

## List of publications

### Publications from thesis

1. **Owais Mehraj**, Bilal M. Pirzada, Niyaz A. Mir, Saima Sultana and Suhail Sabir, *Ag<sub>2</sub>S sensitized mesoporous Bi<sub>2</sub>WO<sub>6</sub> architectures with enhanced visible light photocatalytic activity and recycling properties*, **RSC Advances** 5 (2015) 42910.
2. **Owais Mehraj**, Niyaz A. Mir, Bilal M. Pirzada, Suhail Sabir, and M. Muneer, *In-situ anion exchange synthesis of AgBr/Ag<sub>2</sub>CO<sub>3</sub> hybrids with enhanced visible light photocatalytic activity and improved stability*, **Journal of Molecular Catalysis A: Chemical** 395 (2014) 16.
3. **Owais Mehraj**, Niyaz A. Mir, Bilal M. Pirzada and Suhail Sabir, *Fabrication of novel Ag<sub>3</sub>PO<sub>4</sub>/BiOBr heterojunction with high stability and enhanced visible-light-driven photocatalytic activity*, **Applied Surface Science** 332 (2015) 419.
4. **Owais Mehraj**, Bilal M. Pirzada, Niyaz A. Mir, Mohammad Zain Khan and Suhail Sabir, *In situ synthesis of Fe<sub>2</sub>O<sub>3</sub>/BiOI p/n heterojunctions with improved photodegradation properties and stability*. **(Communicated)**.

### Other Publications

5. Bilal Masood Pirzada, Niyaz A. Mir, Nida Qutub, **Owais Mehraj**, Suhail Sabir and M. Muneer, *Synthesis, characterization and optimization of photocatalytic activity of TiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposite heterostructures*, **Materials Science and Engineering B** 193 (2015) 137.
6. Bilal Masood Pirzada, **Owais Mehraj**, Niyaz A. Mir, Mohammad Zain Khan and Suhail Sabir, *Efficient visible light photocatalytic activity and enhanced stability of BiOBr/Cd(OH)<sub>2</sub> heterostructures*, **New Journal of Chemistry** 39 (2015) 7153.
7. Nida Qutub, Bilal Masood Pirzada, Khalid Umar, **Owais Mehraj**, M. Muneer and Suhail Sabir, *Synthesis, characterization and visible-light driven photocatalysis by differently structured CdS/ZnS sandwich and core-shell nanocomposites*, **Physica E** 74 (2015) 74.

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## Ag<sub>2</sub>S sensitized mesoporous Bi<sub>2</sub>WO<sub>6</sub> architectures with enhanced visible light photocatalytic activity and recycling properties

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To harvest solar energy more efficiently, novel Ag<sub>2</sub>S/Bi<sub>2</sub>WO<sub>6</sub> heterojunctions were synthesized by a hydrothermal route. This novel photocatalyst was synthesized by impregnating Ag<sub>2</sub>S into a Bi<sub>2</sub>WO<sub>6</sub> semiconductor by a hydrothermal route without any surfactants or templates. The as prepared structures were characterized by multiple techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS), UV-vis diffuse reflection spectroscopy (DRS) and photoluminescence (PL). The characterization results suggest mesoporous hierarchical spherical structures with a high surface area and improved photo response in the visible spectrum. Compared to bare Bi<sub>2</sub>WO<sub>6</sub>, Ag<sub>2</sub>S/Bi<sub>2</sub>WO<sub>6</sub> exhibited much higher photocatalytic activity towards the degradation of dye Rhodamine B (RhB). Although silver based catalysts are easily eroded by photogenerated holes, the Ag<sub>2</sub>S/Bi<sub>2</sub>WO<sub>6</sub> photocatalyst was found to be highly stable in the cyclic experiments. Based on the results of BET, PL and DRS analysis, two possible reasons have been proposed for the enhanced visible light activity and stability of this novel photocatalyst: (1) broadening of the photoabsorption range and (2) efficient separation of photoinduced charge carriers which does not allow the photoexcited electrons to accumulate on the conduction band of Ag<sub>2</sub>S and hence prevents the photocorrosion.

