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Luminescence Characterization of the Green Synthesized Terbium Doped Titanium Oxide

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ABSTRACT

Purpose: The purpose of this work is to prepare Titanium Oxide (TiO_2) with eco-friendly synthesis and also to study on structural, morphological, photoluminescence properties on Tb doped TiO_2.

Methodology: Titanium Oxide was prepared by orange fruit aqueous extract as a reducing agent with addition of terbium as its dopant. Characterization of the synthesized TiO_2 was done by XRD proving that the TiO_2 was in the structural form of rutile as evidenced by the sharp peaks. The relationship between the concentration of Tb dopant and the grain size of the film layer was studied. SEM Morphological analysis indicated the formation of particle cluster at 1100°C. EDX spectroscopy was employed to determine the position of elements of the samples while FTIR spectroscopy was in agreement with carbonyl and hydroxyl groups being absent in the prepared samples. Optical characteristics of the samples were evaluated by photoluminescence measurements under the excitation of 400 nm wavelength.

Findings: The results obtained in the present study pointed out how the terbium doping affected the structural and optical characterization of the TiO_2. An increase in the Tb concentration led to an increase in the grain size of the synthesized spherical film. Photoluminescence spectroscopy results showed two separate green and red emissions and was measured to have the highest intensity at 4% terbium concentration. From these results we can see the prospect of using Tb-doped TiO_2 in applications that require certain changes in the optical parameter.

Contribution to Theory, Policy, and Practice: This work contributes to the body of knowledge on green synthesis methods for nanostructures and the effect of RE doping in improving the properties of a material. The results provide insight for green synthesis of photo luminescent materials, optoelectronic devices, and monitoring instruments, identifying ways to pursue environmentally friendly material design.

Keywords: *Green synthesis, Titanium Oxide, Photoluminescence, Nanomaterials, Terbium*

1. INTRODUCTION

Energy crisis is one of the biggest threats to the contemporary society. To meet this challenge, this world has to develop devices that employ energy to the lowest level possible. Many things are visible with visible light in this world. In the past visible light has been obtained in such ways as burning of woods, discharge lamps, candles, halogen tungsten bulbs, fluorescent tubes and now light emitting diodes (LED). Several types of sources emit light, but most of them dissipate a lot of energy in heat or in other forms of light that are imperceptible to the naked eyes [1]. Among these mentioned sources, LED lights are more used from the user end due to its high visible light efficiency. Expenditure of power for small appliances is cut down very much and in market 3 Watt bulbs also available with good visible light efficacy. However, to investigators, there is no exception that there is always a space for improvement in luminescence field [2].

Superior materials for luminescence have been employed in lighting and display based on brightness, colour and efficiency, life span of the material. For this reason, it is required to consider the process of luminescence in these materials. Phosphors received much attention as luminescent materials since the mid of 1990. Efficient white light technology in such solid state materials is based on down conversion of UV or blue light into longer wavelengths in the visible spectrum. Typically, these are inorganic materials such as silicates, sulfides, halides, lanthanide halides, rare earth oxides. The activators are used in a very low concentration with these luminescent materials which then become the host. To obtain a luminescence process, the host material is irradiated by high energy photons, causing this energy to be transferred to the dopants to be emitted as visible wavelengths [3]. But the wavelength emitted also varies with the host crystal surrounding structure of the host up to some extent. At high concentration of the activators various problem arise, one of them is the concentration quenching which is defined as the reduction in luminescence properties [4].

From the literature survey it emerges that available literature is replete with research work in this respect. Among all the known photo catalysts, TiO_2 has been paid the most attention and of interest to many researchers because of the high refractive index and UV light Various activators has been incorporated in different host materials; for example, luminescence of undoped TiO_2, TiO_2 as a host for Erbium (Er^{3+}), Neodium (Nd^{3+}), Ytterbium (Yb^{3+}), tungsten (W), Silver (Ag), Copper (Cu), Tantalum (Ta), Cerium (Ce), Gadolinium (Gd), has been undertaken in this respect. Among all known photo catalysts, TiO_2 has been studied most extensively and is of great interest to many researchers because of its unique properties, including high refractive index and UV light transmittance and absorbance, high incident photoelectric conversion coefficient and dielectric constant, and high photocatalytic activity, photo stability, chemical stability, and anti-corrosive properties, as well as non-toxicity Activators and host material in the above fluorescent compounds have been different and some of the host materials have been discussed such as undoped TiO_2, Erbium (Er^{3+}) doped TiO_2, Neodium (Nd^{3+}) doped TiO_2, Tungsten (W) doped

