Synthesis and characterization of BiOCl–Cu₂ZnSnS₄ heterostructure with enhanced photocatalytic activity

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Abstract

Cu₂ZnSnS₄ QDs (5–7 nm) were synthesized by chemical coprecipitation route. Using prepared Cu₂ZnSnS₄ QDs, a new type of BiOCl–Cu₂ZnSnS₄ heterostructures were prepared using bismuth nitrate as a precursor and potassium chloride as a source of chlorine at 100 °C, 4 h. BiOCl–Cu₂ZnSnS₄ heterostructures were analyzed by XRD, TEM, UV–visible NIR, PL and surface area studies. The diffracted peaks of BiOCl–Cu₂ZnSnS₄ heterostructure show the presence of tetragonal BiOCl and did not show the intense peaks of Cu₂ZnSnS₄ QDs. TEM images of BiOCl–Cu₂ZnSnS₄ showed the deposition of Cu₂ZnSnS₄ QDs on the BiOCl microsphere surface. The surface area of BiOCl, Cu₂ZnSnS₄ and BiOCl–Cu₂ZnSnS₄-1 was of 1.91 m²/g, 3.06 m²/g and 13.39 m²/g, respectively. BiOCl–Cu₂ZnSnS₄-1 had a higher photodegradation rate for Congo red dye than BiOCl and Cu₂ZnSnS₄ QDs under sunlight, and that higher photoactivity was due to the heterostructure effect between BiOCl and Cu₂ZnSnS₄ QDs along with increased optical absorption in the visible region. Scavenger study endorses the involvement of superoxide and holes radicals in the degradation of Congo red.

Keywords BiOCl–Cu₂ZnSnS₄ · Heterostructure · Nanocomposite · Photodegradation · Congo red · Scavengers

Introduction

Semiconductor photocatalysis is a useful, low-cost and environmentally benign technique for solving environmental pollution problems. The scientific community is focused on a very challenging and relevant research's direction, for the synthesis of a better photocatalyst for hydrogen production, environmental pollution and many more. Bismuth oxychloride (BiOCl) is one of the good adsorbents and photocatalyst for the elimination of organic pollutants such as dyes, phenols, bacteria as it possesses a high chemical stability (Li et al. 2017). The good photocatalytic activity is attributed to layered structure consisting of alternate arrangement of [Bi₂O₂]²⁺ monolayer and dual Cl layers (Ao et al. 2016). BiOCl had better photodegradation performance than commercial TiO₂ (P25) under UV light irradiation. However, due to its large band gap (3.17–3.54 eV) decreases BiOCl photoactivity (Liu et al. 2016). Thus, it is necessary to overcome these limitations and it can be performed by forming

heterostructured composites through coupling of BiOCl with another semiconductor having narrow band gap. The designed BiOCl heterostructured composite will possess better visible light response and also facilitate the separation of photoinduced electron–hole pairs due to synergistic effect which eventually provides excellent photodegradation of contaminants.

Copper zinc tin sulfide (Cu₂ZnSnS₄) is a quaternary semiconducting compound of stannite structure. Cu₂ZnSnS₄ is an abundant, non-toxic component in the earth crust. The absorption coefficient of Cu₂ZnSnS₄ is 10⁴ cm^{−1}. Its band gap is about 1.4–1.7 eV (Malerba et al. 2014). Cu₂ZnSnS₄ has shown to be an excellent light energy-harvesting material for solar cells and good chemical stability in the photodegradation of organics (Arbouz et al. 2017; Hou et al. 2014; Barpuzary et al. 2015).