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### 1. Introduction

The growing environment concerns and energy demand are the main driving forces for the sustained fundamental and applied research in the area of semiconductor photocatalysis for organic pollutant degradation and hydrogen generation from water splitting using solar light.<sup>1–3</sup> Semiconductor photocatalysis involves the photoinduced generation of electron–hole pairs, therefore an ideal photocatalyst should have an extended spectral responsive range and low recombination rate of photogenerated charge carriers.<sup>4</sup> Coupling of two photocatalysts to form a heterojunction may provide a chance to develop a new photocatalyst with enhanced separation of photoinduced charge carriers and an extended photoabsorption range.<sup>5,6</sup>

Bi<sub>2</sub>WO<sub>6</sub> is one of the simple aurivillius oxide with perovskite-like slabs of WO<sub>4</sub><sup>2–</sup> and Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup>.<sup>7,8</sup> Owing to its non-toxicity and strong oxidizing power, Bi<sub>2</sub>WO<sub>6</sub> has been used as one of the promising and excellent photocatalyst for the decomposition of organic pollutants under visible light.<sup>9–12</sup> To improve the

photocatalytic activity of bare Bi<sub>2</sub>WO<sub>6</sub>, many different morphologies of Bi<sub>2</sub>WO<sub>6</sub> with different hierarchical architecture and surface area have been reported. These include the development of nanoplates,<sup>13</sup> porous thin films,<sup>14</sup> 3D nest like mesoporous Bi<sub>2</sub>WO<sub>6</sub> architectures<sup>15</sup> and flower sphere like complex structures.<sup>16,17</sup> However there are still two important factors which limits the photocatalytic efficiency and thus hinders the practical application of bare Bi<sub>2</sub>WO<sub>6</sub> (1) the absorption edge of pure Bi<sub>2</sub>WO<sub>6</sub> is *ca.*, 450 nm<sup>18,19</sup> which overlaps a small part of solar spectrum leading to the unsatisfactory photoresponse range and (2) the recombination rate of photoinduced charge carriers is large which leads to the low quantum efficiency because of the short lifetimes of the electron hole pairs.<sup>20,21</sup>

Recent studies have shown that coupling of Bi<sub>2</sub>WO<sub>6</sub> with other semiconductors improves the photocatalytic performance of Bi<sub>2</sub>WO<sub>6</sub> to a substantial extent by promoting the effective separation of photoinduced charge carriers and broadening the visible light responsive range, For *e.g.* α-Fe<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub>,<sup>22</sup> Bi<sub>2</sub>S<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub>,<sup>4</sup> Bi<sub>2</sub>O<sub>3</sub> decorated Bi<sub>2</sub>WO<sub>6</sub> and TiO<sub>2</sub> modified flower like Bi<sub>2</sub>WO<sub>6</sub>,<sup>23</sup> Bi<sub>2</sub>WO<sub>6</sub>/BiOBr,<sup>24</sup> WO<sub>3</sub>–Bi<sub>2</sub>WO<sub>6</sub><sup>25</sup> and CuPc sensitized Bi<sub>2</sub>WO<sub>6</sub>.<sup>26</sup>

As an important chalcogenide Ag<sub>2</sub>S with a narrow band gap of 1.1 eV has been investigated extensively for the numerous applications such as photovoltaic device construction,<sup>27,28</sup>

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# In-situ anion exchange synthesis of AgBr/Ag<sub>2</sub>CO<sub>3</sub> hybrids with enhanced visible light photocatalytic activity and improved stability



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Visible light photocatalysis

## ABSTRACT

AgBr/Ag<sub>2</sub>CO<sub>3</sub> hybrids were synthesized via an *in situ* anion-exchange reaction between Ag<sub>2</sub>CO<sub>3</sub> and NaBr. The obtained hybrids were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), UV–vis diffuse reflectance spectroscopy (DRS) and terephthalic acid-photo luminescence (TA-PL) technique. The as prepared AgBr/Ag<sub>2</sub>CO<sub>3</sub> hybrids exhibited wide absorption in the visible light region and displayed efficient and higher photocatalytic activities towards the degradation of dye molecules (Ponceau BS) as compared to pure AgBr and Ag<sub>2</sub>CO<sub>3</sub> samples under visible light irradiation ( $\lambda > 400$  nm). The enhanced photocatalytic activity of AgBr/Ag<sub>2</sub>CO<sub>3</sub> was related to the efficient separation of electron–hole pairs derived from matching band potentials between AgBr and Ag<sub>2</sub>CO<sub>3</sub>, as well as the good electron trapping role of Ag<sup>0</sup> nanoparticles *in situ* formed on the surface of AgBr and Ag<sub>2</sub>CO<sub>3</sub> particles during photocatalytic oxidation process. The quenching effect of different scavengers of reactive species suggested that  $\cdot\text{OH}$  and  $\text{h}^+$  play major role in the degradation of PBS. The enhanced stability of the hybrid was attributed to the trapping of photogenerated electrons from the surface of catalyst by Ag<sup>0</sup> nanoparticles which suppress the photocorrosion.

