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Guest Editors Dr. Beena G Singh Dr. Apurav Guleria

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Message from the President and Secretary, ISRAPS

Dear ISRAPS members,

Greetings from the ISRAPS Executive Council!

ISRAPS has been actively involved in organizing discussion meetings pertinent to the frontier areas of Radiation & Photochemistry. In this regard, we take this opportunity to acknowledge all the ISRAPS Life Members and other researchers who have contributed in organizing various activities including discussion meetings of ISRAPS at different institutes across the country.

We made a good start of this year by holding the National Symposium on Radiation and Photochemistry in association with the Department of Chemistry, BITS Pilani Goa Campus, Goa during January 5-7, 2023. Leading scientists from various research groups in the country participated and delivered talks in their areas of research. There was also very good response from student participants.

During the last few months, we have been directly involved in the arrangement of organizing the upcoming Trombay Symposium on Radiation & Photochemistry (TSRP-2024), which will be held at DAE Convention Centre, BARC during January 7-11, 2024. More than 25 overseas scientists from all over the world are expected to deliver talks in the field of radiation and photochemistry. On behalf of ISRAPS and the symposium organizing committee, we invite all the researchers working in this twin area of radiation and photochemistry and related areas to participate in the upcoming TSRP-2024 and make the event memorable.

ISRAPS has brought out this ISRAPS bulletin based on one-day discussion meeting (hybrid mode) on "Emerging Role of Radiation in Nanotechnology – Fundamentals to Translational Research" held at the School of Nanoscience and Nanotechnology, Shivaji University, Kolhapur on 15th October 2022 under the auspices of ISRAPS.

Finally, we would like to thank Dr. Beena G. Singh and Dr. Apurav Guleria, the Guest Editors and all the contributors of this issue for their efforts to bring out a very informative bulletin containing articles on the theme of radiation in nanotechnology.

Once more, we wish to express our earnest gratitude to all the life members for their continuous support and cooperation and look ahead to your valued suggestions and active contribution in the upcoming events of ISRAPS.



Dr. Awadhesh Kumar President



Dr. (Mrs.) J. Mohanty Secretary



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ISRAPS Bulletin



A Publication of Indian Society for Radiation and Photochemical Sciences

Editor's Desk ...

Nanotechnology offers a range of possibilities by controlling the properties and functionalities of materials. However, harnessing this potential often requires novel techniques and approaches and radiation plays a significant role in this endeavour. Radiation, encompassing a spectrum from electromagnetic waves to particle beams, has long been employed in various scientific and industrial applications. The emerging synergy between radiation and nanotechnology has the potential to revolutionize various fields, ranging from materials science to medicine.

The Indian Society of Radiation & Photochemical Sciences (ISRAPS) aims to foster research on recent advances in the field of Radiation and Photochemistry. On 15th October 2022, a one-day discussion meeting on "Emerging Role of Radiation in Nanotechnology -Fundamental to Translational Research" was organized at the School of Nanoscience and Nanotechnology, Shivaji University, Kolhapur in hybrid mode, under the auspices of ISRAPS. Continuing with the rich tradition of ISRAPS to bring out bulletins related to talks delivered by esteemed researchers, we are delighted to present the current issue on the theme of radiation in nanotechnology. It contains eight articles that delve on the impact of radiation and its crucial role in the fields of energy, material processing and medicine. Five of the articles focus on photochemical sciences, discussing the fundamental dynamics occurring in Perovskites for solar cell devices, the effect of dopants on the efficacy of phosphors for developing energy-efficient electroluminescent materials, the use of ruthenium complexes in photochemical oxidation of water, different functionalized TiO₂ materials with wide array of applications such as drug delivery and self-cleaning systems, and the role of TiO, thin films as photocatalysts for scalable green hydrogen generation. The remaining three articles highlight the use of high energy radiation in the synthesis of different types of nanomaterials, the processing of functional polymers, and the role of additives in tritium-based nuclear batteries.

On behalf of ISRAPS, we sincerely acknowledge the cooperation from all the contributing authors for this issue. We also thank ISRAPS for entrusting us with the guest editorial responsibility.

Dr. Beena G. Singh and Dr. Apurav Guleria (Guest Editors) Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai, INDIA



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Photocatalyst Thinfilms: A potential, realistic, scalable and sustainable approach for green H₂ generation

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Abstract

An over-reliance on nonrenewable resources like, fossil fuels, has contributed to global warming due to the continuous addition of carbon dioxide into the environment. Finding a sustainable solution to break free from the constraints of non-renewable resources and the polluting environment should therefore be the top focus. This could possibly addressed by putting effort into developing practical substitute fuels and efficient carbon dioxide utilization in value-added chemicals, both of which will promote more sustainable growth. Traditional methods of hydrogen production, such as steam reforming of natural gas, add plenty of CO_2 to the environment. Since hydrogen combustion only produces heat/power and water as the only byproduct, it is regarded as the most promising green fuel or future fuel. Production of economically affordable hydrogen to replace the conventional or non-renewable fuels is therefore the subject matter of extensive research efforts on a global scale. Photocatalysis could be a potential method for producing hydrogen utilizing water as a source by direct conversion of sunlight in order to avoid the aforementioned problems. This is accomplished through the development of photocatalyst thinfilms and artificial leafs, which employ the use of several transition metals (as co-catalysts) over TiO₂ or with other suitable wide band gap semiconductors.

Introduction

Hydrogen represents a potential fuel source that is a carbon-free solution for the sustainable survival of human beings on this planet. Despite interest and development in this field, still, a lot of research efforts are needed to address today's growing energy demands [1]. Traditionally, hydrogen has been generated through the economical process of steam reforming of natural gas (or methane). However, this method inadvertently leads to the release of additional green house gases like CO₂ as byproducts (~10 kg of CO₂ for every 1 kg of H₂ produced). The Paris Agreement, ratified by 196 countries in April 2016, emphasizes the urgent need to combat global warming through emission reduction, thus mitigating the risks associated with climate change. Hydrogen must come from renewable resources, such as solar, wind etc. Thus far, the electrolyzer is the only technology blooming in a promising way to meet the requirement of green H₂; however, this is yet to be commercially viable, in spite of large amount of research efforts in the past few decades. Essentially the amount of input energy required to generate 1 kg H₂ is more than 50 kWh and it also depends on the electrolysis method, while the same amount of H₂ produces 33.3 kWh energy. In addition, it should be noted that green hydrogen production from renewable electricity is still in its infancy and that the electricity needed to produce H, largely comes from thermal-based power plants, which results in grey hydrogen due to the contribution of carbon emissions. Currently hydrogen is exceedingly

expensive due to the electrolyzer need for expensive metals (Pt, Ir) and high price associated with electricity and/or renewable electricity from solar PV (photovoltaics). Currently, the dominant production of green electricity is through solar PV and it is contributing 4.5% of global electricity consumption. However, in the near future, the recycling of Si PV panels is anticipated to emerge as a significant environmental concern. Surprisingly, many now recognize that the green energy label associated with Si PV is somewhat paradoxical. Consequently, it is imperative to continue our efforts in discovering genuinely green solar technology. Embracing diverse energy conversion technologies, even if they come with varying price tags, is essential for operational purposes.

One of the alternative ways of producing green H₂ is the direct splitting of water by sunlight harvesting. During photocatalysis, upon exposure of photocatalyst to sunlight in the presence of water which produces electron-hole carriers, drives the water reduction (by electrons) and oxidation (by holes) to generate H₂. In plants, during the photosynthesis process, utilizes the energy from sunlight (for water splitting) to make carbohydrates (dark reaction) from CO₂; critically, both reduction and oxidation reactions takes place within the leaf, but in the physically separated components. When plants are doing photosynthesis for millions of years nicely, why we struggle and what are the possible ways to improve the efficiency of photocatalysts. It is realized that the low efficiency of hydrogen generation due to the large extent of recombination of photo generated charge carriers, and thus hampering the commercial success of photo (solar) catalytic hydrogen production technology [2].It was understood that, the difference of 3-6 orders of magnitude in time scales of photophysical ($\leq 10^{-9}$ s, charge generation) and photochemical ($\geq 10^{-6}$ s, charge utilization) processes and it is imperative to address bridging the time scale issue by new synthetic strategies.

Since the seminal work demonstrated by Fujishima and Honda in 1972 on rutile-phase titania (TiO₂) surface, a plethora of catalyst formulations such as tungsten trioxide (WO₂), iron oxide (Fe_2O_3), cadmium sulphide (CdS) etc. were developed in order to reach the goal of producing solar hydrogen at a commercial scale [3, 4]. Though TiO₂ is UV-active because of its band gap (3.2 eV), some of its other features such as abundance, high stability, low cost and most importantly, the adequate band edge positions to produce hydrogen have made it the state-ofthe-art material [5]. However, the recombination of generated charge carriers causes pristine TiO₂ as an inefficient catalyst. In this regard, with the help of a cocatalyst, it is possible to increase the life time of the charge carriers or electrons to posses with ample life time to reduce the protons. In principle, cocatalyst (a metal or bimetal) can form a Schottky junction with semiconductor which created the electric field at the interface of metal/semiconductor to help the separation of the electron-hole pairs. As far as our current knowledge, there is a lack of systematic approach to select a specific co-catalyst for a given semiconductor. Often, noble metals are utilized, which proves to be cost-ineffective. Therefore, further research is required to investigate more affordable and abundant co-catalysts, with a focus on making rational choices for their application. Moreover, adding organic substrate as sacrificial agent (SA) into water found to be an efficient way due to effective utilization of holes via photooxidation of SA and therefore leave the electrons to reduce H⁺ ions that produce not only hydrogen (photoreduction) but also value-added products (photooxidation). In view of the sustainable development, production of hydrogen from biomass-derived feedstocks (like methanol, ethanol, and glycerol) is indeed a diligent approach. However, production of H₂ using methanol and ethanol is expensive due to their demand for industrial processing. In this scenario, glycerol as feedstock for hydrogen production is gaining gravity as it is a by-product that produced in large amounts (1 ton of biodiesel

production yields \sim 100 kg of pure glycerol). Recently, with rapid increase of biodiesel production across the globe, the production of glycerol is considered as glycerol glut and therefore it is imperative to find viable scientific and technology solutions to create an asset from this industrial waste [6, 7]. In this regard, the combined efforts of selective glycerol oxidation and hydrogen generation via photocatalysis are considered as promising approach to ensure a more sustainable future. However, because of the simultaneous presence of three reactive hydroxyl groups in glycerol made it difficult to transform it to a specific product with high conversion and selectivity and therefore it remains a significant but challenging task to develop novel and highly selective catalysts.

Why thin films:

The powder form of photocatalysts has been extensively employed for the photocatalysis of various reactions; solar fuels, CO₂ reduction, etc. We deal with charge carriers of ns-fs life time in powder photocatalyst. It is like trying to conduct electricity in broken wires and therefore high quality heterojunctions should be designed for efficient photocatalytic process. More over, powder or suspension form of catalyst evaluation approach is suffering from several issues; a decrease in the efficiency to half when doubling the loading, prevalent light scattering rather than light absorption, and heavy material and infrastructure requirements; all these requirements would lead to expensive hydrogen.

Attributes Conventional Photocatalysis with particulate catalyst based suspension		Conventional Photocatalysis with particulate catalyst based suspension	Thin film photocatalysis		
1.	Test conditions	Powder form of catalyst tested in liquid form of reactants	Thin films will be tested under liquid form of reactants		
2.	Materials utilization	Limited exposure to sunlight	Maximum exposure to sunlight		
3.	Light	Minimum due to	Maximum due to		
utilization		(a) Light scattering by the dynamic nature of suspension under stirring	(a) Light absorption is prevalent instead of scattering		
		conditions, (b) Light absorption losses by the liquid present	(b) minimum possible thickness of liquid (reactants) can be used which avoid the light losses		
4.	Scalability	Difficult due to (1) (2) and (3)	Easy to implement		
5.	Cost of	High due to	Low due to		
	products	(a) less efficient process because of attributes (2) and (3)	(a) more efficient process because of attributes (2) and (3)		
		(b) high infrastructure, reactants and catalyst.	(b) minimum infrastructure and materials requirements		
			(c) flow/continuous process		
			(d) Easy reuse of photocatalyst		
6.	Requirement	Typical batch/continuous process in a chemical industry. However light source needs to be created.	Requires a vast amount of land space to accommodate photocatalyst panels for direct solar light and similar to Si PV.		

Table 1: Salient features of conventional and thin film photocatalysis.



Figure 1. Photographs of thin films of P25 of (a) 1.25x3.75 and Pd/P25 of (b) 1.25x3.85, (c) 2.5x3.75, and (d) 2.5x7.5 cm²[9].

It is important to highlight that, when the total catalyst loading increased from 75 to 150 mg, the apparent quantum yield (AQY) decreased from 6.3% to 2.7%, respectively [8]. This observation directly suggests that the chances of succeeding with powder based suspension method are unlikely to meet success, when it will be scaledup to grams and kilograms. Surprisingly, contrary to the anticipated rise in light absorption with greater powder catalyst loading during standard solution measurement conditions, only a portion of the particles were exposed to photons at any given time, rendering the rest inactive [8]. This is consistent with the findings of Nalajala et al., who reported that testing 25 mg of powder Pd/TiO₂ in 40 mL of aqueous methanol results in low hydrogen production (~9 mmol h⁻¹g⁻¹) compared to using only 1 mg of the same catalyst under similar conditions (~ 32 mmol h⁻¹g⁻¹). These results suggest that when the catalyst's quantity is very small in the solution, a larger portion of particles gets exposed to light due to lower turbidity, leading to the generation of a larger number of active charge carriers [9]. These issues can be successfully circumvented by taking the powder form of the catalyst into a thin film over an ordinary substrate [9-17]. Several issues (represented in Table 1) of the conventional (powder form) photocatalysis can be addressed by the thinfilm form of the catalyst. This strategy is comparable to that of solar Si-PV panel technology, which operates by collecting sunlight using Si-based materials (as a photocatalyst) to generate electricity.

This approach is the inspiration from a leaf where all the components are interconnected towards never ending photosynthesis process. Single leaf can be compared to a thin film, but not to powder. In contrast to solar cell where electrons are needed to travel several microns distance to reach the contact, thin film photocatalysis provide the charge carriers locally and instantaneously complete the reaction and therefore achieve efficient hydrogen production. Moreover, thin films can be scaled to different sizes (Figure 1) without compromising its activity and stability.In order to support the claim that the thin films are better in the context of not only efficient but also scalable H, generation, Domen et al., reported the panel type reactors of size 1 m² and 100 m²[18,19]. During the study, over the glass plate particulate form of aluminium-doped strontium titanate as a photocatalyst and commercial polyimide membrane that for separation of the H₂ and O₂ was demonstrated for overall water splitting for several months. However, the catalyst being used for their study is UV active and it is only 4% of total solar illumination and the calculated STH% is only 0.76 [18, 19].

As mentioned earlier, the thinfilm form of the catalyst materials exhibits better performance. This has been demonstrated with various catalyst materials (Pd, Ag, NiCu, NiFe, Au/C/



Figure 2. Photocatalytic hydrogen production activities of P25 and Pd/P25: P25 powder (25 mg), P25 powder (1 mg), P25 thin film (1 mg), Pd/P25 powder (25 mg), Pd/P25 powder (1 mg), and Pd/P25 thin film (1 mg) [9]

Pd as co-catalyst and TiO2 photocatalyst) by Gopinath et al., [9-17]. The results presented in Figure 2 demonstrate that, thin film form Pd/ TiO₂ exhibited 3 times higher hydrogen yield (~30 mmol/h.g) than that of the suspension of same catalyst under spinning conditions, while the hydrogen yield observed with the thin film is 12 times higher than the conventional method of measuring HER with powder suspension (9.1 mmol h-1 g-1 with 25 mg in 40 mL of aq. methanol). However, the studied materials are only active in UV-region, which is only 4% of sunlight. Hence, it is imperative to develop visible light and near-IR light active catalysts that can utilize the ~55-60% of solar light for efficient and large scale generation of H₂. Such effort was demonstrated by large scale photo-reactor under natural sunlight with mesoporous C₃N₄ catalyst on stainless steel plate and reported 18.2 L H, in 30 days from 0.75 m² area of photocatalyst and TEA as sacrificial agent [20].

Artificial Leaf

During nature inspired sunlight harvesting, Photosystem I (PSI) and Photosystem II (PSII) are energy-arranged in such a way that electron flows in one direction and holes in the opposite direction. Can we design a system that mimic the nature. Photocatalyst should absorb entire range of UV-Vis-NIR range available in sunlight. A composite can absorb maximum range of sunlight wavelengths. However, charge transfer from one to another component and finally to co-catalyst becomes rate limiting. Single material cannot do this. Quantum dots (QDs) possessing tunable band gaps have emerged as promising candidates for the next generation of light harvesting applications, including solar cells and photocatalysis [21, 22].

These nanomaterials have the ability to absorb light across the visible and near-infrared regions. One particularly effective approach for hydrogen generation involves sensitizing a wide band gap semiconductor with a narrow band gap semiconductor, enabling light absorption over a broad range of wavelengths. QDs are commonly utilized as sensitizers due to their high light absorption cross section and the optical properties that depend on their shape and size. Moreover, to bridge the time-scale difference between photophysical and photochemical processes, it is imperative to establish the efficient conduction of electrons (short lived, ≤ns) in an ensemble of particles. Good junctions between particles play a major role in improving efficiency/success. However, junctions in the nature leaf system is generated by assembling the ions/atoms/ molecules and integrated into a system.

How to simulate such an approach in a realworld system is an important question ? Can we assemble ions/atoms/molecular components layer-by-layer and integrate with another wide bandgap semiconductor system. This approach will altogether will avoid any wires, as they create junctions by depositing and integrating of one semiconductor components onto another semiconductor. Such a process was accomplished with the preparation of photoanodes (TiO₂/ PbS/CdS and Au-TiO₂/PbS/CdS) using doctorblade method, and demonstrated much higher hydrogen yield [23, 24]. For TiO₂/CdS/PbS film ten SILAR cycles of CdS followed by 5 SILAR cycles of PbS. Instead of layers, due to



Figure 3. UV-Vis absorption spectra of the AuTiO₂, AuTiO_/PbS, AuTiO_/CdS, TiO_/PbS/CdS, and AuTiO_/ PbS/CdS photoanodes. Note the shift in absorption onset from AuTiO₂ at 560 nm to about 700 nm for AuTiO_/ PbS/CdS. Inset shows a digital photograph of the colours associated with photoanode films, (1) AuTiO₂ and (2) TiO_/ PbS/CdS, and (3) AuTiO_/PbS/CdS [23].

porosity of titania, CdS/PbS quantum dots are assembled in the pores of titania, which leads to bulk heterojunctions. Light absorption up to 700 nm was observed, and supports the electronic interaction of chalcogenide layers with nano-Au (**Figure 3**). The AuTiO₂/PbS/CdS wireless photochemical cell exhibited highly enhanced H₂ evolution rate (HER) at 490 \pm 25 µmol/h and a PCE of 5.6% (just from 2 mg of photoanode material). Integrating semiconductor and QDs in the right order is the critical factor towards better efficiency. From the high resolution transmission electron microscopy (HRTEM) results, metalsemiconductor junction observed between Au and titania suggests the presence of Schottky junctions which helps in electron-hole pair separation. Shift in E_g band of titania to high wave number observed on Au deposition on TiO₂,

emphasizes the electronic integration among them.Visible light absorption from the entire visible light spectrum by Au-SPR andCdS,near-IR by PbS, at different wavelength ensures the maximum light absorption; without Au, this is restricted only to the corresponding wave length regime. The critical factor that increases the light absorption capacity of photoactive material is due to the spatial close proximity of the QDs to the intensifying electric field surrounding the AuNPs in AuTiO₂/PbS/CdS. QDs should absorb visible light at different wave length regime for maximum solar light absorption. On the other hand, due to plasmonic effect, the Au metal nanoparticles produce elevated electric fields with light matter interaction on the surface of nanoparticles, and these electric fields are essential to produce the large number of energetic e^{-}/h^{+} pairs which cause subsequent chemical transformations on the metal surface [25]. It was demonstrated that utilizing AuNPs as a plasmonic sensitizer in conjunction with PbS/ CdS QDs to design a wireless photochemical cell that operates without any applied potential. The produced moist H₂ can be directly supplied to applications like a 1 kW fuel cell. The integration of plasmonic AuNPs, TiO₂, and QDs offers a new pathway for enhancing solar light harvesting. To further improve the efficiency and costeffectiveness of the wireless photochemical cell, researchers may explore the ways to increase the light absorption capacity of the photoanode and incorporate earth-abundant co-catalysts. One potential cost-saving measure is replacing Au with a cheaper surface plasmon resonance (SPR) metal, such as Ag. This substitution has the potential to make the technology more economical while maintaining its performance.

