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Article

Photocatalytic Degradation of Phenol over Highly Visible-light Active BiOI/TiO₂ Nanocomposite Photocatalyst

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Abstract. BiOI/TiO₂ nanocomposites were successfully prepared by the two-step method, co-precipitation/solvothermal method. The amount of BiOI in the composites were varied as 0, 5.0, 7.5, 10.0 and 12.5 mol%. XRD results exhibited sharp and narrow diffraction peaks of both BiOI and TiO₂ in all composite samples. Morphologies of as-prepared samples consisted of spherical shapes of TiO₂ and nanosheets of BiOI. Diffuse Reflectance UV-visible (DR-UV-vis) spectra of composites drastically shifted into the visible range and the reduced band gap energies were observed. The composites obviously showed an enhanced phenol degradation of *ca.* 6 times higher than that of pure BiOI, pure TiO₂ and Degussa P25. The maximum photocatalytic activity of *ca.* 68% was found for 10.0 mol% BiOI/TiO₂ nanocomposite because of its increased visible light harvesting ability and its efficient electron-hole separation efficiency as observed from DR-UV-vis and photoluminescence spectra results.

Keywords: Bismuth oxyiodide, titanium dioxide, nanocomposites, phenol.

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1. Introduction

Phenol is an important toxic organic compound, which is the major source of water pollutant releasing from industrial as herbicide, pesticide, polymeric precursor and paint [1]. Regarding to the major chemical affected water pollution, the wastewater purification is becoming an important major investigation. The typical wastewater treatment including activated carbon or silica-alumina adsorption was used. Semiconductor photocatalytic technique has been utilizing for degradation or mineralization of aquatic phenolic compounds for several decades [2-4]. For this purpose, TiO₂ photocatalyst has been extensively investigated due to its properties such as high physical and chemical stability, non-toxicity and low cost [5]. However, the major limitation of TiO₂ is that it can only be activated under UV light. Therefore, many researchers have focused on an improvement of the light absorptivity of TiO2 usually by forming a heterojunction with other visible-light-active materials, so that an effective utilization of solar light would be attained [6-8]. Moreover, the hybrid material also offers an efficient electron-hole transfer which benefits the separation of photoinduced charge carriers, hence enhancing the photocatalytic activity of the system [9]. Recently, BiOI has attracted a considerable attention due to its narrow band gap of 1.7–1.9 eV [10] which can largely harvest the visible light. Therefore, incorporating TiO2 with BiOI may provide the material with better photocatalytic performance. Previous studies have shown that photocatalytic degradation of dyes over BiOI/TiO2 composite is superior to those over TiO2 and BiOI individually [11, 12]. The reverse microemulsions protocol for BiOI composite synthesis which mainly focuses on the use of surfactants was reported [13]. However, the amounts of BiOI used to composite with TiO2 in those literatures are quite high (50-75 wt.%) and the synthesis method for the composite is rather complicated [14]. Therefore, an investigation on a facile synthesis method for the BiOI/TiO2 heterostructure is mainly focused in this present work. The two-step co-precipitation/solvothermal method was successfully employed as the synthesis method of BiOI/TiO2 composite. The photocatalytic efficiencies of prepared samples were also evaluated by phenol photodegradation under visible light irradiation.

2. Experimental

2.1. Nanocatalyst Preparation

Pure BiOI was prepared by co-precipitation method. Briefly, 1.092 g of Bi(NO₃)₃.5H₂O was dissolved in 30 mL of absolute ethanol and stirred until the clear solution was obtained. An aqueous KI solution was then added into the above solution, keeping Bi:I in 1:1 mole ratio. The suspension pH was adjusted to 4.0 by NH₄OH. Then, the reaction was aged at 80 °C for 5 h. The precipitate was washed and dried at 60 °C for 24 h. Pure TiO₂ was synthesized by modified sol-gel method similar to that reported previously [15]. BiOI/TiO₂ nanocomposites were prepared by the two-step co precipitation/low-temperature solvothermal method. Typically, 1.0 g of as-synthesized TiO₂ powder was sonicated for 1 h and then added carefully into the mixture of Bi(NO₃)₃.5H₂O and KI. A 100 μL of ethylene glycol was subsequently dropped into the mixture. The mol percentages of BiOI were varied as 0, 5.0, 7.5, 10.0 and 12.5%, respectively. The suspension pH was adjusted to 4.0. The suspension was then subjected to solvothermal treatment at 100 °C for 5 h. After the treatment, the sample was washed by DI water for 3 times and dried at 60 °C for 24 h.