TiO_2, Silver (Ag) doped TiO_2, Copper (Cu) doped TiO_2, Tantalum (Ta) and dielectric constant, good photocatalytic activity, photostability, chemical stability, and long-time corrosion resistance as well as nontoxicity. Different activators has been used in different host materials, like luminescence of undoped TiO_2, TiO_2 as a host for Erbium (Er^{3+}), Neodium (Nd^{3+}), Ytterbium (Yb^{3+}), tungsten (W), Silver (Ag), Copper (Cu),Tantalum (Ta), Cerium (Ce), Gadolinium (Gd), Europium (Eu), Yttrium (Y), lithium (Li) , bismuth (Bi) etc has been investigated [5].

On the other side many host materials containing terbium (Tb^{3+}) as an activator have been researched. In the framework of this work the possibility to use TiO_2 as a host for terbium will be described.

Terbium is a soft and malleable element belongs to lanthanide group in the periodic table. Terbium is one of the rare earth elements twice as common as silver but is never found free in nature. It has no environmental threats to animals or plants. Studies has shown that it emits bright green light in the visible region of electromagnetic spectrum due to electronic transition from $^5D_4$ to $^7F_6$ (545nm), which make it a good choice to be used as a phosphor in LED's [6-8].

Titanium dioxide also known as Titania or Titanium-iv oxide having chemical formula TiO_2 is a white powder and is not toxic. It was discovered in 1791 by William Gregar in black magnetic sand. When used as a pigment, it is known as Titanium White. Titanium pigments were prepared commercially in Norway for industrial purposes for the first time. According to an estimate use of Titanium in the world has so much increased that its pigment's use is 2/3rd of all the pigments. Due to its high strength to weight ratio, it is an important material for the air frames used for military purposes [9].

Figure 1: Titanium oxide powder

Titania is utilized in to give coat for papers surface to look more bright and white. It is taken against brittleness, fading and formation of crackling on some material. it is also used in materials which make the face glow and cover skin lesions. [10].it is very transparent and this

quality has been harnessed in protection if foods such as fruits and vegetables from early spoiling through sheltering from ultraviolet and visible light. However, some researches has confirmed its hazards such as carcinogenicity to the worker including during the packing process [11-13].

Natural occurring Titania is available in other three minerals namely Rutile, Anatase and Brookite. It also reveals that the shapes of Rutile and Anatase are tetragonal and that of Brookite is orthorhombic. Among these forms, the rutile form is most common and is commonly distributed across the world. However, when acting as a photo catalyst its absorption edge shifts to 415 nm and has a band gap of 3.2eV on Anatase which produces low level of luminescence in the visible region. To overcome this drawback associated with Tatania it is herein suggested that it can be doped with some the metal or non-metals [14-17].

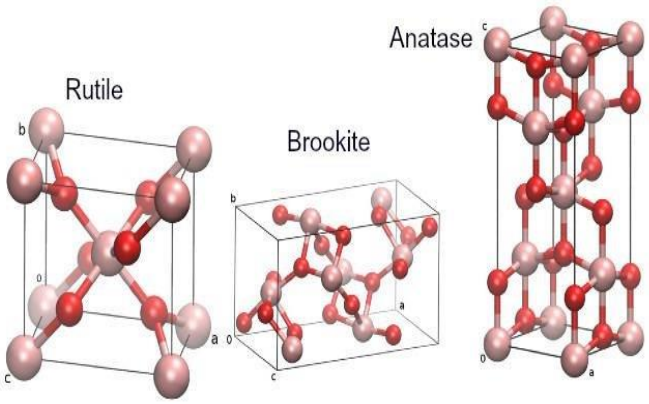

Figure 2: Three crystal structures of Titania

2. MATERIALS AND METHODS

2.1 Preparation of host material

Host material TiO_2 was prepared using this economically viable and environmentally friendly process known as 'Green syntheses. For this preparation 100 fresh oranges were purchase from the market, washed, from which juice was extracted, while the pulp and peels of oranges were sun-dried and grounded. Subsequently; it was mixed with distilled water and was heated at 50 ^{0}C to 60 ^{0}C for 30 to 40 minutes then it was filtered to get an aqueous extract. Pure TiO_2 powder in powder form was provided by the physics laboratory. This was measured and using a weighing balance the amount weighed was 0.04g then added directly to 100ml distilled water. It was then mixed with 20ml for the purpose of bringing down the large size particle into nanoparticles with extract of 5mM solution of TiO_2. The pertaining solution is agglomerated in magnetic stirrer for four hours and is then centrifuged for nearly two hours out of total reaction time of six hours. here, the nanoparticles were precipitated through centrifugation while the particles acquired from the solution were dried through using a hot air oven.