Conclusions

Despite nearly five decades of dedicated efforts in solar water splitting (SWS), a significant breakthrough remains elusive till date. While considerable attention has been given to the three fundamental steps—light absorption, charge carrier separation, diffusion, and charge

utilization at redox sites - many practical aspects that could substantially improve efficiency are often overlooked and under-discussed. Nevertheless, by implementing several small yet meaningful advancements, it is possible to enhance solar hydrogen production by following the below listed points. (i) consider seriously to move from particle suspension to thin filmmeasurement method to increase the rate of reaction through effective light absorption, charge generation and its utilization; (ii) try to mimic nature such as artificial leaf approach with catalyst and experiments; (iii) assemble the catalysts from ionic/atomic species for effective electronic integration and therefore efficient charge generation and utilization; (iv) water splitting experiments may be carried out with cheaper sacrificial agents, such as glycerol, cellulose; (v) carry out the experiments in direct sunlight, as much as possible, as that should be the ultimate goal, (vi) stability (photo corrosion and stability in aqueous medium) of the catalyst should be addressed.

In essence, it is concluded that particulate matter photocatalyst to be made into thin film and measured. It is also expected that such an approach would improve the charge carrier separation as well as utilization, so that renewable energy can be stored in molecules like H_{2} .

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Electroluminescent materials for sustainable lighting applications

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Abstract

Photo and electroluminescence properties of ZnS based phosphors such as ZnS:Cu, ZnS:Cu, Mn have been investigated in detail and their electroluminescent properties have been compared with that of commercially available ZnS based phosphors. Copper doped ZnS samples gave broad emission peak centered around 450 nm, up on both optical (UV) and electrical excitations. Based on the observed linear variation in logarithm of luminescence intensity versus inverse of the square root of voltage, it is confirmed that hot electron induced excitation of luminescence centres is the mechanism involved in electroluminescence. No electroluminescence could be observed from nano-crystals where as yellow emission is observed from annealed ZnS nanoparticles doped with Cu and Mn upon application of alternating current electric fields. Observed yellow emission from the sample has been attributed to the overlapping of blue (due to Cu related centres) and orange (transition between ${}^{4}T_{1}$ excited state and ${}^{6}A_{1}$ ground state of the Mn²⁺) emissions from ZnS:Cu,Mn lattice.

Introduction

Energy efficient and clean (Green or pollution free) technologies are need of the hour and are essential for a sustainable development [1,2]. It is generally said that 1 unit of energy/ electricity saved is equivalent to two units of energy generated. Around 20% of the power generated is used for lighting applications all over the world. It is proposed to reduce the power consumption for lighting to nearly 10% by the end of this decade. Hence development of improved materials for solid state lighting (electroluminescence) technology is one of the approaches for achieving sustainability in energy [1]. Currently electro luminescent (EL) devices/ displays have become indispensable modular elements in various commercially available electronic systems, such as backlighting source in a car control panel [3], advertisement panels, multipurpose displays in buildings, functions etc. EL devices have also been deployed in different fields, such as bio-inspired soft robotics, flexible and stretchable electronics, wearable electronics and sensors [4]. Many inorganic oxides and sulfides in bulk and nano-size dimensions are potential candidates for development of cost effective light emitting or electroluminescent devices. For such applications, materials can be either coated on UV (near UV) light emitting diodes (LEDs) or a device can be fabricated based on Metal-Insulator-Semiconductor (Phosphor) -Metal (MISM) geometry/configurations [4]. In the former case, it is called as phosphor converted LEDs and in the latter case it is considered as a complete (full) electric device. Devices of the latter category can be made either from thin films of phosphor material or by powder coating method. A sandwich type of configuration is generally adopted for such devices and the same can be activated by applying AC and/or DC voltages. Thin film fabrication involves high temperature, vacuum accessories and these invariably lead to costlier devices. Alternatively, powder electroluminescent devices are cost effective options to thin film electroluminescent devices since the former devices can be made based on less costlier screen printing or doctor blade techniques rather than the costlier vapour phase

deposition processes. Powder electroluminescent devices are gaining significant interest and popularity among scientific and industrial community [4].

Powder electroluminescence properties of bulk and nano-materials of inorganic compounds such as ZnS:Cu and Mn²⁺ doped Zn S:Cu have been discussed in this manuscript. In the beginning of this manuscript brief principle of electroluminescence and basic steps involved in powder electroluminescent device fabrication are given and this will be followed by luminescence characteristics of electroluminescent devices. Towards end of the manuscript typical photographs of electroluminescent devices fabricated in authors' laboratory are also given.

What is electroluminescence?

Electroluminescence (EL) is a phenomenon where light is generated when an electric field is applied across a material. The material can be in the form of a pellet, thin film, or powder, and the same can be sandwiched between two electrodes [4]. Schematic diagram of an electroluminescent device is shown Fig. 1(a). Electroluminescent devices can be divided into two categories namely low field and high field devices. Low field devices are also known as light emitting diodes (LEDs), where in light is generated by electron-hole pair recombination at a p-n junction (Fig. 1(b)). In high field devices impact of high energy electrons (hot electrons) excites luminescent centres in phosphor material and the light emission is obtained upon relaxation of excited state of the luminescent centre(s). The electric field in high field devices is of the order of 10^6 Vcm⁻¹. Device configuration is different for both types of systems. High electric field devices can be further classified as alternating current (AC) or direct current (DC) operated devices

Thin film electroluminescent devices

Development of thin film electroluminescent (TFEL) devices [5] began in early 1970s. By 2000, TFEL devices had a solid position in the monochrome flat panel display market for various applications. Advantages of TFEL devices include device structures which are not sensitive to vibrations, temperature variations and dusty environments. Such devices possess wide viewing angle, high contrast even under ambient light, fast response allowing video rate, high resolution and long lifetime. Materials such as ZnS, GaN, InP etc., are generally used for fabrication of such thin film electroluminescent devices. Devices based on ZnS thin films as a green light emitter is available since the early 1980s. Electroluminescent (EL) devices possess other advantages that include low power consumption and low heat generation during operation. They are generally very flat, flexible



Figure 1. Schematic diagram of an electroluminescent device (a) and the principle of light emitting diode (b).

and durable. EL devices have low environment impact and contain no mercury. Many such devices operate in both AC and DC electric fields.

Powder electro luminescent devices

Powder electroluminescent devices are cost effective alternative to thin film electroluminescent devices since the former devices can be made based on powder coating or screen printing or doctor blade techniques [4]. Using a substrate based on organic polymer (like for example ITO coated PTFE) for powder coating, additional advantage of mechanical flexibility for the devices can be achieved. Powder electroluminescent devices operate in either DC or AC voltages and a schematic diagram of powder electroluminescent devices operating under DC and AC voltages are given below (Fig. 2(a and b))

In the case of DC electroluminescent devices, the phosphor (phosphor and binder) is sandwiched between an electron and hole donor layers. Typical examples of electron donating layers include Al, alkali and alkaline earth metals (like for example Ca), etc. The material (mixture) of Poly(3,4-ethylenedioxythiophene) : poly styrene sulfonate (PEDOT:PSS) is a typical hole donor in such devices. ITO coated polyethylene terephthalate act as a transparent window for transmission of generated light due to electron hole combination.

In the case of alternating current electroluminescence devices, powder sample is

mixed with binder and coated (screen printed) on ITO coated glass or PET substrate. Few micron thick BaTiO₂ layer is then coated over the phosphor. It is then dried in an oven at 70°C followed by coating the surface with Ag metal or Ag paste, for making contacts. AC Voltages applied across ITO coated substrate and silver electrode (contact). This configuration is also called as MSIM configuration or structure [4, 6, 7], where "M" stands for ITO, "S" stands for semiconductor (phosphor) and "I" represents insulator or dielectric like BaTiO₂. M Electrons injected in the insulator by the metal migrate towards insulator-phosphor interface at low voltages and eventually occupy traps at the interface. As the voltage increases, electrons gain energy (become hot electrons) and migrates to phosphor matrix and bombards the luminescent centres in the phosphor. Thus the luminescent centre get excited and upon de-excitation gives light output.

Fabrication of electroluminescent devices:

Materials required for fabricating Electroluminescent devices:

Indium-Tin-Oxide (ITO) coated polyethylene terephthalate film (resistivity may be from 10 ohm/sq to 200 ohm/sq), Barium Titanate dielectric ink, phosphor binder with viscosity more than 4,000 cps (without phosphor powder) at 25°C and screen printable silver ink (volume resistivity should be less than or equal to $4.0 \times 10^4 \Omega$ cm) are required in addition to phosphor material for



Figure 2. Powder electroluminescence configuration in (a) DC mode and (b) AC mode



Figure 3. Block diagram for observing electroluminescence using AC or DC source



Figure 4. Variation of the intensity of blue emission from cubic ZnS:Cu (1%) particles as a function of (a) voltage and (b) frequency.

fabricating powder electroluminescent devices. Schematic diagram of the electronic circuit for EL device is shown in Figure 3. Electroluminescent devices can be activated to produce EL by using AC/DC sources. For portable application, battery based DC sources with DC to AC converter are preferable.

As AC voltages are characterised by magnitude and frequency, increase in both leads to improvement in light emission from such devices. Effect of applied frequency and voltage on luminescent properties of ZnS:Cu sample is clearly seen from the plots shown in Fig. 4.

In addition to voltage, frequency also influences the energy gained by the electron and the associated luminescence intensity. Energy gained by an electron, occupying trap levels at the interface of insulator (BaTiO₃) and semiconductor (ZnS:Cu)in powder electroluminescent device, from the applied AC voltage is given by the following expression [8]:

Energy = $eV_{peak}Sin\omega t....(Eqn. 1)$

where V_{peak} is the peak voltage, "e" is the electronic charge, ω is the angular frequency (expressed by the relation $\omega = 2\pi f$, where f is the frequency in Hz). As the peak voltage and frequency increases, energy gained by the electrons occupying trap levels increases, eventually leading to excitation of luminescence centres and increase in luminescence intensity.

For energetic electrons (hot electrons) induced excitation of luminescence centres, intensity of luminescence is expected to have an exponential dependence on applied voltage and can be expressed by the following equation [4, 8, 9].

$$L = L_o \exp(-bV^{-1/2})$$
 (Eqn. 2)

Where "L" is the luminescence intensity and "L₀" and "b" are constants. These constants, depend on factors such as particle size of phosphor, concentration of phosphor in the device, thickness of the layer, dielectric constant of the insulator etc. A plot of logarithm of intensity versus $1/V^{1/2}$ is expected to give a straight line with slope as "b" and intercept related to L₀ (Fig.5(a)). A photograph of a large area display device (with dimensions 2" x3") is shown in Fig. 5(b). Colour coordinates have been evaluated from corresponding emission spectra and it matches closely with the blue colour of industrial standards (colour coordinates: (0.15,0.15))



Figure 5(a). Variation of logarithm of luminescence intensity as a function of the inverse of the square root of the voltage. A photograph of the blue emission from powder electroluminescent display device fabricated from ZnS:Cu(1%) is shown in Fig. 5(b).



Figure 6. Electroluminescence from ZnS: Mn,Cu powder devices at (a) 470V and (b) 486V.

Luminescence studies were also carried out ZnS:Cu sample co-doped with Mn²⁺. Up on excitation by UV light, unlike in the case of ZnS:Cu sample, Mn²⁺ co-doped ZnS:Cu sample showed both blue and orange light emission of almost equal intensity. Similar emission spectrum has been observed for electrical excitation also. Fig. 6(a and b)) shows electroluminescence spectra from Mn²⁺ co-doped ZnS:Cu sample, fabricated in the MISM powder electroluminescent device configuration at two different AC voltages, namely 470V and 486 V at a fixed AC frequency of 10 kHz.

Relative intensity and line shape of emission peaks change slightly with increase in applied voltage as can be seen from Fig. 6. This is understandable as excitation energy changes with applied voltage and subsequently the defect

> centres get preferentially excited leading to variation in their luminescence intensities. A representative photograph of emission from the device is shown in Fig.7(a). Doping copper and manganese together leads to yellow-orange emission due to the combined effect of transitions involving defects in ZnS lattice brought about by Cu substitution and transition between ⁴T₁ excited state and 6A1 ground states of Mn²⁺ ions.

> From the emission spectra obtained at two different voltages colour coordinates have been evaluated and found to be (0.52,0.45). The coordinates correspond to yellow-orange region and is represented in the CIE plot shown in Fig. 7(b).

To compare the luminescence properties of lab prepared samples described above, commercial ZnS phosphor samples have also been procured and its phase purity has been confirmed by X-ray diffraction technique. Detailed photo and electroluminescence studies were carried out on the sample and the results are described in the following section. Figure 8 shows the photo and electroluminescence spectra from commercial ZnS sample. For recording the photoluminescence, sample was excited at 290 nm and for electroluminescence an AC voltage of 200V at frequency of 1kHz was used.

Figure 8(a) shows the photo and electroluminescence (PL and EL) spectra from commercial ZnS sample [10]. The line shapes are nearly symmetric and line widths are identical for both photo and electroluminescence spectra.



Figure 7(a). A representative photograph of emission from ZnS:Cu,Mn(1%) sample subjected to AC powder electroluminescence at an applied voltage of 486V with a frequency of 10kHz. Colour coordinates were evaluated from the electroluminescence spectrum and indicated in the CIE plot in Fig. 7(b).



Figure 8(a). Electroluminescence and photoluminescence (EL and PL) spectra from commercial ZnS phosphor. For PL, the sample was excited at 290 nm and for EL an AC voltage of 200 V with a frequency of 1kHz was applied. Variation of luminescence intensity as a function of inverse of square root of voltage for the same sample is given in Fig. 8(b).



Device in off state

Enlarged view of the device

Figure 9. Representative photographs of the electroluminescent devices fabricated with commercially available ZnS phosphor.

There is a marginal difference of ~ 7 nm between peak maximum of EL (498nm) and PL peaks (505 nm). Unlike the lab made ZnS:Cu sample, symmetric EL and PL spectra observed for commercial sample confirm that the luminescent centres present are of different types in the latter sample. To understand the nature of luminescent centres, decay curves corresponding to emission from commercial sample has been recorded and compared with that of blue emission from lab made sample (not shown). Average lifetime value for the commercial sample is found to be 0.290 ms which is marginally higher than that corresponding to blue emission from lab made ZnS:Cu sample. The results suggest that luminescence occurs mainly due to electron hole recombination involving donor levels (electron traps) in both the samples (lab made and commercial). Variation in luminescence intensity as function of voltage is shown in Fig. 8(b). A straight-line plot observed confirms the fact that hot carrier induced excitation of luminescence centres is the involved mechanism of electroluminescence.

Representative photographs of the devices fabricated with commercial phosphor are given below (Figure 9). It may be noted that the emitted colour is not pure blue but corresponds to cyan colour.

Conclusions

Powder electroluminescent devices based on ZnS:Cu, ZnS:Cu, Mn were fabricated and characterised for its electroluminescent properties. Blue colour of industrial standards with CIE colour coordinates (0.15, 0.15) have been obtained from ZnS:Cu sample. Unlike this commercial ZnS based phosphor gave emission around 500 nm upon both optical and electrical excitations. Detailed studies confirmed that hot electron induced excitation of luminescent centres is occurring in all the ZnS samples and the same is responsible for visible emission upon electrical excitation.

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The phosphine-based Ru(II) complexes for chemical, and photochemical water oxidation

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Abstract

The phosphine based Ru(II) mononuclear polypyridyl complexes $[Ru(tpy)(PP)X]^{2+}$ (PP = dppe, dppp, and POP; X = Cl, and H₂O)such as **1a-c**, **2a-c**, and **3ac** were synthesized. These complexes were characterized by several spectroscopic techniques. The spectrophotometric and electrochemical studies were used to determine the multiple oxidation states and stable intermediates of the **1c**, **2c** and **3c** in aqueous B.R. Buffer solution. The chemical and light-driven oxygen generation using **1c**, **2c**, and **3c** as catalysts was measured by using a pressure transducer and the turnover numbers (TON) were found to be (386, 338, 210) and (170, 155, 135) respectively. The enhanced activities are attributed to the bite angle of P-Ru-P in **3c**, **2c** and **1c** which decreases from 99.45(9)°, 93.18(2)° and 84.02(5)° respectively. Thermodynamic and kinetic stability of Ru(II)-phosphine complexes can be enhanced by introducing the phosphine ligand with suitable electron donating and accepting groups, and changing their bite angle (P-Ru-P).