BiOCl-based constructed heterostructures revealed the enhanced photocatalytic activity, for example, BiOCl–La₂Ti₂O₇ (Ao et al. 2016), Bi₂S₃–BiOCl (Xu et al. 2017), CdS–BiOCl (Pan et al. 2018), BiOCl–ZnFe₂O₄ (Sun et al. 2018), AgCl–BiOCl (Cheng et al. 2014), BiVO₄–BiOCl (He et al. 2014), Co₃O₄–BiOCl (Tana et al. 2014), BiOCl–TiO₂ (Li et al. 2016), Bi₃O₄Br/BiOCl (Gao et al. 2010), BiOCl/C₃N₄ (Huang et al. 2017), α-Fe₂O₃/

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BiOCl (Zheng et al. 2018), BiOCl–Ag₃PO₄ (Cao et al. 2013), BiOCl–Ag₂CO₃ (Fang et al. 2016), Ag-modified BiOCl (Yu et al. 2017), BiOCl–SnO₂ (Sun et al. 2015), Bi₂MoO₆–BiOCl (Zuo et al. 2015), CdS/BiOCl (Lin et al. 2017), BiOCl–Ag₈SnS₆ (Shambharkar and Chowdhury 2018). This inspires us to fabricate a novel BiOCl–Cu₂ZnSnS₄ heterostructure with the hope of boosting visible light absorption capacity for better photocatalytic activity than their single component.

In the present study, chemical coprecipitation method was employed for synthesizing Cu₂ZnSnS₄ QDs (5–7 nm). The prepared Cu₂ZnSnS₄ QDs were used for constructing BiOCl–Cu₂ZnSnS₄ heterostructure through deposition of Cu₂ZnSnS₄ particles on the surface of BiOCl with the help of coprecipitation method. BiOCl–Cu₂ZnSnS₄ heterostructure can extend the response of visible light and separate the photogenerated excitons very effectively and also increases the amount of reactive oxidative species under sunlight. As result, BiOCl–Cu₂ZnSnS₄ heterostructure had a better photocatalytic performance than bare BiOCl and Cu₂ZnSnS₄ QDs. Till date, no study has been conducted on the synthesis of BiOCl–Cu₂ZnSnS₄ heterostructured nanocomposites and evaluated its photocatalytic performance in the degradation of Congo red.

Experimental procedure

Materials

Cu(NO₃)₂·3H₂O, ethylene glycol, Bi(NO₃)₃·5H₂O were procured from Fisher Scientific Ltd. ZnCl₂, SnCl₂·2H₂O, thiourea, potassium chloride were purchased from Merck. Congo red dye was procured from SRL. Distilled water was used to carry out the experiments.

Production of Cu₂ZnSnS₄ QDs, BiOCl and BiOCl–Cu₂ZnSnS₄ heterostructures

Cu₂ZnSnS₄ QDs were prepared by chemical coprecipitation (Shambharkar and Chowdhury 2018; Shambharkar and Chowdhury 2016). 0.1 M Cu(NO₃)₃, (0.05 M) ZnCl₂, (0.05 M) SnCl₂ solutions were taken in a round-bottomed flask, and 50 ml of ethylene glycol (EG) and 10 g of thiourea were added into it and then heated it at 160 °C, 6 h. The black precipitate of Cu₂ZnSnS₄ QDs was acquired and washed with methanol to remove EG and dried.

At the initial stage of reaction, Sn²⁺, Cu⁺, Zn²⁺ ions combine with EG to form Sn–EG, Cu–EG, Zn–EG. When thiourea was added into the reaction system, Sn²⁺, Cu⁺ and Zn²⁺ ions form complex with thiourea and yielded Sn–thiourea, Cu–thiourea and Zn–thiourea complexes. These complexes undergo thermal decomposition at 160 °C

to produce EG-capped Cu₂ZnSnS₄ QDs. The possible reactions occurred during the preparation of Cu₂ZnSnS₄ QDs were as follows:

BiOCl–Cu₂ZnSnS₄-1 heterostructured nanocomposite was obtained from coprecipitation method. 100 mg of Cu₂ZnSnS₄ QDs was mixed with bismuth nitrate solution (0.01 M), 20 ml of EG, and 1 g of KCl. The reaction mixture was stirred and heated at 100 °C, 4 h. Gray color precipitate of BiOCl–Cu₂ZnSnS₄ was formed. Subsequently, the final product was washed to remove EG with methanol and dried at 80 °C. Similar procedure was followed for preparing BiOCl–Cu₂ZnSnS₄-2 using 150 mg of Cu₂ZnSnS₄ QDs. BiOCl microspheres were obtained from our published procedure (Shambharkar and Chowdhury 2018).