2.2 Doping of terbium (Tb_4O_7) in titanium oxide TiO_2

Like in the green synthesis process, titanium oxide and terbium oxide were grinded on aluminum sheets as well. The experiment was performed for five times and terbium is doped in titanium oxide in a ratio of 0%, 1%, 2%, 3% and 4 % of each has been weighed accurately by means digital balance. As for the preparation of homogenous mixture of terbium in titanium oxide ethanol was used. The mixture was prepared on crucibles that have small mass and highly inertial to the reaction that intends to express high temperature. The result in Pencil, for each crucible, was specified as 0%, 1%, 2%, 3% and 4%.

(a) (b)

Figure 3: (a) Samples placed in furnace for calcination (b) Samples heated to 1100^0C

The samples were placed in the furnace at the laboratory of physics, University of Science and Technology Kohat Kust. They wanted to use furnace to raise the temperature through every 30 minutes to 100^0C. The samples were heat treated at a temperature of 1100^0C and kept at this temperature interval for 1 hr. The samples were cooled to near 12 hours to enrich the exothermic process.

The samples were also removed from the furnace. They were in good clarified form now. In preparation of small crystalline for the samples, the samples were grind using mortar pestle. These were then dispensed in bullet vials and labeled in terms of percentage ratio of terbium from 0 to 4% for other different characterizations.

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3. RESULT AND DISSCUSSION

3.1 X-Ray Diffractometer (XRD) Analysis

The XRD pattern of characterized samples of terbium doped titanium oxide with different concentrations is presented below at the Fig.4 This is clear from all the peaks observed which are in fairly well agreement with the standard reference of titanium oxide JCPDS Card No. 89-4920 The graph also establishes the fact that the TiO_2 exists in the most stable phase known as Rutile. There was no diffraction peak of Anatase form present in the pattern which shows that the crystal structure still remains as same after doing terbium. This further confirmed with excellent intensity of the peaks which attributed to calcination temperature of 1100^0C. The outcomes were also comparable with other obvious findings as well. The highest intensity is at 27.73^0 degree attributable to miller indices (110) reflection plane [18]. Other several other high intensities are also achieved at 36.37^0 and 54.58^0 which is in concordance with other researchers conducted. This suggests that the peaks are well defined implying that TiO_2 is in nanoparticles from [19].

It was also noted that in the graph there is no any indication peak of any impurity. This means that in terbium a titanium atom has been replaced by terbium without affecting the formation of the crystal. However, there is an increase in the formation and height of the peaks with an increase in doping concentration. It is also observed that the first intensity peak is reduced in the presence of dopant and it may be attributed to the change in the radii of terbium and titanium ions or due to the change in the mechanical properties of the crystal on doping concentration.