Keywords: Phosphine ligands, mononuclear complexes, water oxidation and bite angle

1. Introduction

Natural photosynthesis by a Mn₄CaO₅ catalyst at the oxygen evolution centre (OEC) in photosystem II (PS-II) has sustained life on the earth for billions of years.¹ Inspired by the natural photosynthesis, photochemical water splitting is regarded as a promising artificial alternative to address the energy challenge and thereby has attracted attention.²⁻⁵ Since "blue dimer", the first well studied dinuclear Ru complex capable of oxidizing water to dioxygen, was investigated by the Meyer group in 19826 several mononuclear and binuclear Ru water oxidation catalysts (WOCs) have been prepared and reported with persistent improvement of catalytic efficiency.7-10 Significant advances have been made in the development of molecular water oxidation catalysts (WOCs). The first mononuclear ruthenium WOC was introduced by Bhattacharya et al.¹¹ in 1997 but detailed mechanistic aspects were not attempted. However, first time water oxidation activity with thermodynamic and kinetic stability of series of mononuclear Ru(II) complexes were reported by Thummel group in 2005.¹² To classify the increasing number of WOCs, based on denticity of the ligands he divided the mononuclear Ru(II) complexes into four classes which was followed by mechanistic insight of WOCs of mononuclear ruthenium complexes by the Meyer group.¹³

The replacement of Ru-N bonds by Ru-O, Ru-S and other pendent groups such as SO²⁻, COOH and -PO₃H₂ in mononuclear Ru(II) polypyridyl complexes enhances the catalytic activities (Figure 1). Sun et al. studied Ru(II) mononuclear complexes involving the M-O coordination of polypyridyl ligand and have discovered a family of highly active Ru-bda (bda2-= 2,2'-bipyridine-6,6-dicarboxylate) moieties at the equatorial position.9,10,14 An interest in developing artificial water splitting to O^2 and H^2 , driven by sunlight, has been motivated by the need for practical and environmentally friendly power generation without the consumption of fossil fuels. The central issue in light-driven water splitting is the efficiency of the water oxidation,

which in the best-known catalysts falls short of the desired level by approximately two orders of magnitude. Here, we show that it is possible to close that 'two orders of magnitude' gap with a rationally designed molecular catalyst [Ru(bda Recently, the Ru-bda core has been used by several groups in order to construct molecular devices and supramolecular systems.15-18 The bda²⁻ ligand on complexation is largely distorted and the Ru-O bond is weakened due to the presence of distortion. Therefore, Ru-bda catalyst suffers from bda²⁻ ligand dissociation under catalytic as well as ambient conditions,¹⁹ leading to issues of prolonged stabilization of metal complexes containing the Ru-bda core. To overcome the ligand dissociation, Duan group reported the Ru-S coordination by replacement of bda2- with 2,2'-bipyridine-6,6'-dicarbothiolate (bct²⁻) ligand.²⁰ The Ru-S (carbothiolate) bond is expected to be stable longer than the Ru-O (carboxylate) bond and therefore the Ru centre should bind bct²⁻ better than bda²⁻. By introducing the negatively charged sulfur donor in the ligand, the Ru-bct displays stronger coordination between the ligand and low valent Ru centre than Ru-bda. The catalytic performance of the Ru-bct is comparable with Ru-bda. Switching from Ru-(NN) and Ru(OO)/Ru-bda to Ru-(SS)/Ru-bct, one can avoid catalyst decomposition issues which often are encountered in preparation, purification and storage of Ru-bda. The influence of the bite present in the O-Ru-O in Ru-bda type molecule over the catalytic activity of the respective complexes were explained by Duan group.21

Concepcion et al.^{22,23} have incorporated the phosphate group by linking to the polypyridyls ligand as bipyridyl diphosphonate. The system provides multifunctionality to the catalyst and forms high-valent metal-oxo species at mild potentials through redox-potential levelling due to charge compensation and δ -donation effect. Besides, phosphonate groups act as proton shuttles to move protons in and out of the catalytic site, thus lowering activation barriers



Figure 1. Depiction of a) Ru-O (Ru-bda), b) Ru-OP(O) OH, (Ru-bpaH2), and Ru-S (Ru-bct²⁻) coordination.

in PCET processes, in particularly, the key O-O bond formation step.

For the first time, in order to outline the effect of phosphine based bidentate ligand (P-Ru-P) on water oxidation catalytic activity herein, we illustrate the synthesis and characterization of series of $[Ru(tpy)(PP)H_2O]^{2+}(PP = dppe, dppp and$ POP) complexes and their spectrophotometric and electrochemical studies. (Scheme 1) These phosphine-based complexes were employed for chemical and light driven water oxidation. The thermodynamic and kinetic stability of 1c, 2c and 3c complexes were observed in the form of TON, TOF and initial rate constant. Further, we also note that effect of the P-Ru-P bite angle and electron donating tendency of phosphine-based ligand on catalytic activity of the 1c, 2c and 3c. The chemical water oxidation by these complexes was found to be greater than parent type 1 [Ru(tpy) $(bpy)H_2O]^{2+}$.

2.Experimental

2.1 Materials and Physical Measurements

The 2,2':6', 2''-terpyridine (tpy), tetrabutyl ammonium perchlorate (TBAP), and ammonium hexafluorophosphate, 1, 2-bis(diphenylphosphino) ethane (dppe), 1, 3-bis(diphenylphosphino)propane (dppp) and bis[(2-diphenylphosphino)phenyl]ether (POP) were purchased from Sigma Aldrich, USA. Potassium iodide, 1, 10-phenanthroline, lithium chloride, potassium bromide, Ceric ammonium nitrate (CAN) and all solvents were purchased from S. D. Fine Chemicals Limited (India).¹H NMR spectra were recorded with Bruker Avance 300 and 500 MHz spectrometer with CDCl₂, DMSO-d_cand D₂O solvents. High resolution mass spectrometry (HRMS) measurements were performed on Bruker, Impact HD ESI-Q TOF mass spectrometer, (Bruker Compass Data Analysis 4.2). Electronic absorbance spectra of solutions in water, methanol and acetonitrile were measured with a JASCO UV-visible spectrophotometer (V-630). IR spectra were recorded on Bruker's ATR-IR spectrometer. The elemental analysis (C, H and N) were carried out with a ThermoQuest microanalyzer. Electrochemical measurements were carried out with CH-electrochemical analyzer model 1100A.

2.2 Synthesis of complexes

Synthesis of $Ru(tpy)Cl_3$ precursor complex and $[Ru(tpy)(PP)H_2O]^{2+}$ (PP = dppe, dppp and POP) complexes werecarried out with modification of previously reported procedure.²⁴ (Scheme **1**)



Scheme 1. Synthetic route of $[Ru(tpy)(PP)H_2O]^{2+}(PP = dppe, dppp and POP)$

$[Ru(tpy)(dppe)H_2O]^{2+}$ (1c)

A mixture of [Ru(tpy)(dppe)Cl]Cl(**1a**) (0.080 g, 0.115 mmol) and aqueous CF_3SO_3H solution (pH = 1.0, 1.89 g) in acetone (3 mL) was heated in an open round bottom flask at 50 °C overnight (12 h) to give a solid residue. Recrystallization of the residue from acetone (3 mL) and water (1 mL) to give dark brown crystalline product. Yield 0.061 g, (63 %). HRMS m/z [M–CF₃SO₃]⁺ calculated 899.8395; found 899.7012 $[M-2CF_3SO_3]^{2+}$ calculated 375.3837, found; 375.0975, Anal. Calcd for $C_{43}H_{37}N_3O_7F_6S_2Ru_1P_2$, C, 49.24; H, 3.55; N, 4.01; S, 6.11found C, 49.62; H, 4.50; N, 4.19; S, 6.40

$[Ru(tpy)(dppp)H_2O]^{2+}$ (2c)

A mixture of [Ru(tpy)(dpp)Cl]Cl(**2a**) (0.080 g, 0.115 mmol) and aqueous $CF_3 SO_3 H$ solution (pH = 1.0, 1.89 g) in acetone (3 mL) was heated in an open round flask at 50 °C overnight (12 h) to give a solid residue. Recrystallization of the residue from acetone (3 mL) and water (1 mL) to give red transparent crystalline product as [Ru(tpy)(dppp)H₂O](CF₃SO₃)₂ (**2c**). Yield 0.061 g, (63 %). MS *m*/*z* [M–CF₃SO₃]⁺ calculated 913.8661; found 913.6045, [M–2CF₃SO₃]²⁺ calculated 382.3970, found; 382.1020, Anal. Calcd. for C₄₄H₃₉N₃O₇F₆S₂Ru₁P₂, C, 49.72; H, 3.70; N, 3.95; S, 6.033found C, 49.23; H, 3.60; N, 4.15; S, 6.20

$[Ru(tpy)(POP)H_{2}O]^{2+}$ (3c)

A mixture of [Ru(tpy)(daf)Cl]Cl(**3a**) (0.080 g, 0.115 mmol) and aqueous CF_3SO_3H solution (pH = 1.0, 1.89 g) in acetone (3 mL) was heated in an open round flask at 50 °C overnight (12 h) to give a solid residue. Recrystallization of the residue from acetone (3 mL) and water (1 mL) to give red crystalline product. Yield 0.061 g, (63 %), MS *m*/*z* [M–CF₃SO₃]⁺ calculated 1023.9810; found 1023.5021, [M–2CF₃SO₃]²⁺ calculated 437.4544, found; 437.2345, Anal. Calcd for $C_{53}H_{41}N_3O_7F_6S_2Ru_1P_2$, C, 54.27; H, 3.52; N, 3.58; S, 5.47 found C, 54.40; H, 3.60; N, 3.70; S, 5.67

3.0. Results and discussions

3.1. Structural Characterization

The complexes were characterized by elemental analysis, IR, NMR, Mass spectroscopy and single crystal X-ray diffraction and their stoichiometry was confirmed.

3.2. Photophysical studies

The UV-visible absorption spectra of complexes **1c**, **2c**, and **3c** were recorded in methanol (Figure 2). The complexes **1c**, **2c**, and

3cshow a prominent peak at 431 nm and 437 nm respectively attributed to a MLCT process involving ruthenium to ligand charge transfer in respective complex. Peaks in the UV region correspond to π - π * transitions in the polypyridyl and phosphine ligand



Figure 2. The electronic absorption spectra of 20 μ M complex **1c**, **2c**, and **3c** in methanol at 25 °C

3.3. Electrochemical Studies

The electrochemical analysis of complex **1c**, **2c** and **3c**exhibits (Figure 3) three metal based redox events at anodic region such as Ru^{II}/Ru^{III}, Ru^{III}/Ru^{IV} and Ru^{IV}/Ru^Vat 0.45 V, 0.92 V and 1.10 V; 0.43 V, 0.84 V, and 1.17 V; 0.63 V, 0.96 and 1.20 V respectively. Similarly, ligand based redox events occurs at cathodic region. The potential difference ΔE and $E_{1/2}$ values of the **1c**, **2c** and **3c** are summarized in the table **2**.

3.4. Pourbiax Diagram of 3c

The oxidation of complex **3c** is sensitive to the electron density around the ruthenium centre. The Pourbiax diagrams (Figure 4) for **3c** obtained from Square Wave Voltammograms in aqueous B. R. Buffer (10 % acetonitrile) exhibits the three-metal based Ru^V/Ru^{IV}, Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} redox couples at 1.6, 1.41 and 0.83 V respectively at pH 1.

Based on the observed potentials of three redox couples from (pH 0-12), the Pourbiax

Complex	MLCT	Ligand base	ed transition
	nm (L mol ⁻¹ cm ⁻¹)	nm (L mol ⁻¹ cm ⁻¹)	
1c	431 (3350)	314 (18000)	265 (22000)
2c	437 (3150)	310 (19500)	266 (24500)
3c	437 (3250)	309 (13500)	274 (18500)

Table 1. Electronic data of complex 1c, 2c and 3c

Complex	Ru ^{II} /Ru ^{III}		Ru ^{III} /Ru ^{IV}		Ru ^{IV} /Ru ^V	
	$\Delta \mathbf{E}(\mathbf{V})$	$\mathbf{E}_{1/2}(\mathbf{V})$	$\Delta \mathbf{E} \left(\mathbf{V} \right)$	$E_{1/2}(V)$	$\Delta \mathbf{E} \left(\mathbf{V} \right)$	$\mathbf{E}_{1/2}(\mathbf{V})$
1c	0.06	0.45	0.2	0.92	0.03	1.10
2c	0.05	0.43	0.07	0.84	0.06	1.17
3c	0.10	0.63	0.26	0.96	0.07	1.20

Table 2. Electrochemical data of complex 1c, 2c and 3c

 $\Delta E = (Epa - Epc) V; E_{1/2} = (Epa + Epc)/2$



Figure 3. *Cyclic voltammogram of complexes a*) **1c**, *b*)**2c** *and c*) **3c***in acetonitrile solvent with ammonium hexafluorophosphate as supporting electrolyte; GC, working electrode; Pt wire, counter electrode and SCE, reference electrode at 25 °C*

diagram is divided into three regions. For pH< 2.0, Ru^V/Ru^{IV} couple having straight line with zero slope, outlines the 1e- transfer process. In the same region, variation in the potential with pH for Ru^{IV}/Ru^{III} couple is linear with slope -112 mV/pH unit, indicating the 1e-/2H⁺ transfer process and Ru^{III}/Ru^{II} couple, it gives the straight line with zero slope, signifying 1e-transfer. For pH <5.2, *E* variation for Ru^{V}/Ru^{IV} couple having straight line with zero slope, indicates the 1etransfer event. In the same region variation in the potential with pH for Ru^{IV}/Ru^{III} couple is linear with slope -60 mV/pH unit, indicating the 1e-/1H⁺ transfer process. Further, in case of Ru^{III}/ Ru^{II} couple, it gives the straight line with 60 mV/ pH slope, signifying 1e-/1H⁺transfer. In the range 5.2 < pH <12.00, the potential remains constant for Ru^V/Ru^{IV} gives straight line with zero slope, outlining the 1e- event. The potential for Ru^{IV}/ Ru^{III} gives straight line with zero slope showing 1 e- transfer process and Ru^{III}/Ru^{II} couple vary linearly with slope approximately -27 mV/pH unit, indicating the 1e-/2H⁺ transfer event. Thus, 3c undergoes proton coupled electron transfer (PCET) processes essential to avoid the charge accumulation in high energy intermediates.

3.5. Water Oxidation

Based on spectrophotometric and electrochemical investigation, the complexes exhibit the essential redox features for water oxidation catalysis. Therefore, **1c**, **2c** and **3c** have been employed for chemical and light-driven water oxidation.

3.5.1. Chemical Water Oxidation

The water oxidation studies were conducted in a 25 mL round bottom flask capped with a septum and equipped with a stir bar. The flask that contained the water-oxidation solution (5 mL) was seated in a thermally controlled water bath (25 °C) and connected to a port of a pressure transducer (PXM409-002BAUSBH) sensor. Subsequently, reactions were initiated by injecting complex 1c into 5 mL of triflic acid (pH 1) solution that contained CAN (550 mg). The dioxygen gas that was generated was monitored by recording the increase of headspace pressure every 10 sec for 5-6 h. The pressure increase was then converted into number of moles of gas using the equation, PV = nRT. The generated dioxygen gas was also quantified by gas chromatography



Figure 4. Pourbiax diagram of 3c in aqueous B. R. buffer containing 10 % acetonitrile



Figure 5. *Kinetics plots of the chemical water oxidation by* (20-100 μ M) *a*) **1c** *and initial rate constant b*) **1c** *in aqueous triflic acid solution* (pH = 1) using CAN as sacrificial reagent at 25 °C



Figure 6. Photoactivated water oxidation by (20-100 μ M) of a) **1c**, initial rate constantb) **1c** in the presence of 0.001 M $Ru(bpy)_3^{2+}$ as photosensitizer and 0.01 M $Na_2S_2O_8$ in pH 7.2 ± 0.2 phosphate buffer at 25 °C

Table 3. Thermodynamic and kinetic stability	of 1c, 2c and 3c from chemical water
oxidation	

Complex	TON	TOF x 10 ⁻² (s ⁻¹)	k x 10 ⁻⁴ (s ⁻¹)
[Ru(tpy)(bpy)(H ₂ O)] ²⁺	178	0.006	0.6
$[Ru(tpy)(bpg)(H_2O)]^{2+}$	833	1.9	2.7
1c	386	1.4	3.8
2c	338	1.6	3.4
3c	255	1.2	4.6

Complex	TON	TOF x 10 ⁻² (s ⁻¹)	k x 10 ⁻⁴ (s ⁻¹)
[Ru(tpy)(bpg)(H ₂ O)] ²⁺	307	0.9	3.0
1c	170	1.8	4.6
2c	155	0.8	3.8
3c	135	0.7	3.4

Table 4. Thermodynamic and kinetic stability of 1c, 2c and 3c by Light-driven water oxidation

(GC). The reaction solution and headspace were purged by Ar to allow accurate measurement of the amount of O_2 produced during the experiment.

During kinetic studies, the catalyst concentration was varied from 20 to 100 μ M for complexes **1c** (Figure 9) while keeping CAN concentration at 0.2 M. This experiment was performed in triplicate. The thermodynamic stability and kinetic stability of the complex **1c** were measured in terms of turn over number (TON) = [generated O₂] / [catalyst] in moles and turnover frequency (TOF) = TON / unit time respectively. Similar studies have been performed using **2c** and **3c**. The comparative activity of **1c**, **2c** and **3c** with complexes are given in table **3**.

3.5.2. Light-driven Water Oxidation

In a typical experiment, (20-100 μ M) of **1c** catalyst was irradiated by LEDs in the presence of 0.001 M Ru(bpy)₃²⁺ as photosensitizer and 0.01 M Na₂S₂O₈ buffered to pH 7.2 ± 0.2 by phosphate buffer, after 3-5 h at 25 °C.

The pressure of evolved gases were measured by Pressure Transducer and confirmed by GC. Similar studies have been performed using **2c** and **3c**. The TON for **1c**, **2c**, and **3c**, found to be 155, 135 and 170 respectively. (Figure 6) The comparative data of light-driven water oxidation activity with complexes from chapter 3 and 4 are shown in Table **4**.

4.0. Conclusion

We have investigated the Ru(II) mononuclear polypyridyl and phosphine based complexes

 $[Ru(tpy)(PP)X]^{2+}$ (PP = dppe, dppp, and POP; X = Cl, and H₂O)such as **1a-c**, **2a-c**, and **3a-c**. The chemical and light-driven activities of 1c, 2c, and 3c were found to be (386, 338, and 210) TON and (170, 155, 135) TON respectively. The increase in the activity have been observed as the bite angle of P-Ru-P in 3c, 2cand 1c increases from 99.45(9)°, 93.18(2)° and 84.02(5)° respectively. The thermodynamic and kinetic stability of Ru(II)-phosphine complexes can be enhanced by derivatizing the phosphine ligand with suitable electron donating and accepting groups, and changing their bite angle (P-Ru-P). On the contrary, phosphorus is coordinated to the Ru centre, seems that the electronic properties of the complexes are not affected much as evidenced by UV-Visible spectra and Pourbiax diagram and water oxidation activity.

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Hot Carrier Cooling Dynamics in Lead Halide Perovskites

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Abstract

Rampant use of fossil fuels for our energy needs have led to a situation where mankind is facing substantial negative impact on society, environment, standard of living etc. Tackling such a challenge would require finding alternative energy resource which is abundant and can therefore replace the quantum of energy generated through fossilfuels, naturally available, and without placing a large impact on already stressed ecosystem. One of the most sought after approaches to mitigating energy needs is by utilisation of solar energy by photovoltaics. In a typical single junction photovoltaic cell, the maximum efficiency is obtained for a material with a band gap of ~1.0-1.3eV as given by detailed balance equation also called Shockley-Quiesser (SQ) Limit. Such photovoltaic cells donot efficiently tap the blue end of electromagnetic spectrum due to thermalisation losses. One approach that can mitigate this is by constructing a hot carrier cell. In the present, we throw light on factors governing this phenomena in halide perovskites and discuss some of our results on HC cooling in lead bromide perovskites.

1. Introduction

Record power conversion efficiency (PCE) of ~26%¹⁻² in polycrystalline thin film based photovoltaics based on lead halide perovskites have led to considerable focus on these materials. While substantial resources have been employed towards the development of the same, the PCE seems to have plateaued and still has a lot to cover to reach theoretical maximum of ~31% as defined by S-Q limit³. One of the major loss factors in a typical photovoltaic cell is the energy lost as heat for any photon of energy greater than the band gap. Avoiding this loss helps one push the PCE beyond the S-Q limit. Devices which can mitigate these thermalisation losses are called Hot Carrier (HC) Solar Cells⁴⁻⁶. Therefore, a single junction photovoltaic cell where this can be achieved helps one breaks the limitation placed by thermodynamics namely S-Q limit. However, such a device would rely on ability to extract charge carriers before they undergo cooling. In a typical semiconductor, this cooling process takes place in the time scale of <<1ps due to strong electron-phonon interactions. Therefore, extracting these carriers before cooling is not that easily feasible. However, in nanomaterials with exotic cooling behaviour can this be achieved remains an open question.