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## 1. Introduction

Energy conversion and environmental accountability are two major challenges to the sustainable development of human society. Over the past decades the various advancements in the field of semiconductor-based photocatalysis have received considerable and prime attention focussed on the view point of solving environment and energy related issues [1–3]. The oldest and conventional TiO<sub>2</sub> catalyst, although still most widely used because of its easy availability, low cost and nontoxicity has relatively wide band gap (3.2 eV) which has significantly limited its application to UV light only (4% of solar spectrum only) [4–6]. To exploit the solar energy, the development of visible light responsive photocatalysts has become one of the imperative and desired topics in the photocatalytic field [7–13]. To exploit the visible light responsive photocatalysts, there are usually two ways. One way is to introduce the intermediate energy levels between valence band and conduction band by doping metal or non-metal elements such as

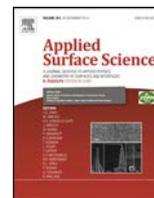
V, Cr, Fe or S, C and N so that the absorption edge shifts into the visible range [14–17]. However in terms of photocatalytic activity this method is not ideal because dopants will serve as centres for electron–hole recombination. The other strategy is to develop novel materials such as BiVO<sub>4</sub> [18,19], Ag<sub>2</sub>MO<sub>4</sub>O<sub>13</sub> [20] and Bi<sub>2</sub>WO<sub>6</sub> [18,21] which can effectively utilize visible light that constitutes 43% of total sunlight.

Lately a feasible and highly efficient strategy of incorporating p-block elements into the narrow band gap oxides was used to design new visible light driven photocatalysts [22]. The incorporation of p-block elements such as P or C into the reported Ag<sub>2</sub>O broadens the narrow band gap of 1.3 eV [23] and enhances the oxidative ability and photocatalytic activity of new visible light driven photocatalyst like Ag<sub>3</sub>PO<sub>4</sub> [22], AgSbO<sub>3</sub> [24], Ag<sub>2</sub>CO<sub>3</sub> [25]. All these silver containing compounds show promising photocatalytic activity. Ag<sub>2</sub>CO<sub>3</sub> with band gap of 2.46 eV has been recognised as one of the most promising visible light driven photocatalyst for its excellent and efficient photo oxidative capabilities [25]. However, the recycle experiments suggested that Ag<sub>2</sub>CO<sub>3</sub> was not stable and displayed photocorrosion which seriously deactivates the photocatalyst [25]. It is therefore necessary to fabricate the original Ag<sub>2</sub>CO<sub>3</sub> for improving its stability. Dai et al. [26] employed a new approach to inhibit the photocorrosion by adding AgNO<sub>3</sub> in the reaction system which helps in trapping the electron from conduction band of Ag<sub>2</sub>CO<sub>3</sub>,

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# Fabrication of novel $\text{Ag}_3\text{PO}_4/\text{BiOBr}$ heterojunction with high stability and enhanced visible-light-driven photocatalytic activity



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## ABSTRACT

Herein, we report a facile and effective method to enhance the photocatalytic activity of bismuth oxybromide (BiOBr) semiconductor through the fabrication of heterojunction with  $\text{Ag}_3\text{PO}_4$ . The as synthesized  $\text{Ag}_3\text{PO}_4/\text{BiOBr}$  microspheres were characterized with transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and UV–vis diffuse reflectance spectroscopy (DRS). The new  $\text{Ag}_3\text{PO}_4/\text{BiOBr}$  heterojunctions exhibited wide absorption in the visible-light region and compared to pure BiOBr and  $\text{Ag}_3\text{PO}_4$  samples displayed exceptionally high photocatalytic activity for the degradation of typical organic pollutants such as Rhodamine B (RhB) and phenol. The optimal Ag/Bi weight ratio in  $\text{Ag}_3\text{PO}_4/\text{BiOBr}$  microsphere (AB7) was found to be 0.7. The enhanced photocatalytic activity was related to the efficient separation of electron–hole pairs derived from matching band potentials between BiOBr and  $\text{Ag}_3\text{PO}_4$  which results into the generation of natural energy bias at heterojunction and subsequent transfer of photoinduced charge carriers. Moreover, the synthesized samples exhibited almost no loss of activity even after 6 recycling runs indicating their high photocatalytic stability. Considering the facile and environment friendly route for the synthesis of  $\text{Ag}_3\text{PO}_4/\text{BiOBr}$  hybrids with enhanced visible-light induced photocatalytic activity, it is possible to widely apply these hybrids in various fields such as waste water treatment.