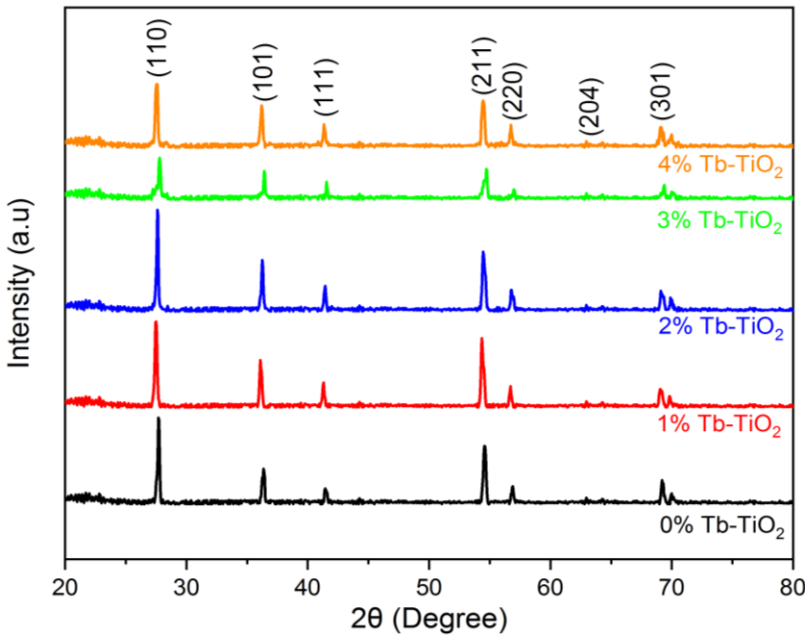

Figure 4: X-ray diffractogram showing the peaks for $Ti_{1-x}Tb_xO_2$

3.2 The Scanning Electron Microscopy (SEM) analysis

These samples were characterized by quantitative and qualitative methods including scanning electron microscopy for grain size and elemental analysis. This from the SEM images as depicted in the figure all the samples are represented by images of equal resolution of 500nm it further confirms the micro size of the particles where we had noted that the nature of the particles was irregular due to aggregation of the initial particles due to high calcination temperature. Spherical like morphology of TiO_2 is reported to be at the low calcination temperature. High calcination temperature has been associated with improvement in the crystalline and grain size [20]. EDX elemental analysis measurement to detect the elemental composition of the synthesized samples reveals the presence of terbium, titanium and oxygen as reflected in the figure but cannot identify any other element. There is presence of oxygen as a hint that the prepare sample is in the form of titanium dioxide. A sample of pure TiO_2 consists of 52.18 % by weight of oxygen and 47.82 % of titanium, while 1% Tb-TiO_2 consists of 52.20% oxygen, 47.75% titanium, and 0.04% Tb; 2% Tb-TiO_2. A high calcination temperature has also been reported to enhance the level of crystallinity and grain size [20]. The EDX measurements carried out confirm the elemental check list and affirm the presence of terbium, titanium and oxygen but no other element as depicted below: It is also evident from the presence of oxygen that the form of the prepare sample is titanium dioxide. Elemental composition of the pure TiO_2 sample has 52.18wt % oxygen and 47.82wt% titanium, 1% Tb-TiO_2 contains 52.20wt % oxygen and 47.75wt% titanium with 0.04wt% terbium,

It is also confirmed that the particle size of the pure TiO_2 sample is 34.6 nm, 1 % Tb-TiO_2 sample is 32.3nm and 2 % Tb-TiO_2 sample is 36.7nm, 4% Tb-TiO_2 sample is 39.8nm and the 5 % Tb-TiO_2 sample is 41.8nm. In general terms there is a direct relation between the dopant concentration and the size of the crystallite and there is always a general tendency of better luminescence with increase in the grain size.