Some common materials employed in solar cells are Silicon, CdTe, CdSe, GaAs etc. Studies in these materials on hot carrier cooling reveals that thin films and confined nanostructures are still fast in the above materials is given in Table 1 are typically in ps timescale for CdSe and GaAs⁷. The hot carrier cooling times in these materials are still orders of magnitude faster than carrier transit time to individual electrodes. Additionally, possibility of carrier trapping during transit cannot also be ruled out. Recently it has been shown that halide perovskites exhibit slow hot carrier cooling with time scales as high as 100s of ps⁸⁻¹⁰. Such slow cooling times along with ability of halide perovskites to sustain substantial defects with defect level alignment closer to individual bands, helps in extraction of hot carriers and thereby extend the PCE and

helping in the breaking the thermodynamic wall imposed by S-Q limit⁷.

In this present article, we help understand what hot carriers are by giving a brief introduction on the same. We highlight the importance of factors governing hot carrier dynamics and mechanism involved in hot carrier cooling process in theseperovskites with a emphasis on some of our recent work. Finally, we discuss the opportunities that perovskites afford towards a hot carrier cell. This review is not extensive and is only a small effort towards understanding HC cooling in halide perovskites.

2. What are Halide Perovksites?

Perovskite term is names after Russian Minerologist C. L. A v Perovski as coined by Gustav Rose¹¹ who discovered them. Typically, perovskites that are naturally found are oxides. A typical oxide perovskite lattice has a formula ABO₃ with a typical crystal lattice consisting of corner sharing BO₆²⁻ (B-Tetravalent cation) octahedra with additional charge balanced by A cation (Divalent).

In case of halide perovskites, which has a chemical formula ABX3 (figure 1), A and B cations are monovalent and divalent, respectively¹². Typically, A cation are large as compared to B cation. In case of halide perovskite one can manipulate the electronic and optical properties of halide perovskites by changing A-cation to Cs, methylammonium (MA), Formamidium (FA) etc¹³. On the contrary one can have a range of divalent cations like Pb, Sn and Cl, Br I for the



Figure 1. Typical Structure of Halide Perovskites.



Figure 2. Schematic showing (a) carrier relaxation after photoexcitation by either trapping or by radiative decay (b) Carrier cooling

halides. In a typical halide perovskite, the structure is seldom cubic and depends on the combination of the sizes of A, B, X. Additionally the A cation can also be a molecular cation as shown in the figure like MA or FA cation. Therefore, depending on the size and shape of the A site cation the lattice can get distorted all the while maintaining the perovskite framework intact leading to orthorhombic or tetragonal structures apart from cubic lattice. One can also modulate properties of perovskites using cation with monovalent and trivalent combination in place of B cation creating 2×2 perovskites (also called double perovskite) or one can use a tetravalent cation to create a vacancy ordered lattice. Each of these modulation helps one creates a variety of lattices

with varied properties. Additionally, one can also play with dimensionality to manipulate properties by quantum confinement effect creating Quantum dots (0D), Nanorods (1D), and nanoplatelets (2D). Each of these manipulations have been known to help modulate optical and electronic properties.

3. What are Hot Carriers?

In a typical semiconductor, the bands of importance for a solar cell applications are the frontier bands called valence and conduction bands which consists of closely spaced discrete levels. The separation between the valence and conduction band is called the band gap. However, within the individual bands, typical density of states ishigh leading to separations between individual levels< thermal energy. On photoexcitation, as shown in figure 2, with energy (E_{hy}) > band gap (E_{h}) of the semiconductor, typically carrier relax to either ground state by a radiative process or by trapping as shown in fig 2a. However, on a faster time scale, the carriers thermalize to reach the band edges via carrier-carrier scattering in a time scale of tens of hundreds of femtoseconds and achieve a distribution governed by Fermi-Dirac statistics with carrier temperature (T_c) greater than the lattice temperature (T_1) . These carriers are called hot carriers. This quasi-equilibrium is achieved because typical electron-hole recombination timesor rate of carrier removal from individual bands are much larger than carrier cooling time. The carriers cool until a thermal equilibrium is achieved with the lattice by equalisation of T_c and T_1 . In a typical semiconductor, this is achieved by initial carrier-carrier scattering and later by carrier-phonon modes and subsequently via phonon-phonon relaxation pathways. In a bulk semiconductor, this phenomenon is fast and therefore, an equilibrium is achieved within few ps⁵⁻⁷. Therefore, rendering any extraction of hot carrier, a futile exercise. Therefore, any possibility of HC solar cells relies on cases where HC cooling takes place in time scales which are larger allowing a meaningful extraction yield. Additionally, material quality which defines the defects in the materials hinders such collection due to trapping of carriers before they reach individual electrodes. Therefore, hindrance towards achieving a HC solar cell are primarily fast HC cooling and presence of defects in materials which acts as trapping centers. Therefore, it is necessary to understand the mechanisms involved in hot carrier cooling to probe and select materials that are more suitable for such a HC carrier solar cell. Therefore, a study of materials that are employed in photovoltaics cells and their relaxation behaviour of hot carriers helps understand process and possibly design materials to tune this process.

The HC dynamics is typically a fast process taking place in the time scale of ps therefore any measurement of the same needs to be monitored in the time scale of fs. HC cooling phenomena is studied by optical techniques like time resolved photoluminescence or femtosecond transient absorption spectroscopy. In the present review, we primarily discuss monitoring hot carrier cooling using transient absorption techniques. In a typical experiment, semiconductor excitation is accomplished with a fs pulse above the band gap. Therefore, a bleach at the band gap energy is observed due to depletion of population and eventual state filling at the band gap energy. The bleach is asymmetric towards the blue side due to hot carrier population⁷. Therefore, the hot carrier population could be fitted to Fermi-Dirac statistics or Maxwell-Boltzmannstatistics as an approximation could be used to extract the carrier temperature after photoexcitation as given below⁸⁻⁹

$$\Delta A(E) = -A_0 e^{\frac{-E}{k_b T_c}}$$

 ΔA is change in absorbance, is the carrier temperature. Carrier temperature for each time slice is used to extract carrier temperature decay. It is seen readily that since the bleach contains contribution from both electrons and holes population, the obtained temperature in general

Chemical	Excess Energy	Parameters Used (Carrier Density, >10 ¹⁸ /cm ³)			Reference
	(eV)	Carrier Density (×10 ¹⁸)	Decay Time to 600K (ps)		
GaAs Film	~1.7	6	~2	TA	15
InN Film	~0.3	6	~1.4	TA	16
CdSe Nanorod	~1.1	22	~3	TRPL	17
MAPbI ₃ Film	~1.5	6	~60	TA	18
FAPbI ₃ Film	~1.5	4.8	30	TA	19
CsPbBr ₃ Colloid	~0.5	3	17	TA	20
MAPbBr ₃ Colloid	~0.5	10	~50	TA	21

Table 1. HC Cooling times for typical material used in photovoltaic cells.

and average temperature. Additionally, the temperature can be skewed toward a particular carrier either electron or hole depending on the effective masses of the carriers and the degeneracy of the individual bands. In case of lead halide perovskites, the effective mases of electrons and holes are similar. Therefore, carrier temperature contribution is equally divided among the two carriers. Information of population of hot carriers is extracted from the blue side shoulder of bleach of lowest absorption band or PL arising from electron hole recombination from band edges. Some of the measurements on the same for commonly used materials for solar cells application is given in Table 1. In all of these materials like GaAs, InN, and CdSe¹⁵⁻¹⁷etc the hot carrier cooling times are significantly fast with typical times <5ps. However recently it has been shown in case of lead halide perovskites these times are orders of magnitude slower as compared to other common photovoltaic materials. For eg the reports show that the hot carrier times are in the range of 10s of ps in both film phase and colloidal phase.

In case of lead halide perovskite one finds that the cooling dynamics compared to conventional semiconductors used in photovoltaics are a lot different. Below we describe the typical mechanisms of slow HC cooling.

4. Slow Hot Carrier cooling mechanisms

HC Cooling is typically investigated by TA studies by monitoring the high-energy region of bleach of the exciton. However, an interpretation also can be complicated by Moss-Burstein effect²²⁻²³& band gap renormalisation. Moss-Burstein effect is essentially a blue shift in absorption band arising due to filling of states are the band edges. This effect is seen at high pump intensities with scaling dependent on density of states or n^{2/3} (where n is the carrier density). Therefore, these effects need to be taken into consideration during interpretation. Below we describe different mechanisms involved in HC cooling process.

4 a. Hot Phonon Bottleneck¹⁸

One of the primary modes of relaxation of charge carriers is by a mechanism called Froehlich interaction. In a polar semiconductor,like lead halide perovskites, a strong interaction exists between a macroscopic electric field due to longitudinal optic (LO) phonon and electrons. Therefore, this interaction is accompanied by release of LO phonon during cooling process. Under low pump intensity the LO phonon is decays by phonon-phonon interaction like Klemens mode, and LO dissipates further to two longitudinal acoustic (LA) phonons. Excitation with pump pulses leading to high carrier densities leads to accumulation of LO phonon if the phonon-phonon interaction decay times are large leading to a non-equilibrium phonon population and hindered cooling. This process is called hot phonon bottleneck. Typical way to describe this is by extracting the energy loss rate as given below,

$$\left(\frac{dE}{dt}\right)_{Phonon} \approx -\frac{\hbar\omega_{LO}}{\tau_{ave}} \left\{ \left(e^{-\frac{\hbar\omega_{LO}}{k_b T_c}}\right) - \left(e^{-\frac{\hbar\omega_{LO}}{k_b T_L}}\right) \right\}$$
(1)

where $\hbar \omega_{L0}$ is the phonon energy, is the HC cooling time and and are the carrier and lattice temperatures respectively⁷.

In case of lead halide perovskites, it is reported that under low carrier densities $<<10^{18}$ / cm³ the decay is found to be fast <1ps and typically can be accounted to Froehlich interaction. However, under high carrier densities $>>10^{18}$ / cm³ the cooling rate is slow ad takes place in the time scale of 10s of ps. Indicating hot phonon bottleneck in play.

4 b. Auger Heating

At higher carrier densities $\sim 10^{19}/\text{cm}^3$, individual crystals can harbour multiple excitons. These multiexcitons interact via coulomb interaction and undergo carrier-carrier scattering where, via an energy transfer process, a single exciton transfers its energy to a carrier leading to creation of a hot exciton as shown in the figure. Therefore, in each of the Auger recombination process the excessenergy becomes the kinetic energy of the carriers and eventually this energy is released by carrier phonon interaction. As one increases pump intensity the distribution of exciton, biexciton and triexciton exists in accordance with Poisson distribution governed by , whereis the average number of excitons/ crystal, is pump fluence and absorption cross section. In a multiparticle system, say for e.g. triexciton, each recombination of triexciton forms hot biexciton, energy equivalent of Eg is converted to kinetic energy of the carriers. Subsequently biexcitons decay to a hot exciton etc. The Auger heating rates are therefore directly proportional to the number of particles within the system as given below in equation 2⁷.

$$\left(\frac{dE}{dt}\right)_{Auger} = E_g R_A (N(N-1))^{-1}$$
(2)

where is the Auger recombination rate.

With a large number of excitons in the system each of the recombination disperse a large amount of energy in the system. Initially the carriers cool at a rate governed by Froehlich interaction for which the energy loss given in eq 1. According to the above equation, as carrier temperature decays the energy loss rate also decreases until this rate matches with the Auger heating rate. Beyond this time, the HC cooling rate is governed by the balance between Auger heating and electron-phonon interaction mediated cooling. Therefore, there is a one to one correlation between Auger recombination and the T_{c} .

4 c. Acoustic-Optic Phonon Up-conversion

Under still higher carrier densities, LO phonon decays to Acoustic modes and these Acoustic phonons propagates through the solid and dissipated heat³⁰. However, if a given materialhas a low thermal conductivity, propagation of the Acoustic modes is hindered. This in turn leads tolocalisation and therefore longer lifetime for Acoustic phonons and thereby increasing the probability of up-conversion of Acoustic phonons back to optic phonon by a process called Acoustic-Optic phonon upconversion. The probability of up-conversion is also enhanced if there exist a significant overlap between low energy optic modes and acoustic modes.In a lead halide perovskite with organic A cation, a substantially low thermal conductivity accompanied by strong overlap between low frequency modes of organic cation with lead halide phonon modes lead to high probability for an up-conversion to occur.

HC Cooling in Lead Bromide Perovskites

Typically, HC cooling is studied by using either TA spectroscopy or TRPL. The samples are excited by a pump energy greater than band gap and then a pulse intensity dependent variation in the spectra is used to index the $T_{c'}$ carrier temperature. The blue side of the exciton bleach or PL correspond to distribution of hot carriers and a MB approximation is used to extract $T_{c'}$. Slow HC cooling in Lead halide perovskites have been investigated by several groups Xing et al, Sum et al, Beard et al. Here we present some of our results on HC cooling studies by



Figure 3. (a) & (b) TEM Images and UV-Vis. Absorption Spectra of MAPbBr3 NCs respectively. (c) & (d) Normalised $\Delta T/T$ spectra for MAPbBr₃ at carrier density 1.5×10^{17} /cm3 & 10^{18} /cm³ respectively

TA spectroscopy on colloidal methylammonium (MAPbBr₃) and caesium (CsPbBr₃) lead bromide perovskite Nanocrystal (NCs).

Methylammonium Lead Bromide

The figure 3 a & b give TEM image and absorption spectra of MAPBBr₃. The nanocrystals are typically cubic in shape with a typical edge

length of ~15nm and exciton peak position ~510nm (~2.34 eV). The figures 3c& d also represent the femtosecond spectra at two different pump intensities corresponding to carrier density of 1.5×10^{17} / cm³ & 10^{18} /cm³. The spectra in both the cases shows exciton peak at ~510nm, broadened towards the blue side which correspond to HCs, with greater broadening seen at higher intensity.Additionally, the recovery of broadening is also seen faster at lower pump



*Figure 4. Carrier temperature vs Time for different carrier densities for MAPbBr*₃

intensity indicating different regimes of HC cooling. The time dependent T_c was extracted by fitting the blue side of the exciton bleach to MB statistics for each to the time slices asextracted values are shown in figure 4.

HC Cooling as seen from T_c vs time in figure 4 clearly shows multiple regimes of cooling in play. Under low pump intensity, T_c decays with a mono-exponential decay with a time constant of ~0.14-0.3ps. This decay is associated with electron-LO interactions also called Froehlich interaction as discussed earlier. Under low pump intensity N << 1, each of the NCs only possess single excitons.
However, on increasing pump intensity, the T_c decay times were prolonged with decay times of ~10-11 ps and~100 ps for carrier densities > 10^{18} /cm³. Under these pump intensities, each of the NCs can contain multiple excitons. These multiexcitons decay via Auger recombination, further heating up the system. To verify the role of Auger process, decay of the exciton bleach was used to extract τ_{Auger} which comes out to be ~30ps for carrier density ~ 10^{18} /cm³. Typically, of the HC cooling rate arising from Auger heating scales as ~ $\frac{\tau_{Auger}}{3}$ 10ps. This value is in agreement with second decay component and with previous reports on MAPbBr₃. Therefore, the second decay

component can be assigned to Auger heating. We now focus on the slowest decay component, with higher pump intensity, Auger heating leads to accumulation of LO phonons which subsequently decays to Acousticphonons. However,we see here that the T_c decay at higher intensities takes place in 100s of ps. Typically the propagation of acoustic phonon dissipates the heat through the system. However, if the thermal conductivity of system is low, then this propagation is hindered and leads to up-conversion of these acoustic phonons. In lead halide perovskites, the thermal conductivity of hybrid organic inorganic perovskites is <1 W/K/m which results



Figure 5. (a) Fits of TA spectra for different time slices (b) Carrier temperature vs Time. Inset: Extracted Quasi Fermi Level vs Time. (c) Carrier Temperature vs Time for different carrier densities.



Figure 6. (a) Energy Loss Rate vs TC. Solid Lines are fits to corresponding model, Dots are the data points. (b) Auger and HC Cooling Rates with respect to volume

from anharmonic phonon-phonon scattering. This in turn leads to inability of the system to dissipate heat and therefore resulting in higher up-conversion efficiency. The HC cooling is slow at high intensities and hints at potential of this material towards HC solar cells.

Caesium Lead Bromide

Below we discuss how HC cooling behaves in all-inorganic perovskite specifically CsPbBr₃. This study was conducted on colloidal samples of 3 different sizes with edge length of 8.1, 10.7, 13.4nm respectively. The fits to exciton bleach and extracted carrier temperature for 3 different carrier densities are represented in figure 5. It is clear from figure 5 that the T_c decay is single exponential for low carrier density of ~2×10¹⁷/ cm³. However, at the highest carrier density, 3×10^{18} /cm³, we observe that the T_c decay is biexponential. This is in contrast to MAPbBr₃ as seen above which showed a third decay component even at carrier density of ~10¹⁸/cm³.

The slowest decay component has a lifetime of ~0.2-0.3ps and this lifetime is typically due to Froehlich interaction. Therefore, role of LO cooling was explored by studying the carrier energy loss rate according to eq 1. The energy loss rate with respect to T_c showed a phonon lifetime of ~0.4ps with a phonon temperature of ~ 300K. The energy loss rate of ~ 0.3 eV/ps upto 500K, which drops to <10⁻² below 350K. These values are in accordance with LO cooling models and therefore ascertains the role of electron-LO interaction towards cooling.

However, under high carrier densities, it is observed from figure 6, that the Tc decay is biexponential upto 3×10^{18} /cm³ with decay times of ~0.3ps & 17-20ps. The energy loss rate also shows that while initial energy loss rate matches well with LO filling model, beyond 600K the loss rate drops orders of magnitude further. Second Tc decay component is ~17-20ps which matches well with Auger component. Typically for an Auger process energy loss rate which scales with $\Delta T_c^2 (\Delta T=T_c-T_L)$. A good fit for Auger heating as shown in the figure 5a ascertains the role of Auger heating. In the present study, we have conducted hot carrier cooling for three different size of CsPbBr₃ NCs. The Auger time has a sublinear scaling and HC cooling, this sublinear scaling has been observed before and HC cooling times has a one to one correspondence with Auger times, this ascertains role of Auger process. Typically, A-site cation has been known to have little influence on nature of frontier bands (Valence and conduction band) as valence and Conduction bands are primarily composed of Pb and X orbitals. However, the HC cooling dynamics is shown to be dramatically different in both these cases.

Conclusion

Lead halide perovskites are a class of materials that have immense potential not only in optoelectronics but also in electronics, sensors etc. Their use in thin film photovoltaics has been extensively investigated. The study of HC cooling dynamics only adds to the potential of these material in beating S-Q limit. While it has been shown previously that extraction of HC ischallenging owing to their fast decay times, the possibility of longer T_c in these materials shows their untapped potential. Our studies as described in this review is just one of many on HC cooling perovskite colloids. Here we showed that hot carrier cooling depends on materials properties. For e.g. in case of MAPbBr₃ the HC cooling have been shown to exhibit multiple regimes of decay with the fastest times assigned to Froehlich interaction. The slowest time governed by Acoustic Optic phonon upconversion extending to 100s of ps. However, in the case of CsPbBr, the decay is predominantly governed by Auger heating. Such contrasts show subtle variation in A-site leads to drastic change in HC cooling. Additionally, both B-site and Halide site changes also have been shown to impact HC cooling. These studies suggest that halide perovskites have immense potential in HC solar cells with immense potential to be manipulated with change in ions.