Characterization techniques

Crystallinity and purity of Cu₂ZnSnS₄ QDs, BiOCl and BiOCl–Cu₂ZnSnS₄ were determined by conducting X-ray diffraction (XRD) on Bruker AXS D8 ADVANCE X-ray diffractometer. Transmission electron microscope was performed on JEOL Model JEM-2100 to assess the morphology of samples. Band gap energy was obtained from UV–visible diffuse reflectance spectra (Varian, Cary 5000 UV–Vis NIR spectrophotometer). Surface area of the samples was determined from N₂ adsorption–desorption isotherms (Micromeritics ASAP 2020), and photoluminescence (PL) spectra were recorded by JY Fluorolog-3-11 fluorescence spectrofluorimeter with Xenon Lamp (450 W) as excitation source with excitation wavelength 310 nm.

Photocatalytic activity of BiOCl, Cu₂ZnSnS₄ QDs and BiOCl–Cu₂ZnSnS₄ was evaluated by conducting degradation studies using Congo red dye (20 mg/l) under direct sunlight irradiation. BiOCl–Cu₂ZnSnS₄ powder (100 mg) was added in 80 ml of Congo red solution and agitated in the dark to ensure adsorption–desorption equilibrium before light irradiation. A solution of 5 ml from the mixture was taken out after irradiation time was over and centrifuged.

Absorbance the dye was measured at $\lambda_{\max} = 497$ nm on Cary 100 Bio UV–Vis spectrophotometer. The similar technique was accepted for BiOCl and $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles, and the photodegradation performance of samples was studied.

Results and discussion

XRD, TEM, UV–visible NIR, PL and BET studies

XRD pattern of BiOCl, $\text{Cu}_2\text{ZnSnS}_4$ QDs and BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ is shown in Fig. 1a–c. The diffracted peaks of the synthesized $\text{Cu}_2\text{ZnSnS}_4$ QDs were matched with JCPDS file 00-026-0575 (Kesterite, syn) with crystal system tetragonal. The crystallite size of $\text{Cu}_2\text{ZnSnS}_4$ QDs was obtained from Debye Scherrer formula, $D = 0.99\lambda/\beta \cos \theta$, where β is full width at half maximum of the diffracted peak, λ is the X-ray wavelength and θ is the angle of diffraction and it was found to be 7 nm. BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ heterostructure displayed the typical BiOCl signals (JCPDS file 01-085-0861). Characteristic peaks of $\text{Cu}_2\text{ZnSnS}_4$ QDs were not seen in the pattern of BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ which may be due to low content of $\text{Cu}_2\text{ZnSnS}_4$ QDs in the composite (Fig. 1c). The surface morphology and the interaction of $\text{Cu}_2\text{ZnSnS}_4$ QDs with BiOCl were studied from TEM (Fig. 2a–f). From Fig. 2e–f, it was seen that $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles (5–7 nm) were

deposited on BiOCl microsphere surface to form interface linking between BiOCl and $\text{Cu}_2\text{ZnSnS}_4$ QDs. The EDX data (Fig. 3) of BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ revealed the presence of elements O, S, Cl, Cu, Zn, Sn and Bi and were distributed homogeneously in the composite.

UV–Vis NIR absorption spectra of BiOCl, $\text{Cu}_2\text{ZnSnS}_4$ QDs and BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ are shown in Fig. 4. $\text{Cu}_2\text{ZnSnS}_4$ QDs absorbed UV–visible light up to near infrared region, while UV radiation was absorbed by BiOCl and BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ composites exhibited a mixed absorption (Fig. 4b). The band gap energy (E_g) for BiOCl microspheres, $\text{Cu}_2\text{ZnSnS}_4$ QDs and BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ was obtained from Tauc equation (Xiao et al. 2018), and the plots are shown in Fig. 5a–d. The obtained E_g value of BiOCl microspheres was closed to 3.46 eV (Zang et al. 2006). The E_g value was decreased on loading of $\text{Cu}_2\text{ZnSnS}_4$ QDs in composites (Table 1) which may be aroused from synergistic effect between $\text{Cu}_2\text{ZnSnS}_4$ QDs and BiOCl in lowering the band gap.