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## 1. Introduction

The increasing concerns of environment deterioration have stimulated the progresses in the contemporary research to exploit the solar energy for the environmental remediation [1,2]. Majority of the oxide semiconductor photocatalysts are only UV light active which constitutes about 4% of the solar spectrum [3] therefore development of visible-light responsive photocatalysts has become a highly desirable topic in contemporary research. Bismuth oxybromide (BiOBr) has been recognised as one of the most promising photocatalysts owing to its lamellar structure [4], high photocatalytic activity and photocorrosion stability [5–10]. The good chemical stability and eco-friendly nature makes BiOBr as one of the choicest catalysts for degradation of toxic organic pollutants [11–15]. However, its band gap (2.9 eV) limits the absorption above 430 nm [16].

Several strategies such as impurity doping [17], surface decoration [18,19] (metal deposition or heterojunction), photosensitization [19] and morphology controlled synthesis

[20–24] have been employed to broaden the visible-light absorption range of such photocatalysts. Though doping has proved to be effective in shifting the absorption edge into the visible range but the sensitivity of photocatalysts to doping level and homogeneity makes it a less suitable method [25]. Construction of heterostructures by combination of two semiconductors with matching band potentials, such as BiOCl/Bi<sub>2</sub>O<sub>3</sub> [26], AgI/BiOI [27], BiOCl/BiOI [28], BiOBr/BiOI [29–31], Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/BiOI [32] and Bi<sub>2</sub>S<sub>3</sub>/BiOI [33] has turned out to be more flexible and effective strategy for broadening the visible-light absorption of photocatalysts because heterojunction can effectively tune the electronic properties of composites [26] and are less sensitive to component homogeneity. For an effective heterojunction with increased visible-light absorption and efficient separation of photoinduced charge carriers, the semiconductors should have the matching band structure, requisite band gap energy and suitable molar ratio [19,34–36].

$\text{Ag}_3\text{PO}_4$  is a visible-light responsive photocatalyst and exhibits extremely high photooxidative capability for O<sub>2</sub> evolution from water and decomposition of organic dyes [37,38]. Unfortunately, pure  $\text{Ag}_3\text{PO}_4$  has low structural stability which limits its environmental applications [39]. To the best of our knowledge no significant effort has been made for the preparation of

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# Synthesis, characterization and optimization of photocatalytic activity of TiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposite heterostructures



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TiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposite

## ABSTRACT

Titanium dioxide/zirconium dioxide nanocomposites were synthesized using a simple and modified sol–gel method. The synthesized particles were characterized through SEM, TEM, XRD, and DTA/TGA. SEM analysis shows micrographs with irregular and sharp edged particles. TEM analysis shows spherical particles of average diameter 10.5 nm. Tetragonal structure of TiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposite particles with stabilized anatase phase was confirmed by XRD studies. The average crystallite size was calculated from XRD, using Scherrer's formula. Band gap was calculated from the DRS spectra using Kubelka-Munk function and Photoluminescence (PL) was done to study the recombination rate of charge carriers. Results showed a considerable increase in band gap on ZrO<sub>2</sub> addition and subsequent decrease in recombination rate. Impedance study showed a significant decrease in dielectric characteristics on ZrO<sub>2</sub> addition. Photocatalytic activity of the synthesized catalysts was studied by degradation of an azo-dye, Ponceau BS, using ultra-violet source of light. Optimum activity was observed on 6.0% ZrO<sub>2</sub> loading.