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Radiation-processed functional polymers

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Abstract

Radiation-processed functional polymers represent a growing field in materials science, offering transformative potential across various industries including healthcare, automotive, environmental conservation, and advanced manufacturing. This article explores the multidisciplinary fusion of radiation processing techniques with functional polymers, revealing avenues for controlled alterations at the molecular level to achieve desired characteristics and functionalities. Through specific examples, this paperdemonstrates applications of high energy radiation in modifying the physical, chemical, or biological properties of polymers. Exploration spans a range of applications such as drug delivery systems, chemical sensors, and fuel-resistant elastomers, elucidating their underlying principles, innovative approaches, and real-world implications.

Keywords: Radiation Processing, Functional Polymers, Drug Delivery Systems, Chemical Sensors, Fuel-Resistant Elastomers

Introduction

The sphere of polymer science has witnessed a revolutionary transformation heralded by innovations that have transcended traditional boundaries. Among these advancements, the domain of radiation-processed functional polymers has emerged as a paradigm-shifting frontier, blending the realms of physics, chemistry, and engineering to foster unique applications[1]. Within this interdisciplinary relationship, the functionalization of polymers through radiation processing has evolved as a vital methodology, unlocking a multitude of capabilities and functional characteristics that conventional polymers can scarcely offer [2-5].

Radiation processing, a method employing various forms of radiation, such as gamma rays, electron beams, or X-rays, serves as a sophisticated tool to modify the physical, chemical, or biological properties of materials. When applied to polymers, it paves the way for controlled alterations at the molecular level, enabling the enhancement of certain attributes or integration of entirely new functionalities. The appeal of radiation processing lies not only in its precision, but also in its versatility, accommodating a wide spectrum of materials and applications. Functional polymers are polymers endowed with specific functions that may be responsive, adaptive, or specific to particular applications. The ability to design polymers with the desired characteristics has profound implications across various industries, from healthcare and environmental conservation to advanced manufacturing. Radiation processing takes this functionalization to novel heights, offering control and finesse that traditional chemical processes often struggle to achieve [6].

In the field of healthcare, radiation-processed functional polymers facilitate innovations, such as controlled drug release systems and novel sensors. By modifying the properties of the polymer, researchers can control the release of drugs into the body or detect specific chemicals, offering personalized treatments and real-time monitoring. In the automotive industry, the development of fuel-resistant elastomers compatible with both biodiesel and petrodiesel signifies a remarkable stride towards sustainability and energy diversity. The environmental advantages of radiation processing are noteworthy, providing a greener alternative to conventional methods. The lack of harmful solvents and the potential for waste reduction underscores its alignment with contemporary sustainability goals. Moreover, the scalability of radiation processing ensures its suitability for large-scale industrial applications.

Despite their immense promise, the field of radiation-processed functional polymers is not without challenges. The complex interplay between radiation type, dose, polymer selection, and desired functionality demands a profound understanding of the underlying mechanisms. A delicate equilibrium must be maintained to achieve the intended outcome without unintended alterations or damage. This requires not only technological prowess, but also a nuanced appreciation of the material's behavior under radiation.

This article delves into the world of radiationprocessed functional polymers, elucidating the scientific principles behind their synthesis, exploring their applications across various domains, and examining the challenges and prospects that lay ahead. By combining insights from cutting-edge research, this study provides a comprehensive overview of a field that stands at the intersection of innovation, functionality, and sustainability, setting the stage for in-depth exploration of a subject that is as intriguing as it is impactful.

Radiation processed flexible polymeric shielding materials for soft gamma

Advancements in flexible polymeric shielding materials have emerged as a focal point of research, particularly in fields requiring protection from soft gamma rays. These applications necessitate meticulous exploration of the mechanical properties and gamma attenuation characteristics of the materials [7, 8]. Recent studies have focused on the nuanced analysis of radiation-induced crosslinking and the impact of filler compositions, with particular attention to Bi₂O₃, on the integrity and gamma shielding efficacy of polymer composites. To understand the mechanical properties, researchers have uncovered that the application of reinforcing fillers and radiation-induced crosslinking offers a remarkable enhancement in the physical structure of polymers. A comprehensive examination of the elongation at break (EB) of the composites revealed a decrease in EB corresponding to an increase in the Bi₂O₂ fraction and absorbed dose. This decrease reflects the intricate formation of intermolecular crosslinked networks, impeding chain slippage, and subsequently diminishing elongation. The correlation between filler content, absorbed radiation dose, and elongation at break not only provides vital insights, but also sets the stage for precise manipulation of the material structure to attain specific mechanical attributes. Moreover, the increase in Young's modulus with both the absorbed dose and Bi₂O₃ loading adds to the understanding of material stiffness.A macroscopic model, intricate weaving factors such as filler and matrix moduli, serves to enrich the theoretical interpretation of these discoveries.

When shifting the focus to attenuation studies, the performance of the PDMS/Bi₂O₃ composites in shielding gamma radiation from Am-241 was noteworthy. Interestingly, the shielding efficiency remained relatively unaffected by the increase in the radiation dose, whereas the filler loading played a pivotal role. Even a modest 10 wt% Bi₂O₃ loading yielded 50% attenuation, which increased to 70% with 30 wt% loading, yet only resulted in a 40% increase in density over the unfilled PDMS. This finding emphasizes the exceptional potential of flexible polymeric composites to provide potent radiation shielding, capitalizing on the unique attributes of Bi₂O₃.Figure 1 shows the changes in the mechanical and attenuation properties of the processed PDMS- Bi₂O₃ composites.

In encapsulating these multifaceted evaluations, the harmonization of mechanical properties with gamma attenuation studies is a ground-breaking step towards the evolution of flexible shielding materials for soft gamma rays. The tailored orchestration of radiation-induced crosslinking with specific filler loadings provides a strategic pathway for fabricating materials with mechanical robustness and effective radiation shielding.This innovation holds promise for safer applications in nuclear fuel processing and space exploration, in which managing radiation exposure is critical.

These pioneering developments in understanding the interplay between gamma radiation, mechanical properties, and gamma attenuation in polymeric shielding materials signify a landmark in radiation-protection technology.Insights derived from optimizing the balance between crosslinking, filler composition, and mechanical integrity form the foundation for future innovations. These advancements have led to a new era in safety and sustainability across applications, where gamma radiation exposure is a pertinent concern. This reinforces the potential of flexible and proficient shielding materials tailored to the diverse demands of different industries, thereby setting the stage for further exploration and refinement in this critical field.

Radiation processed strain sensors

Radiation processing of polymers represents a significant advancement in the



Figure 1: (1) Variation in elastic modulus of composites with absorbed dose (a) 100 kGy (b) 200kGy (c) 400 kGy (2) Variation in attenuation of different composites irradiated to different doses. Inset: Variation in counts with Bi_2O_3 (wt. %) at two different radiation doses[9].

field of functional materials, and among its many applications, the development of strain sensors is a particularly exciting area of research[10, 11]. This process involves the use of high-energy gamma radiation to induce controlled crosslinking in thermoplastic-elastomeric blends and composites, such as those containing conducting carbon nanoblack (CCNB) and graphene. This crosslinking is instrumental in enhancing the mechanical properties of the material, potentially leading to marked increases in attributes such as the elongation at break and gauge factor. This transformation offers the possibility of fine-tuning the mechanical properties of the material, thereby allowing for a new level of customization. The graphene integration at specific weight fractions further contributed to these enhancements. The interplay between radiation, graphene content, and crosslinking density opens a pathway for adjusting the essential properties, such as the elastic modulus. The discovery of the optimal conditions for such integration could lead to further advances in the field.

One particularly innovative aspect of radiation processing is the control of percolation dynamics, in which conducting particles interconnect within the insulating polymer phase. This phenomenon can be precisely controlled by radiation exposure, allowing for substantial resistance changes.Such control over percolation dynamics has wide-ranging implications for strain sensing and other potential applications. Another critical area of exploration is the effect of radiation on the crosslinking density within the material. The ability to manipulate radiation doses to induce variations in gauge factors and interfacial bonding may lead to a deeper understanding of the functional properties of the material. The intricate relationship between the radiation-induced crosslinking density and the overall behavior of the material adds another layer of complexity and opportunity for research. Moreover, the focus on radiation processing does not reside solely within the laboratory.Its potential applications in automotive, healthcare, and aerospace industries demonstrate the realworld implications of this technology.Strain sensors developed using this method can become integral components in various advanced systems, providing more accurate and reliable measurements. In figure 2 response of a strain sensor irradiated to different doses is elucidated.

Overall, the development of radiationprocessed strain sensors is an exciting frontier in the field of functional polymers.By leveraging the unique capabilities of radiation processing, researchers have explored new avenues for constructing advanced strain sensors and other functional materials.The complexity of interactions, possibility of customization, and real-world applications all contribute to a rich and promising area of study.This overview points to a future in which the role of radiation in material science continues to evolve and expand, offering novel solutions to longstanding challenges, and leading to innovations that could reshape numerous industries.



Figure 2: Effect of dose on cyclic strain sensing of a polyolefin based conducting polymer composite at 10% strain (a) 50 kGy (b) 200 kGy.

Drug delivery systems

The field of drug delivery has experienced transformative advancements, particularly with the integration of radiation processing in the development of polymer nanocomposites. Among these are matrices reinforced with graphene composed of materials such as carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), tailored for controlled drug release[12].The synthesis of these materials generally involves intricate processes, such as solution blending and sonication-assisted dispersion.What sets this approach apart is the application of varying high-energy radiation doses to induce specific degrees of crosslinking, which appears to have a profound impact on the drug release kinetics. This technique shows that radiation plays a substantial role in modulating drug release. One of the core observations centers on the correlation between the radiation dose and the rate of drug release. An increase in radiation dose appears to slow down drug release, with a marked difference between the various absorbed radiation doses (figure 3). This pattern may open doors to highly customizable drug delivery systems, allowing medical professionals to tailor treatments more precisely according to individual patient needs.

However, the role of graphene in this matrix is complex. While it significantly enhanced the elastic modulus, its influence on drug release timing was comparatively minimal. These findings suggest a marginal delay in drug release at certain concentrations of graphene, but the overall effect seems limited. These insights contribute to a more nuanced understanding of how radiation and graphene interact to control drug-release mechanisms. The selection of polymers such as PVA and CMC further contributes to the effectiveness of this system. PVA's inherent hydrophilic qualities and adaptability through gel formation and crosslinking methods, paired with CMC's water uptake and customizable properties, create a balance between drug release and mucoadhesive behavior. This combination, coupled with the pronounced effects of radiation, represents a significant step in the field. Moreover, this approach to drug delivery offers a glimpse into its potential future applications in medicine. Controlled and targeted drug delivery has long been a focal point of research, and the use of radiation-induced crosslinking paired with



Figure 3; Effect of absorbed radiation dose on doxycyline release Kinetics for PVA-CMC (4:1) nanocomposites loaded with 3 wt% graphene (A) 25 kGy (B) 75 kGy (c) 150 kGy[12].

graphene reinforcement provides a promising pathway.

Radiation processed chemical sensors

The field of radiation-processed functional polymers opens up numerous possibilities for innovation and technological advancements. Among these diverse applications, the enhancement of chemical sensors through radiation processing is particularly notable. Chemi-resistivity, where the resistance of a material changes upon exposure to specific chemicals, is an intriguing phenomenon that can be harnessed for chemical detection. This feature is pivotal in various contexts, such as the detection of volatile organic compounds, and is becoming an essential component of modern chemical sensing technology[13-15]. Enhancing the chemiresistive response of conducting polymer composites (CPCs) requires an understanding of the complex interplay between various elements. The exploration of different combinations of unfunctionalized and functionalized carbon nanotubes (CNT), polydimethylsiloxane (PDMS), and gamma radiation reveals that these components can be manipulated to create marked enhancements in chemiresistive properties. Through the preparation of various chemiresistors using different CNT combinations with gamma radiation, insights into the role of functional groups and their interactions with polymer matrices have been gathered.Specific functionalizations, such as CNT-COOH, appear to result in superior interfacial interactions, shedding light on the influence of chemiresistivity.

The choice of functional groups on CNT and radiation dose affect the properties of chemiresistors in a dose-dependent manner. The correlation between these factors provides a glimpse into how radiation-induced grafts and immobilization techniques can be implemented.A more in-depth understanding of how chemiresistivity can be controlled and enhanced is offered by examining the response and sensitivity at specific dose levels.The evidence of radiationinduced linkages and variations in the polymer chain density contributes to the comprehensive knowledge of interfacial characteristics.

Radiation effects have also been thoroughly examined, with observations highlighting an increase in chemi-resistivity with dose and discerning differences based on the functionalization of CNT. These findings emphasize the primary role of the CNT-PDMS interfacial characteristics rather than the radiation-induced changes in the bulk material. Overall, the exploration of the chemiresistive properties of CPCs, the influence of CNT functional groups, and the strategic application of gamma radiation contribute to the broader field of radiation-processed functional polymers (figure 4). This underscores the potential of modifying the chemiresistive properties of CPCs through controlled adjustments, fostering the creation of reproducible and precise chemical sensors.



Figure 4: Change in A_r (Change in resistance/Initial resistance) after exposure to successive air-toluene cycles, three cycles of a fixed concentration were used followed by increased concentrations[14].

Radiation Processed Fuel resistant elastomers

The development of elastomers capable of withstanding both biodiesel and petrodiesel is central to the growth and sustainability of biofuels.Within the context of radiationprocessed functional polymers, this subject is of paramount importance, as it intersects with renewable energy, environmental sustainability, and material science. Traditional elastomers have struggled to provide resistance to both biodiesel and petrodiesel owing to their differences in polarity.The distinctive chemical properties of these fuels pose challenges that demand innovative solutions for compatibility, particularly in automotive applications, where elastomers are essential in fuel-sealing systems.

The use of Ethylene Propylene Diene Monomer (EPDM) and acrylic acid (AA) in grafting polymers is a promising approach. This method facilitates the creation of materials with differing polar and dispersive components, thereby enhancing the fuel resistance and tensile strength without compromising elongation.The mechanism behind this success revolves around the orientation of the polar group of biodiesel, which forms a barrier against further diffusion of fuel molecules (figure 5). This discovery forms a cornerstone in the advancement of materials compatible with fuels with diverse solubility profiles, thereby addressing a significant obstacle in automotive engineering. Contrary to the success of EPDM and AA grafting, traditional elastomers, such as acrylonitrile butadiene rubber (NBR), exhibit limitations.While historically used for its resistance to petrodiesel, NBR's vulnerability to biodiesel underscores the deficiency of conventional elastomers. The disparity in the polarity of biodiesel and petrodiesel leads to significant mechanical deterioration, revealing the shortcomings of traditional methods. The quest for elastomers suitable for biodiesel and petrodiesel blends is further complicated by the challenges of blended fuels. Although some approaches based on solubility parameters might propose certain nonpolar or polar elastomers for specific fuel types, they falter when applied to blends. Altering the composition of biodiesel for compatibility also becomes a daunting task because of the diversity of production processes. In the broader picture, this research emphasizes the significance of biodiesel as a renewable fuel derived from biomass, highlighting its environmental merits and global efforts to foster its usage.Although intricate, the compatibility challenge is not insurmountable. By leveraging the principles of radiation-processed functional polymers, this research paves the way for the design of advanced elastomeric materials that perform effectively in both biodiesel and petrodiesel environments.

The methodologies explored, particularly the innovation in modification and grafting, reflect the adaptability and potential of radiationprocessed polymers[16-18]. These methods represent emblematic achievements for both industrial and sustainability initiatives. By providing practical solutions to complex problems, this research contributes significantly to automotive engineering and represents a compelling model for interdisciplinary exploration. Overall, the endeavor to create fuel-resistant elastomers resonates as a vibrant example of how radiation-processed functional



Figure 5: Fuel uptake by AA-g-SiEP (acrylic acid grafted, silica/EPDM composite) (A) Effect of fuel blend ratio on fuel uptake (B) Schematic representation of preferred arrangements due to orientation of biodiesel molecule[19].

polymers can offer transformative solutions. The intersection of material science with environmental considerations presents a fascinating area for continued investigation, contributing not only to technological advancement, but also to the broader goals of renewable energy and environmental stewardship.

Conclusion

The exploration of radiation-processed functional polymers has illuminated the vast potential of these materials in a diverse array of applications, from the medical realm to the industrial and environmental sectors. Through meticulous study and innovation, researchers have harnessed the unique properties and transformative capabilities of radiation to craft polymers that address some of the most pressing current challenges. Whether it is the meticulous modulation of drug delivery kinetics or the design of resilient elastomers compatible with biofuels, the role of radiation in enhancing polymer functionality remains unknown.

This comprehensive analysis of radiationprocessed functional polymers, spanning their use in drug delivery systems, chemical sensors, and fuel-resistant elastomers, offers a profound understanding of the intricate interplay between radiation and polymer characteristics. It is evident that as we navigate the demands of a rapidly evolving technological landscape, the significance of these advanced materials will be amplified. Their versatility, combined with the precision with which their properties can be modified through radiation, positions them as pivotal tools for shaping future innovations across multiple disciplines.

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Shri. C.V.Chaudhari has been working on the modification of polymers by using radiation induced grafting of hydrophilic or hydrophobic monomers on the polymer backbone to improve oil resistance, thermal properties, solvent resistance, compatibility between the incompatible polymers and radiation processing of polymer blends for desired applications. Radiation induced grafting of monomers on the polymer backbone includes grafting of methacrylic acid on ethylvinyl acetate, grafting of glycidylmethacrylate on low density polythene, glycidylmethacrylate on Teflon scrap.
Dr. K.A Dubey is working as a scientist in Radiation Technology Development Division, Bhabha Atomic Research Centre. His research interest includes radiation processing of polymer blends, alloys and nanocomposites for advanced applications. Presently he is engaged in radiation processed conducting polymer composites for various advance applications, biodegradable polymers, over current protection devices, toxic volatile sensors and high modulus composites.
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Tapping the Potential of Ionizing Radiations in the Synthesis of Nanomaterials

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Abstract

Given the imminent applications of nanomaterials, it is imperative to develop methodologies that incorporate eco-friendly, scalable, time-efficient and cost-effective attributes, whilst ensure precise control over their morphologies *vis-à-vis* properties. In this perspective, radiation-assisted approach for the synthesis of nanomaterials can contribute a lot in addressing these challenges. This article presents an overview of the application of high energy ionizing radiations (such as e-beam or γ -rays) in the production of a variety of nanomaterials with unique features which otherwise necessitate intricate and laborious procedures in conventional techniques. The core principle in radiation-assisted synthetic approach lies in the radiolysis of solvent, and subsequent reactions of formed radicals/intermediates with dissolved precursor compounds. Therefore, a brief discussion is provided on radiolysis and the proficient utilization of the radicals generated in-situ for the synthesis of various nanomaterials. Furthermore, the role of various experimental parameters, especially absorbed dose, dose rate, host matrix, and capping agent has been explained in the manipulation of nucleation and growth mechanisms, which ultimately director control the characteristics of nanomaterials. Lastly, the challenges pertaining to the radiation-based synthesis are delineated, alongside the proposed improvements aimed at surmounting said challenges.

1. Introduction

Nanomaterials are different from bulk materials and their relevance stems mainly from the unique physicochemical properties (such as, mechanical, optical, thermal, magnetic, biological, electrical, and chemical) that emerge at the nanoscale due to quantum effects [1-5]. More so, high surface area-to-volume ratio is one of the main characteristics of materials at nanoscale dimensions. Needless to say, in the last three decades, the field of nanotechnology has witnessed tremendous advancement in terms of innovation and development [1-5]. Some of the prominent applications of nanotechnology today (with examples) are presented in Figure 1.