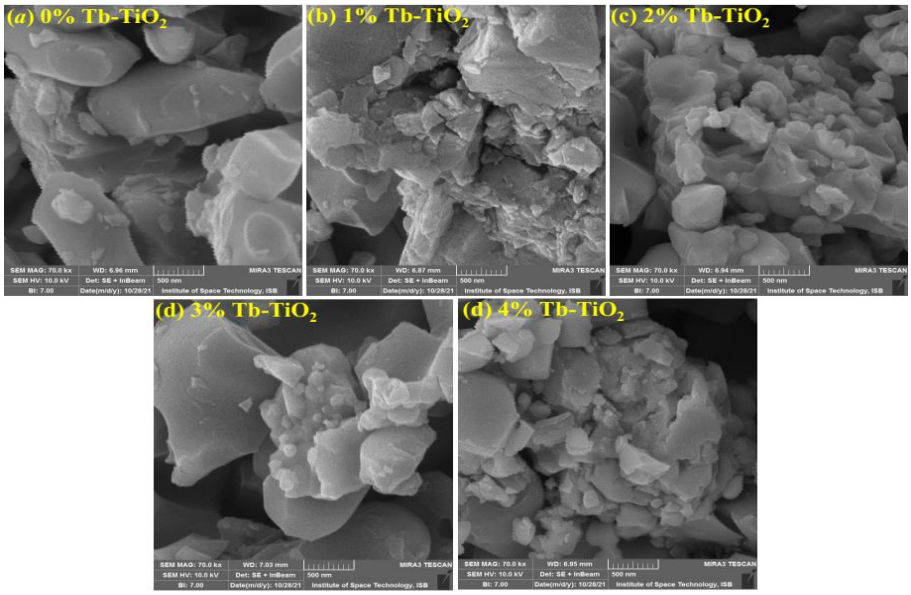

Figure 5: SEM micrographs of Tb doped titanium oxide

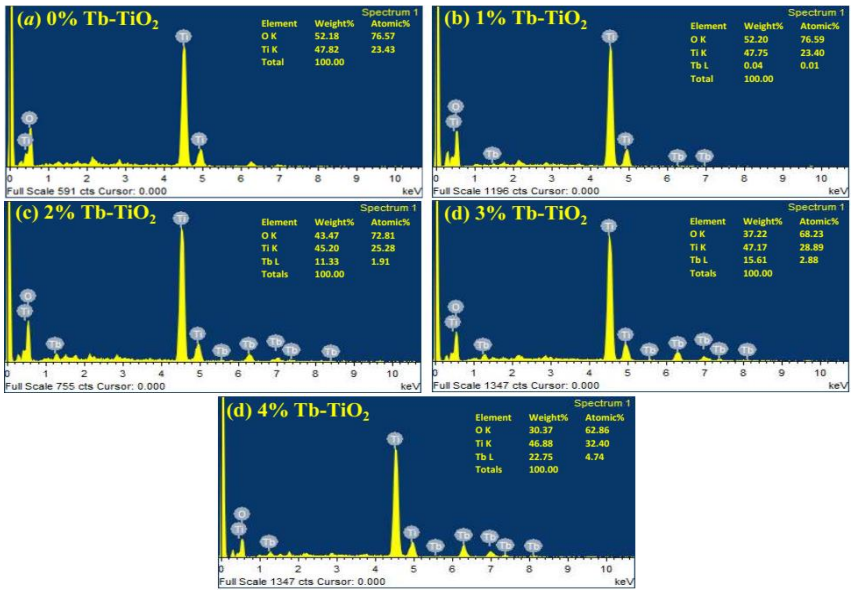

Figure 6: EDX analysis of Tb doped titanium oxide.

3.3 FTIR analysis

FTIR, in this case, revealed very clearly the various functional groups, organic and inorganic substances that are present in the given sample. It provides information about the substance of the object. Figure shows the FTIR spectra of terbium doped green synthesized TiO_2 nanoparticles in the region of 500-4000 cm-1. Because of calcination temperature (1100°C), there is no signal of stretching vibration of Ti-OH.

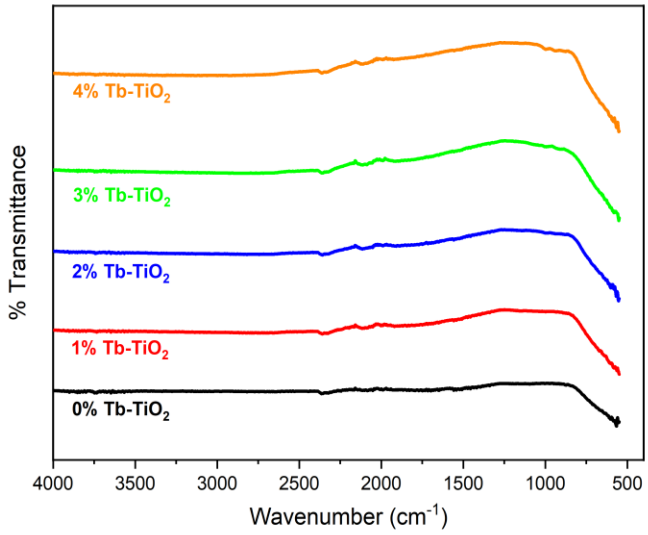

Figure7: FTIR spectrum of Tb doped titanium oxide

3.4 Photoluminescence analysis

Fig 8 shows the emission spectrum of TiO_2 The photoluminescence spectrum of Tb^{3+} phosphor, when the material is exited at 400nm. At 590nm and 690nm two large changes with regards to the measure of light transmitted were observed to occur.

Yellow transition from ($^5H_7$ to $^7F_4$) level emitted in the range of 578-620nm while the red transition from ($^5H_7$ to $^7F_0$,1,2) level emitted in the ranges 660-730nm.

These emission peaks are in well consensus with the emission spectrum reported in the literature [21-24]. Fig. 9 is the energy level diagram indicate the general transitions of Tb^{3+} ion from various phosphor.