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## 1. Introduction

The un-abating use of organic dyes in different industries is a serious problem in terms of environmental concerns. Extensive use of organic dyes (mostly azo dyes) in textile industries is a big threat to water bodies and severely affect water quality parameters. To overcome this issue, several treatment methods, such as, Chemical Oxidation, Wet Oxidation, Biological Treatment, Ozonolysis and Activated Carbon Adsorption have been proposed for the removal of organic pollutants from industrial effluents. Moreover, photocatalysis proved to be promising due to the use of easily available solar energy [1–3].

In photocatalysis, the catalyst absorbs photons of light to undergo excitation of electrons from the valence band to the conduction band, generating electron-hole pairs. These electron hole pairs act as redox centres and readily initiate oxidation-reduction processes on catalyst surface, resulting in the degradation of toxic pollutants [4–6].

To look for a feasible and efficient photocatalyst, metal oxide nanomaterials are being explored as semiconductor photocatalysts for the degradation of organic pollutants. These semiconductor catalysts are able to degrade pollutants into easily biodegradable compounds and eventually mineralize them into carbon dioxide and water. TiO<sub>2</sub> has received much attention as a photocatalyst after Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO<sub>2</sub> electrode under ultraviolet (UV) light [7,8]. TiO<sub>2</sub> gained priority due to its abundance in the geosphere, high photochemical stability, low cost, non-toxicity, biological inertness, reusability and the possibility of its activation by sunlight [9–11]. However, a large band gap (~3.2 eV) in TiO<sub>2</sub> makes it responsive in the ultra-violet light which makes only about 5% of the solar spectrum. Hence, efforts are being put to make it active into the visible region, in order to make the best use of solar energy [12].

Moreover, pure titania is poor in quantum efficiency due to prevailing photo-corrosion by rapid recombination of electrons and holes. To circumvent, development of reliable composite photocatalyst is a priority in today's research [13]. In order to effectively control photo-corrosion, the various attempts include encapsulation of electron acceptors on functionalized semiconductors, immobilization of semiconductor photocatalyst in redox functionalized polymers and electrostatic association of electron acceptors at the semiconductor surface. The efficiency of photocatalyst is considerably enhanced by coupling with a foreign metal oxide. Usually,

Abbreviations: TTIP, Titanium tetra-isopropoxide; PBS, Ponceau BS.

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## Efficient visible light photocatalytic activity and enhanced stability of BiOBr/Cd(OH)<sub>2</sub> heterostructures†

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Novel BiOBr/Cd(OH)<sub>2</sub> heterostructures were synthesized by a facile chemical bath method under ambient conditions. A series of BiOBr/Cd(OH)<sub>2</sub> heterostructures were obtained by tuning the Bi/Cd molar ratios. The obtained heterostructures were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). Optical properties were studied by UV-visible spectroscopy, diffuse reflectance spectroscopy and photoluminescence (PL). Photocatalytic studies on rhodamine B (RhB) under visible light irradiation showed that the heterostructures are very efficient photocatalysts in mild basic medium. Scavenger test studies confirmed that the photogenerated holes and superoxide radicals (O<sub>2</sub><sup>•−</sup>) are the main active species responsible for RhB degradation. Comparison of photoluminescence (PL) intensity suggested that an inhibited charge recombination is crucial for the degradation process over these photocatalysts. Moreover, relative positioning of the valence and conduction band edges of the semiconductors, O<sub>2</sub>/O<sub>2</sub><sup>•−</sup> and <sup>•</sup>OH/H<sub>2</sub>O redox potentials and HOMO–LUMO levels of RhB appear to be responsible for the hole-specificity of degradation. Photocatalytic recycling experiments indicated the high stability of the catalysts in the reaction medium without any significant loss of activity. This study hence concludes that the heterojunction constructed between Cd(OH)<sub>2</sub> and BiOBr interfaces play a crucial role in influencing the charge carrier dynamics and subsequent photocatalytic activity.

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### 1. Introduction

Heterogeneous photocatalysis has evolved as a viable technology for the control of environmental pollution related issues and energy conversion.<sup>1</sup> To date various kinds of catalyst semiconductor materials, including metal oxides,<sup>2</sup> sulphides,<sup>3</sup> nitrides,<sup>4</sup> and their mixed solid solutions,<sup>5,6</sup> have been used as photocatalysts responsive to both the UV and visible light wavelengths. Primarily, TiO<sub>2</sub> received wide attention due to its excellent photocatalytic activity, chemical stability, and non-toxicity.<sup>7</sup> However, it has limited practical application due to a large band gap of ~3.2 eV and rapid recombination of photogenerated charge carriers.<sup>8</sup>