Nanomaterials are poised to revolutionize numerous sectors, including energy, healthcare, and the environment, in the near future. However, it is crucial to develop a sustainable and eco-friendly protocol for their synthesis with minimal use of corrosive, flammable reagents and toxic/hazardous chemicals (i.e., reducing and capping agents). In this perspective, ionizing radiation (e.g., e-beam, γ -ray) assisted synthesis of nanomaterials is a well-known technique, and offer many advantages [6-22], as shown in Figure 2.

2. Radiolysis: Core principle of radiationassisted approach

Till now, variety of nanomaterials have been prepared using radiation-assisted approach, which include metals, metal oxides, metal alloys, core-shell systems, carbon-based, ceramics, polymer, organic and semiconductor-based [6-23]. The core principle of radiation-assisted approach is based on radiolysis of the solvent medium. In aqueous solution, the radiolysis by high energy ionizing radiations lead to the formation of various species (radicals, ions,



Figure 1. Schematic representation of the prominent applications of nanotechnology.



Figure 2. Schematic illustration of the advantages of radiation-assisted approach.

molecular), which is generally represented as [6-11,24,25]:

$H_20 \longrightarrow e_{solv}^-, H^\bullet, \bullet OH, HO_2^\bullet, H_2O_2, H_3O^+$ (1)

The solvated electrons, esolv-and H• are strong reducing agents with redox potentials of -2.9 and -2.3 V_{NHE}, respectively. The 'OH radicals are highly oxidizing in nature with a redox potential of +2.7 V_{NHE} in acidic media, while +2.18 V_{NHE} at pH 7.0. In strongly alkaline solution (e.g., at pH 14), 'OH rapidly transforms to 'O⁻. Since, esolv⁻ and •OH possess strong redox potentials and highest radiolytic yield (represented by G-values in per 100 eV; G $(esolv^{-}) = G(\bullet OH) = 2.7, G(H \bullet) = 0.6$ they are the major redox agents used in the radiationinduced synthesis of nanomaterials in aqueous solutions. Obviously, radiation-assisted synthesis of nano materialsis driven (in general) by either reducing or oxidizing a soluble precursor to the desired oxidation state, as can be seen from these reactions [6-11,26-28]:

$$M^+ + e_{solv}^- \rightarrow M^0 \tag{2}$$

 $M^+ + H^{\bullet} \rightarrow M^0 + H^+$ (3) (3)

 $M^{x+} + HO^{\bullet} \rightarrow M^{(x+1)+} + OH^{-}$ (4)

It is feasible to manipulate the redox conditions (either oxidative or reductive) of irradiated aqueous solutions by the addition of selective radical scavengers. For instance, to scavenge H[•] and 'OH radicals produced during aqueous solution radiolysis, *tert*-butanol is added to the reaction mixture. Their scavenging would allow only the esolv-to react with precursors, causing the reaction to proceed according to the equation below [24,25]:

 $CH_{3}(CH_{3})_{2}COH + {}^{\bullet}OH (H^{\bullet}) \longrightarrow {}^{\bullet}CH_{2}(CH_{3})_{2}COH + H_{2}O (H_{2})$ (5)

The organic radical formed in the above reaction is less reactive (than) and thus, remains unaffected for carrying out further reaction with precursor compound. Also, the organic radical formed from *tert*-butanol has an additional advantage of absorbing very weakly in the UV region, thereby minimizes any potential interference (it may cause) in the measurement of absorption spectra pertaining to other product species.

The redox condition of the irradiated system can be adjusted to purely oxidative by simply saturating the solution with N_2O (saturation

solubility of N_2O in water is ~ 25 mM), which converts to 'OH radical [24,25]:

$$e_{\rm solv}^{-} + {\rm N_20} \rightarrow {\rm N_2} + {\rm 0^{--}} \xrightarrow{{\rm H_20}} {\rm 0H^-} + {\rm ^{-}OH} \ (6) \ k = 9.1 \times 10^9 \ M^{-1} \ s^{-1}$$

The reaction of N₂O with H[•] is slow (k = 2.3×10^{6} M⁻¹ s⁻¹), and majority of the radicals available in N₂O saturated aqueous solutions are [•]OH radicals. The pH of the solution also plays a crucial role. At pH > 11, H · reacts with OH⁻ (H · + OH⁻ \rightarrow esolv⁻), which leads to an increase in G (•OH) by up to 0.6 (i.e., by G (H•)). Whereas, at pH < 3 reaction, the fraction of the oxidizing radicals decreases due to the competition of reaction (6) with the reaction (7) [24,25]:

$$e_{solv}^- + H_3 0^+ \rightarrow H^{\bullet} + H_2 0$$
 (7)

Thus, in order to carry out a synthesis (or to study its reactions) with OH radical in acidic conditions (especially pH< 3), the solutions are generally saturated with oxygen (O_2). As a result, H• and esolv- reacts readily with O_2 and get scavenged from the system resulting in an oxidizing condition.

3. Radiation-assisted synthesis of Nanomaterials

A schematic depiction of a general scenario representing the radiation-assisted synthesis of nanomaterials is shown in Figure 3.

As mentioned earlier, one of the main advantages of this approach is the availability



Figure 3. Schematic depiction of a general scenario representing the radiation-assisted synthesis of nanomaterials.

of various experimental parameters for tuning/ controlling the features of nanomaterials (such as size, shape, surface area, composition, size distribution, etc.) [6-23,26-28]. These experimental parameters include absorbed dose, dose rate, irradiation source (type or nature of ionizing radiation used for irradiation), precursor concentration, capping agent, and host matrix. The role of some of the main parameters in influencing the size, shape and composition of nanomaterials has been briefly discussed in the following sections.

3.1. Nature of irradiation source

In general, accelerated electron-beam and γ -rays have been mostly used as the irradiation sources for the synthesis of nanomaterials. However, there are few reports where researchers have also used X-rays, proton beams, and heavy ion beamsas irradiation sources [29-32]. Essentially, these irradiation sources can be classified based on their linear energy transfer (LET), which decides the penetration of the radiation and the radiolytic yield of species formed on ionization. X-rays, y-rays and accelerated electron beams (1-10 MeV) are low-LET ionizing radiations, while ion beams are high LET radiations. The LET effect of different irradiation sources on the properties of nanomaterials have been reported in the literature [29-32]. For instance, Remita et al. [29] investigated the LET effect of different ionizing radiations (y-rays, electron or C⁶⁺ ion beam irradiation) on the synthesis of silver nanoclusters in aqueous solution. It was observed that the LET influences the shape of the particles as well as their formation yield. Specifically, it was noticed that the radiolytic reduction yield decreases at higher LET values. In a comparative study conducted by another research group [30], the synthesis of silver nanoparticles using y-rays, electron-beam, and synchrotron X-ray irradiation was carried out. The study found that the former two irradiation sources resulted in smaller nanoparticles with a narrower size distribution compared to the latter

one.Varma et al. [31] reported the formation of Cu nanoparticles in fused silica glass using swift heavy ion beams (i.e., 120 MeVAg⁹⁺ ions). Kim et al. [32] reported the formation of Pt nanomaterials by using a proton beam. Additionally, the authors demonstrated morphology tuning of the Pt nanoparticles by simply varying the average beam current and duration time.

The aforementioned studies clearly demonstrate "irradiation sources" as a potential tool for manoeuvring the characteristics of nanomaterials. However, there remains a scarcity of research pertaining to the utilization of high LET ionizing radiations in the synthesis of nanomaterials.

3.2. Absorbed dose

In order to quantify the radiolytic products as a result of radiolysis, it is imperative to ascertain the precise amount of energy absorbed by a substance with a specific mass. This quantification of energy is accomplished using the absorbed dose, which essentially measures the absorbed energy by a substance per unit mass. The SI unit of dose is Gray (Gy). 1 Gy equals to 1 joule of energy absorbed per kilogram of matter (1 Gy = 1 J kg⁻¹) [24,25]. In radiationassisted approach, the determination of absorbed dose necessary for the complete transformation of precursors into nanomaterials is of utmost importance. Furthermore, it is imperative to optimize the absorbed dose, as an excessive or insufficient amount can bed etrimental for the resulting nanomaterials. For instance, an excessive amount of absorbed dose (than the optimized one) can result in the decomposition of nanomaterials, or the emergence of defects within them. Additionally, excessive dose can lead to the formation of unwanted by products [6-11,26-28]. On the contrary, when a lower absorbed dose is administered than what is optimized, it leads to the presence of unreacted residual precursors. Both of these scenarios may result in low yield as well as poor quality (such as purity) of the nanomaterials.

Absorbed dose has been a handy tool for the researchers for manoeuvring the morphology of nanomaterials. In general, it has been observed that the average particle size decreases with increasing absorbed dose due to the domination of nucleation over the growth process, whilst particle size distribution increases [6-22,26-28]. It has also been reported by our group where CdSe QDs synthesized in AOT microemulsions (schematic illustration in Figure 4A) exhibited blue-shift in their excitonic peak with the increase in the absorbed dose, which clearly signifies decrease in their size (Figure 4A (a)) [14]. Similar findings were obtained in another work on the synthesis of β -cyclodextrin (β -CD) coated CdSe QDs, where the excitonic peak undergoes blue shift with the increase in absorbed dose (see Figure 4B (b)) [17].

Besides, the influence of absorbed dose on the shape of nanomaterials has also been reported in the literature. Abedini et al. [33] reported the formation of small spherical Ag nanoparticles (in the presence of PVA) by γ -ray irradiation at low irradiation doses, while it transformed to triangular nanoplates at higher absorbed doses (Figure 5).

Based on the aforementioned studies, it is evident that the absorbed dose exhibits potential as an effective tool for manipulating size and shape, thereby facilitating the pursuit of desirable properties (e.g., optical, electrical, magnetic, etc.) for diverse applications.

3.3. Dose rate

Dose rate refers to the quantity of radiation absorbed per unit of time. Dose rate serves as a pivotal factor in governing the intricate nucleation-growth reactions. Essentially, the effect of dose rate is similar to that of absorbed dose in modifying the nanoparticles size. As a rule of thumb, in solution, a higher dose rate promotes the creation of multiple nucleation centres, resulting in the synthesis of small nanoparticles with a narrow distribution [6-11,26-28]. Conversely, when the reaction solution is exposed to low dose rates, the growth of the nanoparticles is enhanced which leads to the formation of larger nanoparticles. This is attributed to the fact that the rate at which reducing radicals are produced is slower than the rate at which ions associate with atoms. The effect of dose rate on the size of nanoparticles is schematically represented in Figure 6.

Researchers have utilized dose rate in the formation of nanomaterials with tunable morphologies and compositions. For instance, dose rate has been effectively used to create coreshell or alloyed clusters of bimetallic compounds. Remita et al. [34] reported the radiolytic synthesis of mixed Au^{III}/Pd^{II} solutions at different dose rates. It was found that a bilayered cluster of Au core-Pd shell is formed at low dose rate, while, genuine alloyed clusters are formed at high dose rate. Likewise, Treguer et al. [35] conducted the radiolysis of mixed Au^{III}/Ag^I solutions at different dose rates. It was observed that at low dose rate, silver-coated gold aggregates are formed. On the contrary, at high dose rate, bimetallic alloyed Ag/Au clusters are formed. Apart from the size and composition, dose rate has been found to influence the shape of nanomaterials also. For instance, Okamoto et al. [36] reported the synthesis of Au nanorods with larger aspect ratio at higher dose rate, while at low dose rate, slow reduction rate leads to formation of quasispherical Au nanoparticles (Figure 7).

Our group has also reported the significant effect of dose rate during the synthesis of CdSe nanoparticles in room temperature ionic liquid (RTIL) [15]. The observation of the formation of CdSe islands embedded within a porous structure composed of entangled Se nanofibers was noted under conditions of high dose rate (in electron beam irradiation), while, an equivalent dose of γ -radiation resulted in the formation of predominantly nanosheet like structures in conjunction with a relatively homogeneous distribution of CdSe nanoparticles.

Evidently, varying dose rate offers a convenient tool in tuning the morphology and the composition of the nanomaterials.



Figure 4.Panel (A): Schematic illustration of AOT water-in-oil microemulsion. Absorption spectra **(a)** of CdSe QDs synthesized in water-in-oil AOT MEs via electron-beam irradiation with variable radiation doses at fixed precursor concentration and W_0 value. Inset of **(a)**: Tauc plot of $(\alpha'h\nu)^2 vs$. hv for the determination of band gap values (E_g). Taken from [14]. **Panel (B)**: Schematic illustration of β-cyclodextrin (β-CD) coated CdSe QDs. UV-VIS absorption spectra **(b)** of β-CD coated CdSe QDs at various doses. Inset of **(b)** shows the Tauc plot.Taken from [17].



Figure 5. *TEM images of Ag colloids at different gamma dose. (a) At 30 kGy the spherical shape is dominant, (b) at 60 kGy the resultant shape is anisotropic, and (c) at 100 kGy triangular nanoplates are dominant. Picture taken from [33].*

3.4. Host matrix

As mentioned earlier, radiation-assisted approach overcomes many undesirable conditions associated with other conventional chemical and physical methods. However, lack of appropriate host matrices may lead to poor control over the size, shape, phase and composition of nanomaterials. In this perspective, supramolecular assemblies can contribute significantly as host matrices or soft templates in the controlled synthesis of nanomaterials using radiolytic approach [7,10-12,14,15,23,26-28].



Figure 6. Schematic illustration of the effect of dose rate on the size of nanoparticles.



Figure 7. *TEM images of Au nanoparticles synthesized by gamma-ray irradiation at varying dose rates. Picture taken from* [36].



Figure 8. SEM images of CdSe nanostructures synthesized by electron beam (a) and γ -ray irradiation. Taken from [15].

Some examples of supramolecular assemblies which have been explored as host matrices in the radiolytic synthesis of nanomaterials (by various researchers) are microemulsions (or reverse micelles), and room temperature ionic liquids (RTILs). So far, variety of nanomaterials of metals (e.g., Au, Ag, etc.), metal oxides (e.g., iron oxide), alloys (e.g., Cd–Ag), semi conductor (e.g., CdS, ZnS, PbS, CdSe) have been synthesized by this hybrid approach [7,10-12,14,15,23,26-28]. Our group has also reported the radiolytic synthesis of nanomaterials (especially, semiconductorbased) in these supramolecular assemblies [12,14,15,37,38]. These are briefly discussed as follows.

Radiolytic synthesis of CdSe quantum dots (QDs) was carried out in an anionic surfactant (AOT, i.e., aerosol-OT or sodium bis(2ethylhexyl) sulfosuccinate) based water-in-oil microemulsion [14]. Since, the water pool size of the microemulsions varies proportionately with the water to surfactant concentration ratio (W_{o}) , the size of the nanoparticles synthesized also increased accordingly. The absorption spectra of the CdSe QDs (shown in Figure 9a) exhibited red shift in the excitonic peak position with the subsequent increase in the W₀ values of the microemulsions. This categorically indicates an increase in the average size of QDs. Apart from this, the photoluminescence properties of the QDs were also tuned by varying different experimental parameters such as absorbed dose and precursor concentration. It can be observed from the chromaticity diagram shown in Figure 9b.

The CTAB (Cetyl trimethyl ammonium bromide, i.e., cationic surfactant) based quaternary water-in-oil microemulsions were also explored as the soft template for the radiolytic synthesis of CdSe nanoparticles [12,38]. Interestingly, in microemulsions with lower water content (i.e., $W_0 \le 10$), the rod-shaped nanostructures were produced. Whereas, cubic shaped nanostructures were formed upon increase in the water content (higher W_0 values) of these microemulsions. These cubes further get separated with increase in the W_0 values. Thus, a tuning of the shape of CdSe nano particles synthesized through electron beam irradiation was easily achieved by varying the water content, i.e., W_0 values of CTAB-based microemulsions [38].



Figure 9. Schematic representation of the synthesis of CdSe nanoparticles in water-in-oil AOT microemulsions using electron-beam irradiation approach. Absorption spectra (a) of CdSe QDs synthesized in AOT microemulsion with variable W_0 values at fixed absorbed dose and precursor concentration, (b) Photoluminescence tunability displayed by the QDs as shown in the chromaticity diagram at various experimental conditions. Taken from [14].



Figure 10. *TEM images of the CdSe nanomaterials* synthesized by electron-beam irradiation in water-inoil CTAB microemulsions with water to surfactant concentration ratio (W_0) as: (a) $W_0=10$, (b) $W_0=30$ and (c) $W_0=40$. Taken from [38].

Apart from microemulsions, RTILs also possess organized structure with polar and nonpolar regions co-existing in them. Thus, it could be anticipated that RTILs as host matrices might provide more opportunities to have a better control over the composition and morphology of the nanomaterials. Our group has synthesized variety of semiconductor-based nanomaterials (Se, CdSe, SnSe), in the RTILs by using high energy ionizing radiations. Unique nanomorphologies with heterogeneous composition of particles could be conveniently synthesized. For instance, morphologies such as, islands of CdSe within the Se nanofibres (explained above, see Figure 8a) [15] and porous nanostructures of SnSe [39] were formed on irradiating the RTIL containing respective precursors. Recently, we have shown how the ion-pair combination in RTILs can be exploited to control the size of Se nanoparticles [37]. The RTILs used were 1-ethyl-3-methyl imidazolium boron tetrafluoride ([EMIM][BF,]), 1-(2-hydroxyethyl)-3-methy limidazolium boron tetrafluoride ([EOHMIM][BF₄]) and 1-ethyl-3methylimidazolium methanesulfonate ([EMIM] [MS]). The size of Se NPs@[EOHMIM][BF₄] was found to be the smallest (~32 nm) followed by Se NPs@[EMIM][BF₄] (~57 nm) and Se NPs@ [EMIM][MS] (~60 nm), respectively, as can be shown from Figure 11. The observed trends could be correlated with the strength of interionic interactions in the respective RTILs as well as their packing order (density). Importantly, the RTILs played the role of a solvent, a stabilizer, and an *in-situ* source of reducing species.

In addition to the size, and the shape, the phase of nanomaterials can also be controlled by the suitable choice of the host matrix. Off late, we have shown the synthesis of Se nanoparticles in amorphous phase by using radiolytic approach [37]. Essentially, amorphous Se (a-Se) possess inherent advantages in numerous applications, such as cosmetics, electronics, photovoltaic cells, X-ray detectors, xerography and biomedical field. Taking this into account, a-Se nanoparticles are highly desirable. However, applications of a-Se nanoparticles are limited by its meticulous synthetic procedures and rapid phase transformation (due to thermodynamically unstable nature resulting in low glass transition temperature, i.e., 31°C) leading to poor stability [37,40]. Nonetheless, RTILs proved to be an excellent host matrix for stabilizing a-Se nanoparticles for longer periods of time as compared to a few *minutes-to-days*, known hitherto [40].

3.5. Capping/stabilizing agent

Capping agent play a pivotal role in the stabilization of nanomaterials by forming a protective layer around them, there by minimizing their surface energy. In general, capping agents stabilizes nanomaterials mainly through two mechanisms, i.e., electrostatic and steric stabilization [1-5]. This layer acts as a shield against aggregation, or agglomeration, which is essential to prevent uncontrolled growth of nanomaterials. Additionally, capping agents are crucial in controlling the size and shape, toxicity mitigation, chemical and biological functiona lizationof nanomaterials. Some common examples of capping agents are polymers, amphiphilic compounds, surfactants, biological molecules, etc [1-5]. In radiolytic approach, the capping agent is generally added



Figure 11. *TEM images of Se nanoparticles synthesized in RTILs: (a) [EOHMIM][BF4] (~ 32 nm), (b) [EMIM][BF4] (~ 57 nm), and (c) [EMIM][MS] (~ 60 nm). Taken from [37].*

to the sample along with precursor compounds. So, an important criterion for capping agent in this approach is radiation stability. Our group has synthesized nanomaterials using capping agents which are biocompatible, cost-effective and also inherit certain radiation stability [16-22]. Some examples are briefly discussed as follows.