As shown from above data, the intensity of yellow emission spectrum is much higher than that of red emission spectrum. Consequently, the synthesized phosphor can be used as yellow emission phosphor.

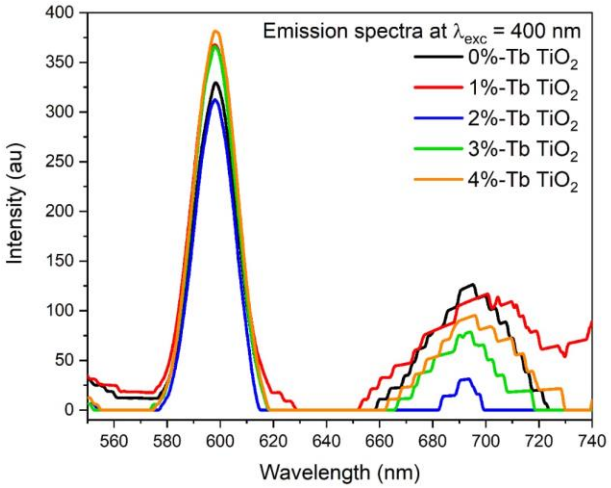

Figure 8: PL emission spectrum of TiO_2 with different concentration of Tb

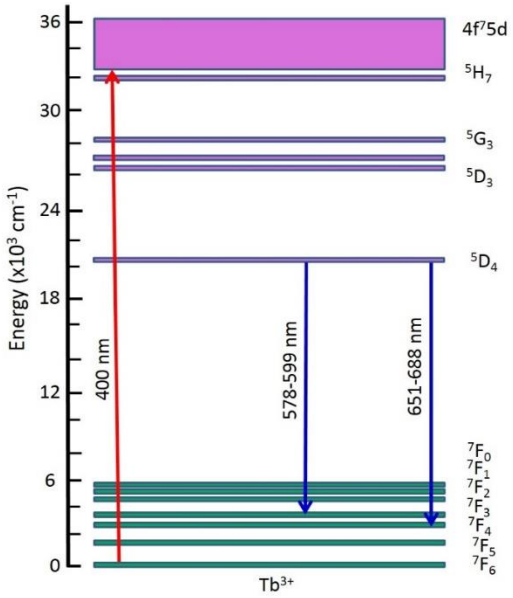

Figure 9: Energy level diagram of Tb^{3+} with various possible transitions.

4. Conclusion

Green synthesis is a cheaper and environmental friendly approach to synthesize TiO_2. The uniformly sharp and well matching peaks of XRD pattern also bear the testimony of the fact that the prepared sample is crystalline in nature. This is accompanied by a narration of the crystal size with regards to the dopant concentration and therefore enhanced luminescence outcomes. In the present case, no such stretching vibrations have been observed, particularly because of the high calcination temperature involved. The prepared sample emits yellow and red light. This is due to

transition from $^5H_7$ to $^7F_4$ The intensity of yellow light is high. It is clearly seen that the highest intensity is shown by 4% of Tb doped in TiO_2. However, in the present case photoluminescence intensity is observed to be less for other concentration of Tb as well. Thus, use of Tb doped titanium oxide as phosphor is recommended for yellow color.

RECOMMENDATION

The study presents the possibility of Tb-doped TiO_2 synthesized using an ecofriendly green synthesis approach with orange fruit extract as a reductant. The excellent properties of emission, especially the high photoluminescence intensity at 4% doping with Tb, make this material a good candidate for phosphor utilization in all applications that require yellow emission such as lighting systems and display technologies. The synthesis method needs to be scaled up and extended to produce other doped oxides with minimal environmental impact. Further optimization of dopant concentration and investigations into the long-term stability and performance of the material under various conditions are suggested to enhance its practical applicability. Its potential for advanced applications, including bioimaging, photocatalysis, and energy-efficient lighting, also warrants further research

Authors' Contribution

Majid Ali, as a first author, was responsible for conducting the research, performing experiments, analyzing data, and preparing the manuscript. Niaz Ur Rehman and Muhammad Bilal, as corresponding authors, supervised the study, ensured its quality, and managed journal communication. Shahzad Nawaz Malik, Shamaila Fatima, and Hammad Haider contributed by refining the methodology, reviewing literature, organizing the manuscript, and validating data.

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