In order to overcome the limitation and effectively control photocorrosion, various attempts including encapsulation of

electron acceptors on functionalized semiconductors, immobilization of semiconductor photocatalysts in redox functionalized polymers and electrostatic association of electron acceptors at the semiconductor surface were made. Transition metal ion doping is one approach for acquiring visible response by introducing intermediate impurity energy levels.<sup>9,10</sup> The efficiency of the photocatalyst is considerably enhanced by coupling with a foreign metal oxide.<sup>11,12a</sup> Currently, coupling of semiconductors with graphene is widely recognized to be a viable strategy to improve the photocatalytic performance of an electronically conductive 2D platform enabling the acceptance and shuttle of photogenerated electrons from band-gap-excitation of semiconductors.<sup>12b–d</sup> Recent studies have also revealed that some physical and chemical properties of TiO<sub>2</sub>, such as light absorption, photocatalytic reactivity, selectivity, *etc.*, can be modulated by its defect disorder.<sup>12e</sup>

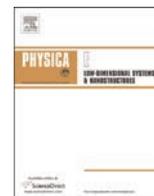
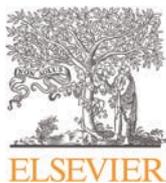
Heterostructure construction between two different semiconductors has also been extensively applied in many fields including photocatalysis and solar energy conversion,<sup>13,14</sup> because heterojunctions control the behaviour of photogenerated charges, such as the direction of transportation, the distance of separation, and the recombination rate.<sup>15,16</sup> Furthermore, the

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# Synthesis, characterization and visible-light driven photocatalysis by differently structured CdS/ZnS sandwich and core–shell nanocomposites



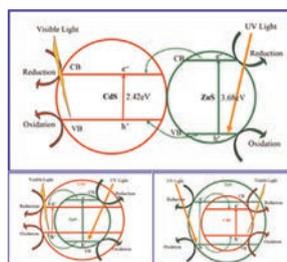
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## HIGHLIGHTS

- CdS–ZnS sandwich and core–shell nanocomposites.
- Visible light response in CdS–ZnS nanocomposites.
- Reduction of charge recombination and leaching.
- Higher photocatalytic activity in core–shell nanocomposites.

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Acid Blue

## ABSTRACT

CdS/ZnS sandwich and core–shell nanocomposites were synthesized by a simple and modified Chemical Precipitation method under ambient conditions. The synthesized composites were characterized by XRD, SEM, TEM, EDAX and FTIR. Optical properties were analyzed by UV–vis. Spectroscopy and the photoluminescence study was done to monitor the recombination of photo-generated charge-carriers. Thermal stability of the synthesized composites was analyzed by Thermal Gravimetric Analysis (TGA). XRD revealed the formation of nanocomposites as mixed diffraction peaks were observed in the XRD pattern. SEM and TEM showed the morphology of the nanocomposites particles and their fine particle size. EDAX revealed the appropriate molar ratios exhibited by the constituent elements in the composites and FTIR gave some characteristic peaks which indicated the formation of CdS/ZnS nanocomposites. Electrochemical Impedance Spectroscopy was done to study charge transfer properties along the nanocomposites. Photocatalytic properties of the synthesized composites were monitored by the photocatalytic kinetic study of Acid Blue dye and p-chlorophenol under visible light irradiation. Results revealed the formation of stable core–shell nanocomposites and their efficient photocatalytic properties.

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## 1. Introduction

Zinc sulfide (ZnS) is an important II–VI semiconductor material with wide direct band gap,  $E_g = 3.68$  eV (336 nm) [1–3], high index

*Abbreviations:* NCs, nanocomposites; NPs, nanoparticles; QDs, quantum dots; CB, conduction band; VB, valence band; AB 29, Acid Blue 29

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of refraction, high transmittance in the visible range [4], and large exciton binding energy (40 meV) [5,6]. At ambient conditions, ZnS can have two different crystal structures, zinc blende (cubic) and wurtzite (hexagonal) [2]. One more crystalline phase “Rock Salt” can occur at high pressure but only in case of nanosized ZnS [7]. Surprisingly, hexagonal ZnS displays much better optical properties than the cubic phase, however, cubic phase is more stable [8]. As decreasing the particle size lowers the temperature boundary, the nanosized hexagonal can be synthesized at temperatures