For the first time ever, our group reported the synthesis of photoluminescent amorphous Si-based nanomaterials in aqueous media using radiolytic method [13,18]. It was revealed that the nanomaterials were formed via hydroxyl radical (•OH) induced reaction. The bare Sibased nanomaterials exhibit poor colloidal stability and photoluminescence quantum efficiency. Therefore, in situ capping of Sibased nanomaterials was carried during the irradiation of sample solutions. The capping agents chosen were biocompatible and exhibit radiation stability to a certain extent. In different set of experiments, the nanomaterials were capped with polyethylene glycol-10000 (PEG-10k) [19], α -cyclodextrin (α -CD) [16] and Triton X-100 (TX-100) [20]. Interestingly, not only the composition but the optical properties of Si-based nanomaterials formed were significantly different from each other. For instance, organosilicon oxide nanoparticles (OSiNPs) were formed in case of PEG-10k and TX-100, when used as capping agents. However, using α -CD as a capping agent favoured Silica nanoparticles. Furthermore, the significant difference in the photoluminescence properties of Silicon oxide nanomaterials coated with these capping agents could be realized from Figure 12. The PEGylated OSiNPs exhibited maximum photoluminescence intensity at ~425 nm for an excitation wavelength of 360 nm (Figure 12a). In case of TX-100@OSiNPs, maximum photoluminescence intensity peak was observed at~410 nm for an excitation wavelength of 340 nm (Figure 12b). Nonetheless, these nanomaterials were explored for various applications such as cell labelling, anticounterfeiting and sensing of toxic metal ions (e.g., Cr (VI)) [19] and explosive compounds (e.g., picric acid).

Interesting tunability in the photoluminescence properties of α -CD@SiO, NPs was



Figure 12. Excitation-wavelength-dependent photoluminescence spectra of PEG-10k@OSiNPs (a) [19], TX-100@OSiNPs (b) [20] and α -CD@SiO₂ NPs (c) [16]. Photoluminescence quantum efficiencies (QE) of the nanomaterials are provided in the table.



Figure 13. Schematic illustration of the formation of α -CD@ SiO_2 NPs using electron-beam irradiation and tuning of their photoluminescence with the absorbed dose. The chromaticity diagram also reflects the photoluminescence tunability. Taken from [16]



Figure 14. *Schematic illustration of the formation of*α-CD@ *TeNCs using electron-beam irradiation and their proposed photoluminescent mechanism. Taken from* [22]

observed with the absorbed dose (Figure 13), which could be attributed to the formation of a particular kind of 'defects' at a proportionate absorbed dose.

Lately, Te-based nanomaterials have gained a lot of attention due to the recent reports suggesting their promising applications in biomedical field. However, anisotropic property of Te makes it difficult to control phase and morphology of its nanomaterials. Radiolytic approach with high dose rate facilitated formation of α -CD coated photoluminescent size controlled, amorphous Te-nanocomposites (α -CD@TeNCs). Figure14 shows the schematic representation of the formation of α -CD@TeNCs through a solvated electron driven reaction (as evident by pulse radiolysis studies). Remarkable concentrationdependent killing was observed only in the case of cancerous cells, while no such trend was seen in normal healthy cells.

Radiolytic approach was used for the facile preparation of Palladium (Pd) nanoparticles coated with cyclodextrin molecules [21]. The nanomorphology varied considerably as a function of dose rate, wherein spherical-shaped nanoparticles were formed in case of high dose rate electron-beam assisted synthesis, while nanoflakes self-assembled to form nanoflower-shaped morphologies in γ -ray mediated approach involving low dose rate. Implications of morphology control was observed from the superior catalytic (in 4-nitrophenol



Figure 15. Schematic illustration of the formation of spherical and flower-shaped cyclodextrin coated Pd nanoparticles using electron-beam and γ -ray irradiation, respectively. Taken from [21]

to 4-aminophenol conversion) and anticancer properties of flower-shaped Pd nanoparticles as compared from spherical ones.

It is evident from aforementioned examples that the interplay of various experimental parameters involved in the radiation-assisted approach, such as absorbed dose, dose rate, host matrix, nature of ionizing radiations, precursor concentration and capping agent, the nanofeatures of materials can be conveniently controlled for their desirable applications.

4. Conclusions and Future Scope

The field of nanotechnology has witnessed remarkable advancements in recent years, and undoubtedly, nanomaterials are highly expected to play a significant role in our various aspects of day-today life. However, there is still dearth of an economic, eco-friendly, time-efficient methodology for the synthesis of nanomaterials with precise control over their morphology. In this perspective, radiation-based approach may address these concerns. This article presents an overview of the radiation-assisted synthesis of nanomaterials with a brief initial discussion on the fundamental aspects of water radiolysis. The generation of various primary radicals and the flexibility to create either oxidizing or reducing conditions, depending on the requirement in the synthesis of nanomaterials, have been described. This is followed by the discussion on the availability of various experimental parameters in the radiolytic approach for controlling the characteristics of nanomaterials. It has been explained how by controlling the dosage and treatment rate in radiolysis facilitatesmanoeuvring of the size, shape, composition, and other features of nanomaterials. Further, the influential role of host matrix and capping agent in directing the aforementioned characteristics of nanomaterials and their optical properties have been presented.

Evidently, radiation-assisted approach is a versatile and promising method for producing nanomaterials with tunable properties, however, there are challenges associated with this methodology. These are mentioned as follows.

- **a.** Precision in nanomaterial engineering: Although, radiation-assisted approach provides controllability mainly over the size, shape, and composition of the nanomaterials. However, precise creation of nanomaterials with specific attributes for desirable applications is still a challenge.
- **b.** The yield of radicals produced during radiolysis is very important factor in the synthesis of nanomaterials. Undoubtedly, radiolytic approach is mainly limited to the creation of nanomaterials in aqueous media and there are still very few reports on their preparation in non-aqueous media.
- **c.** Creating desirable nanostructures through radiolytic approach require more R & D into the development of novel radiation-resistant host matrices with well-defined features to guide the growth and organization of nanoparticles.
- **d.** Determining the optimum absorbed dose is critical step in this approach to achieve the desired nanoparticle properties without generating unwanted byproducts. Excessive radiation dose can lead to increased defect formation, particle aggregation, and unwanted chemical changes.
- e. Radiolysis can introduce defects and impurities in the synthesized nanomaterials, which can affect their properties and performance, making it necessary to develop purification and post-synthesis treatment methods to minimize or remove these defects.
- f. The majority of the papers pertaining to the synthesis of nanomaterials by radiationassisted methods have utilized electronbeam or γ -rays as ionizing radiation sources. There remains a significant amount of unexplored potential in the utilization of alternative ionizing radiation sources, such as proton and heavy ion-beams, in the synthesis of novel nanomaterials. In

addition, these alternative ionizing radiation sources can be explored in controlled defect engineering, induce phase transformations, crystal structure changes and post-synthesis treatment in nanomaterials.

- **g.** Transition from laboratory-scale synthesis to large-scale production can be challenging due to issues related to radiation safety, and maintaining consistent nanoparticle properties at larger scales.
- **h.** The use of ionizing radiation poses radiation safety concerns for both researchers and the environment. Careful consideration and implementation of safety protocols are necessary to mitigate risks associated with radiation related accidents.

With new advances in radiation chemistry, the radiolytic approach can certainly contribute significantly in providing a "green" and "economic" platform in the design and development of nanomaterials with tailored properties.

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Tritium based betavoltaic nuclear battery using β -SiC nanowires

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Abstract

A betavoltaic nuclear battery using randomly oriented β -SiC nanowire arrays is developed. The synthesized nanowires are characterized using UV-Vis spectroscopy, XRD, Raman spectroscopy, and SEM techniques. The formation of β -SiC nanowires on Si substrate in Ar gas environment using tubular furnace is discussed as a possible mechanism. A sandwich-type metal/ β -SiC nanowires/ metal structure with a built-in contact potential difference is used to investigate the effect of beta radiation on voltage production. The radioactive source with specific activity is used to develop betavoltaic nuclear battery based on the wide band gap β -SiC nanowires semiconductor. Ultra-long β -SiC nanowires immobilized on a Si substrate is integrated with a tritium radioisotope planar source on a Cu substrate (Cu-H-3/SiC/Al).

Keywords: β-SiC nanowire, betavoltaic nuclear battery, tritium and wide bandgap semiconductor

1. Introduction

Betavoltaic micro-batteries are attractive for powering miniature autonomous devices and wireless sensors that are used in implanted medical microelectromechanical systems (MEMS) devices, as well as defence and industrial applications that demand long-term operation [1, 2]. These batteries use radioisotopes to produce high-energy beta particles, which create electronhole pairs in the active region of a semiconductor. The electron-hole pairs are separated by a builtin electric field and delivered to the external circuit to drive the load. The working principle is similar to that of a solar cell, but betavoltaic nuclear batteries have lower efficiency and power output per unit area than solar cells. The first semiconductor-based betavoltaic nuclear battery using Si was invented by Rappaport in 1954 [3], and since then, many efforts have been made to enhance the energy conversion efficiency [4-8]. Recently, betavoltaic nuclear batteries based on wide bandgap semiconductors such as silicon carbide (SiC) and gallium nitride (GaN) have been reported [5, 7], but they still use conventional planar diode structures that limit the active area.

A 3D porous silicon p-n diode structure was used to create a betavoltaic device that showed a higher energy conversion efficiency than a planer device [9]. This suggests that nanostructures with a high aspect ratio can enhance the betavoltaic effect by increasing the active area and the beta radiation absorption. However, silicon is not an ideal material for this purpose, as it has a small energy bandgap, a high leakage current, and a low absorption capacity for high-energy beta particles. Therefore, wide bandgap semiconductors are needed to improve the performance of betavoltaic nuclear batteries. These materials can absorb high-energy beta particles without degradation and have a low leakage current. Moreover, wide bandgap semiconductors with morphological structures could further increase the energy conversion efficiency of betavoltaic devices.

In the present work, we have developed a betavoltaic nuclear battery using tritium (H-3) as the radioactive source and ultra-long β -SiC nanowires as the semiconductor material. The β -SiC nanowires are suitable for this application because they have a wide band gap, high radiation resistance and low leakage current.

Our work demonstrates the potential of β -SiC nanowires for betavoltaic devices.

2. Experimental details

2.1. Synthesis and characterization of β -SiC nanowires for nuclear battery

The process of thermal evaporation involved preparing n-type Si wafer by cutting them into required size (2.5 cm × 2.5 cm × 0.0625 cm), and cleaning it by ultrasonication in acetone, double distilled water and isopropyl alcohol each for 15 min to remove surface contamination. Then the substrates were dried in air at room temperature. After that, the substrate was loaded into the middle horizontal quartz tube furnace placed at the centre of an electric tube furnace. Graphite powder (1 g) on a quartz boat was mounted 0.5 cm before the silicon substrate. The argon (99.999%) gas was then flushed inside the quartz tube (to get rid of all other gases) and kept at a flow rate of 20 sccm. The temperature was then raised up to 1200 °C at a heating rate of 5 °C/sec and kept for 4 hours. When the room temperature was reached the sample was removed from tubular furnace and characterized by different techniques to confirm β -SiC.

2.2. Characterization:

The main objectives of the characterization of β -SiC nanowires were to study crystal structure, vibrational, surface morphology and optical bandgap properties. The substrate of β -SiC were characterized by (i) UV-Vis spectroscopy, (ii) XRD, (iii) SEM and (iv) Raman spectroscopy.

- (i) The bandgap of β-SiC nanowires was calculated using a Tauc plot, with UV-vis spectra recorded on a JASCO V-670 UV-Visible spectrophotometer.
- (ii) A Bruker AXS D8 Advance X-ray diffractometer was used to study the crystal structure of β -SiC nanowires using XRD technique. The XRD patterns were recorded at an angular resolution of 0.1° in the 2 θ range from 10° to 80°.

- (iii) The morphology and size of β -SiC nanowires were examined using SEM on a JEOL JSM-6360 electron microscope. The microscope was operated at accelerating voltages ranging from 3 kV to 20 kV and a beam current of approximately 50 to 70 μ A. SEM uses an electron beam to image the surface morphology of the specimen.
- (iv) A Renishaw inVia laser Raman microscope, equipped with a 532 nm Ar laser, was used to record the Raman spectra of β -SiC. The Raman spectrum of each sample was recorded over a period of ten seconds.

2.3. Use of radioactive source

Thin layer of titanium on 25 mm diameter of Cu substrate saturated with H-3. The radioactive source used in this experiment is H-3, which is a hydrogen isotope that undergoes beta decay. The activity of the H-3 source is approximately 1 Curie, which means that it emits about 3.7×10^{10} beta particles per second. The H-3 source is prepared by depositing a thin layer of titanium on a copper substrate with a diameter of 25 mm.

2.4. Fabrication of β -SiC betavoltaic nuclear battery using H-3 as radioactive source

To form a metal-semiconductor Schottky junction, one side of the substrate was contacted with Cu, while the other side was coated with Al using PVD method in a vacuum environment. The chambers vacuum pressure was maintained at 5.5×10^{-6} Torr and the substrate was kept at room temperature. Figure 1 illustrates the preparation process for the β -SiC nanowires-based betavoltaic nuclear battery structure.

To test the ability of β -SiC to convert beta energy into electrical energy, a Cu/ β -SiC nanowires/Al sandwich structure was assembled by compressing a planar beta source onto the β -SiC nanowires layer, bringing the β -SiC nanowires into full physical contact with the H-3 layer on the conducting copper substrate. A sandwich-type metal/ β -SiC nanowires/metal structure under a built-in contact potential



Figure 1: A schematic view of development of Schottky junction type betavoltaic nuclear battery using β -SiC nanowires arrays.

difference was used to investigate the effect of beta radiation. The sandwiched structure was integrated by immobilizing β -SiC nanowires on an Al metal contact with a radioisotope H-3 planar source on a copper substrate (Cu-H-3/ β -SiC nanowires/Al). Under irradiation from an 18.6 keV end-point energy beta particle radioactive source with an activity of ~1 Ci, the output voltage was measured on a multi-meter for a specific time interval. The measurements were performed in dark conditions and at room temperature.

3. Results and discussion

3.1. Growth mechanism of β -SiC nanowires

The growth mechanism for SiC nanowires is a Vapour-Solid (VS) process, without the use of a catalyst. Oxygen from the SiO₂ layer on the Si substrate and surviving oxygen in the furnace reacts with graphite powder to form CO vapour. As the temperature increases, graphite powder vaporizes to form C vapour, which reacts with the SiO₂ layer to produce SiO vapor. The SiO vapor then reacts with solid graphite and CO to form SiC crystal nuclei, which are believed to form at defects or impurities on the Si substrate. These nuclei then act as seeds and interconnect to form SiC nanowires along the preferential crystalline direction.

3.2. UV-Vis spectroscopy

The UV-Vis absorption spectrum of β -SiC nanowires grown on Si wafer at 1200 °C for 4 hrs is shown in Figure 2 (a). The nanowires have an optical absorption peak at ~ 406 nm. Figure 2 (b) shows the plot of $(\alpha hv)^{1/2}$ vs energy (eV) to determine the indirect band gap of the β -SiC nanowires. The band gap value is obtained by extrapolating the linear part of the plot to the zero absorption edge. The calculated indirect optical band gap for SiC nanowires is 2.30 eV.

3.3. XRD

Figure 3 shows the XRD pattern of β -SiC grown on Si wafer at 1200 °C for 4 hrs. The peaks at 35.5°, 41.4°, 60.1°, 71.8°, and 75.65° correspond to the (111), (200), (220), (311), and (222) planes of cubic β -SiC with a lattice constant of 0.4358 nm, as identified by the JCPDS data (no. 74-2307). The crystallite size of β -SiC nanowires was determined using the Debye-Scherers formula and the XRD peak of plane <111>. The average crystallite size is calculated to be around 40.55 nm.



Figure 2: (*a*) *UV-Vis absorption spectrum of SiC nanowires and (b) Tau plot of* β *-SiC nanowires.*



Figure 3: the XRD pattern of β -SiC grown on Si wafer at 1200 °C for 4 hrs.



Figure 5: *The Raman spectrum of the* β *-SiC nanowires synthesized by horizontal tubular furnace.*

3.4. Raman Spectroscopy

A typical Raman spectrum of β -SiC nanowires is shown in Figure 4. The highest intensity peak at 794 cm-1 corresponds to the β -SiC-3C zone center transverse optical (TO) phonon mode. The longitudinal optic (LO) phonon mode is identified by a peak appeared at 946 cm-1. The Raman spectrum confirms the synthesis of pure β -SiC nanowires using tubular furnace.

4.5.SEM

Figure 5 shows SEM micrographs of the surface view of randomly oriented β -SiC nanowires grown using a simple tubular furnace. Images (a) to (d) show straight and curved nanowires densely grown on the Si substrate. The nanowires are several hundred microns long (200-400 µm) with uniform diameters between 50 and 100 nm. The average diameter of the randomly oriented β -SiC nanowires is 64 nm. Image (d) shows a cross-section view of the β -SiC nanowires on the Si substrate, with a total thickness of ~7.5 µm.

3.6. Performance of a betavoltaic nuclear battery based on β-SiC nanowires

Figure 1 shows the schematic view of a Schottky-junction type nuclear betavoltaic device. To test the conversion of beta energy to electrical energy, the device was exposed to an H-3 beta



Figure 5: The images (a)-(c) show SEM micrographs of β -SiC nanowires at different magnifications. The cross-sectional view of β -SiC on Si substrates is shown in image (d).



Figure 6: The graph of output voltage (V) vs time (hr) of performance of the Schottky-junction type nuclear betavoltaic battery.

source. The output voltage was measured on a digital multi-meter for a specific time interval, with the radioactive source placed over the β -SiC region. Figure 6 shows the output voltage vs time performance of the fabricated betavoltaic device. The readings were taken every 0.5 hr. The initial output voltage was 20 mV when the beta source was applied. The voltage increased with time

and reached a constant value of around 478 mV after 5 hrs. The short circuit current was ~ 0.097 μ A. The active area of the device was 2.4 cm × 2.4 cm and the H-3 beta source was used as the radioactive source. The total output power of the β -SiC nanowires Schottky junction type nuclear betavoltaic battery was around 46.36 nanowatt.

Figure 7 shows the actual set-up of a β -SiC nanowires based Schottky-junction type betavoltaic nuclear battery, with the output voltage measured using a digital multimeter. Using an H-3 radioactive source with 1 Ci activity, the β -SiC nanowires generate a maximum output voltage of around 478 mV.



Figure 7: A photograph of the experimental set-up for a β -SiC nanowires-based Schottky-junction type betavoltaic nuclear battery is shown, with the output voltage displayed on a digital multimeter.