To study the charge recombination over BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ heterostructures, PL responses were taken and the plots were presented in Fig. 6. At excitation wavelength of 310 nm, BiOCl shows PL intensity with emission peaks at 313 nm, 360 nm and 625 nm. The emission intensity was decreased on incorporating $\text{Cu}_2\text{ZnSnS}_4$ QDs in the BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ -1. This was occurred due to

Fig. 1 XRD pattern of **a** $\text{Cu}_2\text{ZnSnS}_4$ QDs, **b** BiOCl and **c** BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ -1

Fig. 2 TEM images of BiOCl (a, b), Cu₂ZnSnS₄ QDs (c, d) and BiOCl-Cu₂ZnSnS₄-1 (e, f)

Fig. 3 EDX spectra of BiOCl-Cu₂ZnSnS₄-1

the isolation of electrons and holes by coupling BiOCl with Cu₂ZnSnS₄. On further addition of Cu₂ZnSnS₄ in BiOCl-Cu₂ZnSnS₄-2, the PL intensity was increased because of the recombination of isolated electrons and holes. Thus, our findings have shown that BiOCl-Cu₂ZnSnS₄-1 heterostructure exhibited the best e^- - h^+ pair separation.

N₂ adsorption-desorption isotherms of Cu₂ZnSnS₄ QDs, BiOCl and BiOCl-Cu₂ZnSnS₄ were of type III (Fig. 7), and the surface area of BiOCl-Cu₂ZnSnS₄ was increased after adding Cu₂ZnSnS₄ QDs in composite (Table 1). The pore volume of BiOCl-Cu₂ZnSnS₄ was of 0.076 cm³/g.

Fig. 4 UV–visible light-NIR absorption spectrum of BiOCl microspheres, BiOCl–Cu₂ZnSnS₄-1, BiOCl–Cu₂ZnSnS₄-2 and Cu₂ZnSnS₄

Fig. 5 Tauc plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) of **a** BiOCl microspheres, **b** Cu₂ZnSnS₄ QDs, **c** BiOCl–Cu₂ZnSnS₄-1 and **d** BiOCl–Cu₂ZnSnS₄-2

Table 1 Rate constant, band gap energy and surface area of prepared BiOCl microspheres, Cu₂ZnSnS₄ QDs and BiOCl–Cu₂ZnSnS₄

Samples	Indirect band gap (eV)	E_{VB} (eV)	E_{CB} (eV)	Surface area (m ² /g)	Rate (k) (min ⁻¹)
Cu ₂ ZnSnS ₄ QDs	1.29	1.435	0.145	3.06	0.011
BiOCl	3.49	3.60	0.11	1.91	0.0019
BiOCl–Cu ₂ ZnSnS ₄ -1	3.45			13.39	0.0265
BiOCl–Cu ₂ ZnSnS ₄ -2	3.37			–	0.0012

Fig. 6 Photoluminescence spectra of BiOCl, BiOCl-Cu₂ZnSnS₄-1 and BiOCl-Cu₂ZnSnS₄-2

Fig. 7 N₂ adsorption-desorption isotherms of as-prepared BiOCl microspheres, Cu₂ZnSnS₄ QDs and BiOCl-Cu₂ZnSnS₄-1

Photocatalytic performance

After sunlight irradiation, absorbance spectra of Congo red dye solution in the presence of BiOCl microspheres, Cu₂ZnSnS₄ QDs and BiOCl-Cu₂ZnSnS₄ were measured (Fig. 8a–d). The Congo red molecules were degraded completely in the presence of BiOCl-Cu₂ZnSnS₄-1 photocatalyst, and the degradation efficiency was represented in Fig. 9a. BiOCl-Cu₂ZnSnS₄-1 showed higher photodegradation and degraded 94.9% of Congo red dye after 90 min of sunlight irradiation. The photodegradation rate constant of Congo red was higher for heterostructure than for bare BiOCl and Cu₂ZnSnS₄ QDs (Fig. 9c). The improved photocatalytic activity of BiOCl-Cu₂ZnSnS₄ was endorsed to the formation of heterostructure between BiOCl and Cu₂ZnSnS₄ QDs that improved separation and transport of photogenerated charge carriers. The degradation behavior

of BiOCl-Cu₂ZnSnS₄ was compared with commercial P25 TiO₂ and it was observed that the degradation efficiency of BiOCl-Cu₂ZnSnS₄ was lesser than that of P25 TiO₂ towards Congo red (Shambharkar and Chowdhury 2018).

The band edge positions of BiOCl and Cu₂ZnSnS₄ (Zheng et al. 2018; Cao et al. 2013) were determined (Table 1). The χ value for Cu₂ZnSnS₄ QDs was calculated to be 5.29, and χ value for BiOCl was calculated to be 6.36 (Sun et al. 2015). The CB of Cu₂ZnSnS₄ QDs was higher than CB of BiOCl. Therefore, the photoinduced electrons from the conduction band of Cu₂ZnSnS₄ QDs were inserted to the conduction band of BiOCl. Meanwhile, the photogenerated holes on the valence band of BiOCl were moved to valence band of Cu₂ZnSnS₄. This process resulted in heterojunction at the interface of the two compounds (Fig. 10). The holes react with H₂O and generate $\cdot\text{OH}$ radicals. The electrons combine with O₂ to yield active superoxide radical anion of oxygen and decomposed the Congo red dye on the catalyst surface. The degradation experiment was repeated using the BiOCl-Cu₂ZnSnS₄. BiOCl-Cu₂ZnSnS₄ heterostructure had retained its stability up to four cycles.

Various scavengers like isopropanol (Pr) for $\cdot\text{OH}$ radicals, ammonium oxalate (AO) for h^+ , 1,4-benzoquinone (BQ) for O₂ $\cdot^-$ radicals were mixed with Congo red solution containing BiOCl-Cu₂ZnSnS₄ compound, and the photocatalytic activity was executed. From Fig. 9b, it was observed that AO and BQ were inhibited the photodegradation reaction. Therefore, the possible reactions happened over BiOCl-Cu₂ZnSnS₄ heterostructure in the degradation of the dye were given below.

Conclusions

Facile coprecipitation method was employed for constructing a new BiOCl-Cu₂ZnSnS₄ heterostructure. BiOCl-Cu₂ZnSnS₄-1 heterostructured composite showed superior photocatalytic activity in the degradation of Congo red than single phase BiOCl and Cu₂ZnSnS₄ QDs

Fig. 8 UV–visible absorbance spectra of Congo red before and after solar light irradiation in the presence of **a** BiOCl microspheres, **b** $\text{Cu}_2\text{ZnSnS}_4$ QDs, **c** BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ -1 and **d** BiOCl– $\text{Cu}_2\text{ZnSnS}_4$ -2

Fig. 9 **a** Percentage efficiency of photodegradation of Congo red with time. **b** Effect of different scavengers. **c** Plot of $\ln(C_0/C)$ versus irradiation time. **d** Recyclability

Fig. 10 Scheme of electron transfer in BiOCl–Cu₂ZnSnS₄ heterostructure

in the presence of sunlight. The degradation of Congo red was achieved 94.9% in 90 min of sunlight irradiation. The photoactivity of BiOCl–Cu₂ZnSnS₄-1 was due to the generation of heterostructure between BiOCl and Cu₂ZnSnS₄, which separates the photoexcited electron–hole pairs in the interface of BiOCl and Cu₂ZnSnS₄ on absorption of visible light radiation. The recombination of e^- and h^+ in BiOCl was removed by constructing BiOCl–Cu₂ZnSnS₄ heterostructure. The created BiOCl–Cu₂ZnSnS₄ heterostructure can be used as a promising photocatalyst for environmental cleanup.

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