4. Conclusion

In this study shows that β -SiC nanowires can be synthesized in a tubular furnace using an argon gas atmosphere at 1200 °C for 4 hours. The indirect optical band gap of the β -SiC nanowires is 2.30 eV, as determined by Tau. The XRD results reveal that the β -SiC nanowires have a cubic structure. The SEM micrographs show that the nanowires are ultralong, with an average diameter of 64 nm. These randomly oriented β -SiC nanowires, a wide gap semiconductor, were used to develop a betavoltaic nuclear battery. A sandwichtype metal/ β -SiC nanowires/metal structure with a built-in contact potential difference was used to investigate the effect of beta radiation. The structure consists of immobilized β -SiC nanowires on a Si substrate with a radioisotope H-3 planar source on a Cu substrate (Cu-H-3/ SiC/Al). Under irradiation with beta particles from ~18.6 keV source with an activity of ~1 Ci, the structure produces an open-circuit voltage of 0.478 V and a short-circuit current of 97 nA. The β -SiC nanowires have great potential for betavoltaic batteries due to their ability to absorb beta particles and transport charge carriers. By connecting multiple betavoltaic nuclear batteries, a voltage up to 6 volts can be achieved with a current limit of $\sim 1 \mu A$. The sandwich-type metal/semiconductor/metal structure (Cu-H-3/SiC/Al) plays an important role under the built-in electrical field created by the contact potential difference between Cu and Al. The enhanced betavoltaic mechanisms of the metal/ semiconductor/metal structure and its optimized design are presented.

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Multifunctional TiO₂ Nanostructures for Photochemical Transformation Applications

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Abstract

The world has faced major challenges in the field of energy, health, and environmental pollution. Numerous efforts have been devoted to addressing these issues, among which nanostructured titanium dioxide (TiO₂) is recognized as one of the most promising approach. The photocatalytic process of nanostructured titanium dioxide is a conceptually simple and promising technology. Nanostructured modified titania has high chemical stability, environmental benign and good heat resistance. It is highly promising to be used in electronic, photocatalysis, solar cells, airwater purification, drug delivery, antibacterial and self-cleaning applications. Pristine titania can only work under ultraviolet (UV) light (wavelength < 388nm) due to its wide band gap of 3.2eV. Various synthesis strategies have been adopted to enhance photocatalytic performance of titanium dioxide nanostructures. The structural, optoelectronic, and photocatalytic properties of modified titanium dioxide nanostructures have been investigated in detail. This article focused on the research findings from ourgroup on multifunctional titania and then explain its applications in air-water purification, solar cells, drug delivery and self-cleaning systems.

1. Introduction

In the newly expanding subject of nanotechnology, materials, technologies, and systems with dimensions typically less than 100 nm are studied, manipulated, created, and used[1]. By modulating their size, materials can have their qualities engineered via nanotechnology[2]. The versatile semiconductor material titanium dioxide (TiO_2) has received a lot of attention in a number of scientific and technical domains[3]. It is a viable contender for many uses, including environmental cleanup, energy conversion, and healthcare, because to its special features, which include great chemical stability, low toxicity, and remarkable photocatalytic activity[4].

The photocatalytic capability of titania has been thoroughly studied in the context of environmental remediation. It can produce electron-hole pairs when exposed to ultraviolet (UV) or even visible light[5]. These redox processes help different organic contaminants, such as volatile organic compounds (VOCs), dyes, and even some microbes, to degrade[6]. The development of sustainable and environmentally friendly solutions for air has given substantial emphasis to this capacity to effectively digest hazardous chemicals.

The versatile semiconductor material titanium dioxide has received a lot of attention in a number of scientific and technical domains[7]. It is a viable contender for many uses, including environmental cleanup, energy conversion, and healthcare, because to its special features, which include great chemical stability, low toxicity, and remarkable photocatalytic activity[8].

For the development of modified titania nanostructures, a variety of synthesis techniques including sol-gel, hydrothermal, solvothermal, solid state reaction, and coprecipitation are available[3]. To improve the photocatalytic abilities of titania, these techniques allow for the insertion of dopants, surface alterations, and hybridization with other substances. By adjusting elements including composition, shape, dopant concentration, and surface changes, these synthesis techniques enable flexible tailoring of the attributes of modified titania nanostructures. The desired alterations, the particular application requirements, and the scalability of the synthesis process all influence the selection of the best synthesis method[9].

Additionally, surface alterations might boost target pollutant adsorption by promoting charge separation, preventing electron-hole recombination, and increasing surface area by the deposition of metal nanoparticles or chemical sensitizers[10].Graphene, metal oxides, or carbon-based nanomaterials are a few examples of materials that can be hybridised with titania to increase its photocatalytic efficacy. By fusing the special qualities of titania with those of the added components, these hybrid structures can produce beneficial synergistic effects that boost charge transfer, prolong light absorption, and increase stability[11].

We hope to give a thorough overview of the most recent developments in titania and its modification for photocatalytic applications in this review. We will go over the several methods used to alter titania, such as doping, surface changes, and hybridization. We will also investigate how these alterations affect photocatalytic activity, stability, and selectivity. Finally, we will discuss modified titania's potential uses in healthcare, energy conversion, and environmental remediation.

2. Phases of titania

Titania occurs in a variety of phases or crystal forms, each with its own special qualities and uses. Rutile, anatase, and brookite are some of the most often investigated phases of titania as depicted in Fig.1[12,13].

At ambient temperatures, rutile is the most thermodynamically stable phase of titania. It has a tetragonal crystal structure and is distinguished by tightly packed oxygen and titanium atoms. Rutile type has a high refractive index, great chemical stability, and strong electrical conductivity. Rutile titania is used in areas including solar cells, gas sensors, and catalysis because of these characteristics[15]. Due to its wide bandgap (about 3.0 eV) and high charge carrier mobility, it can be used as a photocatalyst for water splitting as well as in photoelectrochemical cells[16].

Another significant phase of titania is anatase. It is metastable at room temperature and has a slightly deformed tetragonal crystal structure[12]thanks to their particularly high surface area, con-trolled porosity, high flexibility in composition, and surface design, are promising candidates in different application fields such as sensors, self-cleaning coatings, lithiumion batteries (LIBs). Due to its smaller energy bandgap (about 3.2 eV) and higher surface reactivity, anatase titania has a bigger surface area and more photocatalytic activity than rutile. In photocatalytic processes including pollutant degradation, water splitting, and self-cleaning surfaces, this phase is frequently employed. Due to its strong surface reactivity, anatase phase is also well suited for use in supercapacitors, lithium-ion batteries, and dye-sensitized solar cells[12,17,18]the present study demonstrates a novel method involving fabrication of self-doped TiO² NTAs by a simple cathodic polarization treatment on the pristine TiO2 NTAs to achieve improved conductivity and capacitive properties of TiO².

The least frequent and least researched phase of titania is brookite. It is metastable at ambient temperatures and has an orthorhombic



Fig. 1. Crystal structure of titania (a) anatase, (b) rutile and (c) brookite [12,14]we present a combined density functional theory and many-body perturbation theory study on the electronic and optical properties of TiO(2.(© 2012 IOP Publishing Ltd.)

crystal structure. Unique characteristics of brookite phase include a large bandgap (about 3.3 eV), high thermal stability, and strong chemical resistance[19].

Numerous industries, including photocatalysis, energy storage, and optoelectronics, are very interested in the capacity to control and change the phase of titania.

3. Modified titania for air-water purification

Due to its outstanding photocatalytic qualities and capacity to effectively destroy a variety of contaminants, modified titania has attracted considerable interest as a promising material for air and water cleaning. Titania is a prime option for environmental remediation applications because to the alterations that can increase its photocatalytic activity, widen its light absorption spectrum, and improve its stability[7]. Here, we go through modified titania's potential for purifying both air and water.

By using the sol-gel process, our team has created titania nanoparticles that are Fedoped (0.0-3.0% mol%). These nanoparticles' photocatalytic activity was investigated for the photodegradation of Rhodamine 6G as well as the conversion of p-nitrobenzaldehyde to p-nitrobenzoic acid[20].Similarly, Cr-doped titania photocatalysts have been made by our team using the sol-gel process[21]. The degradation of MB under UV and visible light irradiations was used to assess the photocatalytic activity of the produced samples.Chromium concentration in the titania host lattice is increased, which promotes the photocatalytic destruction of MB. Titania was doped with Cr cations to enhance its photocatalytic activity when exposed to visible light[21].

In another report, we have created SiO_2 -TiO thin films by spin coating and the sol-gel process[22]. These thin films were extremely clear and antireflective. The photocatalytic performance of the these thin films deposited on glass substrates is significantly influenced by the presence of an intermediary SiO₂ layer.The intermediary SiO₂ layer facilitates methylene blue's photocatalytic breakdown[22].

Most frequently, titania has been utilised to pure air and remove various chemical contaminants. We used a two-step solvothermal approach to create graphene oxide and anatase titania nanocomposites[23]. Under UV irradiation, the photocatalytic destruction of benzene gas was assessed. The outcomes showed that the presence of GO facilitated the photocatalytic benzene breakdown in gaseous form and facilitate the separation ofphotogenerated charge carriers along with high stability, which ultimately enhance the photocatalytic activity under ultravioletirradiation[23].

4. Modified titania for solar energy conversion

Titania is a vital component of solar cells and is essential to the effective operation of these devices. The perovskite solar cells are used to turn sunlight into power and titania serves as the semiconductor material in these solar cells, enabling effective charge carrier transfer and light absorption. Titania is a commonly used material in perovskite solar cells. It is primarily utilized as an electron-transporting layer (ETL) in the device structure[24].

In perovskite solar cells, titania is typically applied as a thin film on the transparent conducting substrate, such as indium tin oxide (ITO)[11]. The titania layer serves as a scaffold for the perovskite material, facilitating efficient charge transport and extraction.

Titania possesses several favorable properties that make it suitable for this application. It has a high electron mobility, allowing for efficient electron conduction from the perovskite layer to the electrode. Titania also has a wide bandgap, enabling it to transmit visible light while reflecting ultraviolet (UV) light. This property helps to minimize losses due to absorption of UV photons by the perovskite layer.

There are different types of titania materials used in perovskite solar cells,
including mesoporous and compact titania films. Mesoporous structures provide a large surface area, enhancing the interface between the perovskite and titania layer and improving charge extraction. On the other hand, compact titania films are employed when a planar heterojunction structure is desired, where the perovskite layer directly contacts the titania layer[11,15].

Our group has prepared low temperaturebased titania nanoparticles as electrontransporting layer for perovskite solar cellsusing a non-hydrolytic sol-gel approach[25]. We were able to produce Nb doped titania with uniform film coverage, great transparency in the visible range, a wide optical bandgap, and outstanding electrical conductivity by methodically optimising the reaction duration, thermal annealing temperature, and Nb doping concentration. These titania nanoparticles demonstrated outstanding performance as an electron-transporting layer in perovskite solar cells under an ambient environment. On solid glass and flexible plastic substrates, these solar cells obtained high efficiency of 18.97% and 13.51%, respectively (Fig. 2)[25].

Titania has been used widely in third generation dye sensitized solar cells (DSSC). Depending on its crystal phase (anatase or rutile),



Fig.2.J–V characteristics of the flexible perovskite solar cell. Inset figures show the IPCE spectrum, table of device performance and picture of the flexible devices[25]. (© 2019 International Solar Energy Society)

titania has a wide bandgap that is typically 3.0-3.2 eV. Titania is able to absorb a sizeable amount of the ultraviolet (UV) region of the solar spectrum due to its wide bandgap[11]. However, it only absorbs a little amount of visible light. In DSSCs, organic dyes or sensitizers are utilised to get over this restriction. These colours cause titania to adsorb, bringing the range of light absorption into the visible spectrum. The dye molecules' excited electrons are then injected into titania's conduction band by the absorbed photons[10].

In DSSCs, titania makes charge separation and transfer more effective. A current flow when dye-derived electrons are introduced into the titania's conduction band and travel in the direction of the electrode[26]. The charge transfer cycle is finished simultaneously with the regeneration of the dye molecules through electron donation from a redox electrolyte. Effective charge transport is made possible by titania's high electron mobility and low recombination rate, which also help to cut down on energy losses in the DSSC system.

Titania's surface area is crucial for DSSCs because it creates a significant dye adsorption interface and boosts light harvesting effectiveness. High surface area nanocrystalline titania films can be produced using a variety of methods, including sol-gel synthesis, nanoparticle deposition, and screen printing. With the use of these techniques, a porous structure may be created, increasing the quantity of dye that can be absorbed and improving overall light absorption[27].

Excellent chemical stability and compatibility with the electrolyte and other DSSC parts are displayed by titania. It resists corrosion and keeps working effectively for lengthy periods of time. For DSSCs to be effective and durable over the long term, especially in a variety of environmental conditions, this stability is essential. Similarly, titania plays a critical role in facilitating efficient charge transport and extraction in perovskite solar cells[24], contributing to the overall performance and power conversion efficiency of the devices

5. Functionalised titania for drug delivery application

Due to their distinctive characteristics, biocompatibility, and capacity for regulated release, functionalized titania nanoparticles have demonstrated remarkable potential for drug delivery applications[28]. Nano-titania's interaction with pharmaceuticals can be improved by altering their surface, which enables effective drug loading, protection, and targeted delivery to particular body regions. Here, we go over applications for functionalized titania in drug delivery.

To enhance their drug delivery capabilities, titania nanoparticles can be functionalized with a variety of compounds, including polymers, surfactants, or proteins[28]. Better drug encapsulation, stability, and controlled release are made possible through surface modification. Drugs can be successfully encapsulated in or on the surface of functionalized titania nanoparticles. Titania nanoparticles' huge surface area and excellent adsorption capacity allow for the effective loading of medicinal medicines[29].

Our group has reported preparation of modified titania nanocorals by solvothermal approach[30]. These nanocorals were functionalised with methoxy polyethylene glycol (mPEG). These nanocorals effectively attached with chemotherapy drugs (DOX) on their surfaces and exhibit biocompatibility.Upon exposure to UV light, the titaniananocorals generate free radicals, making them valuable for targeted drug release in cancer cells. Notably, the duration of UV light irradiation can be manipulated to control the release of medication, thereby enabling precise regulation of the anticancer effect. Through a combination of stimuli and light activation, the multimodal titaniananocorals offer a promising approach for eradicating cancer cells (Fig. 3) [30].

Drug delivery that is prolonged and targeted is made possible by the regulated drug release kinetics that can be achieved with titania nanoparticles. The factors such surface charge, function type, and nanoparticle size can affect towards drug delivery. Targeting ligands or antibodies can be added to the surface of functionalized titania nanoparticles to create them for targeted medication delivery[31]. These ligands bind specifically to the target cells' receptors or biomarkers, enabling site-specific medication administration and minimising side effects.



Fig. 3. Schematic for the modification of titania and its anticancer activity [30].(©*The Royal Society of Chemistry* 2017)

When used in drug delivery applications, functionalized titania nanoparticles provide controlled release, targeted distribution, and imaging capabilities.

6. Modified titania for photocatalytic antibacterial activity

Significant promise for photocatalytic antibacterial applications has been shown for modified titania[32]. The photocatalytic antibacterial activity of titania can be improved by adding particular changes, such as doping, surface functionalization, or hybridization with other materials, allowing for effective and targeted bacterial eradication. Here, we discussed the application of modified titania for antibacterial photocatalytic activity.



Fig. 4.Schematic showing photocatalytic reaction under (a) UV light and (b) the visible light[32]. (© *The Korean Institute of Chemical Engineers*)

The photocatalytic antibacterial activity of titania can be considerably improved by doping it with specific elements like copper (Cu)[33], nickel (Ni), iron (Fe) or other transition metals[32]. When exposed to light, these dopants' role as electron traps improves the formation of reactive oxygen species (ROS) and increases charge carrier separation (Fig. 4). The ROS, which have potent oxidative capabilities and can harm bacteria's cell membranes, DNA, and proteins, rendering them inactive, include hydroxyl radicals (OH) and superoxide ions (O_2^{-}) (Fig. 5).



Fig. 5. The schematic for photocatalytic killing of bacteria [32].(© *The Korean Institute of Chemical Engineers*)

Titania primarily absorbs UV light, but it can be modified to increase its ability to do so in the visible spectrum as well. Doping, surface sensitization with dyes or quantum dots, or the use of plasmonic nanoparticles to increase light absorption and enable visible light-driven photocatalysis can all be used to achieve this. Visible light activation makes it possible to use solar or indoor lighting, expanding the usefulness of modified titania for antibacterial applications[9].

Our group has reported effect of Cu doping in titania towards photocatalytic antibacterial application against pathogenic bacteria Escherichia coli and Staphylococcus aureus under visible light irradiation. We studied role of hydroxyl radicals towards inactivation of bacterial by photoluminescence technique[33]. We have also reported photocatalytic inactivation different bacterial pathogens such as Staphylococcus aureus, Bacillus subtilis, Escherichia coli, and Salmonella abony with nickel modified titania nanoparticles under weak intensity visible light [34]. In another report, we studied the photocatalyticin activation of E. coli under different physico chemical conditions such as effect of concentration of dopant, light intensity, weight of catalysts etc. [35]. We found that the photocatalytic activity improved with increasing Fe concentration in titania host and the maximum inactivation was achieved for 3.0 mol% Fe-doped titania nanostructures under fluorescent light compared to 1.0 and 2.0 mol% Fe-doped titania[35].

Our team has developed chitosan and Cu modified titania composites(CS-CT) using the sol-gel and ultrasonication methods[36]. When compared to control, CS-CT displayed aexcellent light-mediated photocatalytic antibacterial activity against *E. coli* and *Staphylococcus aureus*. As a result of the synergistic impact of organic and inorganic materials enhancing one another's activities, it is discovered that the antibacterial activity of CS-CT nanocomposite in the presence of light is increased compared to that of its constituents[36].

The creation of effective and long-lasting antibacterial compounds is made possible by modified titania with increased photocatalytic activity[11]. Titania can be used in a variety of situations, such as water treatment, air purification, antibacterial coatings, and healthcare facilities, by using dopants, surface functionalization, hybridization with other materials, and visible light activation. The goal of ongoing research and development in this area is to enhance the antibacterial activity of modified titania systems while maintaining their biocompatibility and environmental safety [37].

7. Conclusions

In conclusion, multifunctional titania nanostructures have emerged as a highly promising approach for various photochemical transformation applications. The unique properties of titania, such as its high chemical stability, environmental benignness, and remarkable photocatalytic activity, make it a versatile material for addressing challenges in energy, health, and environmental pollution.

The research findings presented in this article highlight the significant progress made in the synthesis and modification of titania nanostructures to enhance their photocatalytic performance. Various techniques, including sol-gel, hydrothermal, solvothermal, solid state reaction, and coprecipitation, have been employed to tailor the structural, optoelectronic, and photocatalytic properties of titania. These modifications have led to improved efficiency, expanded light absorption spectrum, and enhanced stability, making titania nanostructures suitable for diverse applications.

The applications discussed in this article demonstrate the potential of modified TiO² nanostructures in several areas, including airwater purification, solar cells, drug delivery, and self-cleaning systems. In air-water purification, modified titania has shown exceptional photocatalytic activity in degrading organic contaminants and purifying air and water. In solar energy conversion, titania plays a crucial role in perovskite solar cells and dye-sensitized solar cells, facilitating efficient charge carrier transfer and light absorption. Furthermore, functionalized titania nanoparticles have demonstrated great promise in drug delivery applications, enabling controlled release and targeted delivery of pharmaceuticals.

The continuous advancements in the field of multifunctional titania nanostructures offer exciting opportunities for addressing global challenges. Further research and development efforts are needed to optimize the synthesis methods, explore novel modifications, and unlock the full potential of titania nanostructures for a wide range of photochemical transformation applications. By harnessing the capabilities of titania nanostructures, we can contribute to a sustainable future by providing innovative solutions for energy, environmental, and healthcare needs.

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