2.2. Sample Characterization

XRD pattern was characterized to confirm the crystalline phase of the prepared samples by X-ray diffractometer Rigaku MiniFlex II ($Cu-K_{\alpha}$ radiation). BET N_2 adsorption for specific surface area determination at the temperature of liquid nitrogen was investigated by Autosorb–1MP–Quantachrome. Optical property of the photocatalysts was analyzed by DR–UV–vis Spectrophotometer (Shimazu, UV–3101PC) and photoluminescence spectroscopy (PL, Avantas-2048TEC). Morphology and microstructure of the as-prepared samples were examined by scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM–EDS, JEOL JEM–2010) and transmission electron microscope (TEM, Philips TECHNAI 12).

2.3. Photocatalytic Activity Studies

The photocatalytic degradation of phenol was evaluated under visible light irradiation (λ > 400 nm). For comparison, the photocatalytic degradation of phenol over Degussa P25 and direct photolysis were also investigated under the same conditions. The photocatalytic degradation of phenol was evaluated under visible light irradiation (λ > 400 nm) using a 50 W of halogen lamp with an intensity of 640 W/m². The initial concentration phenol solution was 10 mg/L. The suspension pH was adjusted to 8.0±0.30 by using 0.1 M NH₄OH and HClO₄ solution. A 0.8 g/L of catalyst suspension was kept in the dark for 30 min to obtain adsorption/desorption equilibrium. After irradiation, 4 mL of suspension was withdrawn periodically in every 45 min and filtered by a Millipore filter (0.22 µm). Then, the phenol solution was dyed by the 4–aminoantipyrine colorimetric method (APHA, 1992) [16]. The maximum absorbance at 504 nm was analyzed using UV–vis spectrophotometer (PG Instruments, T90).

3. Results and Discussion

3.1. Crystal Phase and Microstructure Analysis

The XRD patterns of pure BiOI, pure TiO₂ and BiOI/TiO₂ nanocomposites are shown in Fig. 1. The peaks at 20 of 9.6°, 19.5°, 29.6°, 31.6°, 37.0°, 39.3° and 45.3° correspond to (001), (002), (012), (110), (013), (014) and (112) crystal planes of tetragonal BiOI (JCPDS file No.10–0445). Sharp and narrow XRD peaks of pure BiOI indicate that the sample is well crystallized [17]. Pure TiO₂ calcined at 600 °C exhibits the characteristic peaks at 25.3°, 37.8°, 48.0°, 53.9°, 54.9° assignable to the (101), (004), (200), (105) and (211) crystal planes of anatase TiO₂ (JCPDS file No. 21–1272) [18]. The XRD spectra of BiOI/TiO₂ nanocomposites present the characteristic peaks of both TiO₂ and BiOI, indicating the composite nature of the prepared samples. As the BiOI content in BiOI/TiO₂ composite is increased, the relative peak intensity of BiOI also increases. By using the strongest peaks of anatase TiO₂ (101) and BiOI (012) planes, the average crystallite sizes of TiO₂ and BiOI, calculated according to the Scherrer's equation (Eq. (1)), can be obtained as presented in Table 1 [19].

$$L = 0.89\lambda/\beta(\cos\theta) \tag{1}$$

where λ is the wavelength of the X-ray in nanometer (0.154 nm), β is the width of the XRD peak at half peak-height (FWHM) in radian, θ is the angle between the incident and diffracted beams in degree, and L is the average crystallite size of the sample in nm. Specific surface area (S_{BET}) of all synthesized photocatalysts is also shown in Table 1. Upon increasing BiOI content, the S_{BET} of the composite significantly decreases due to the low surface area nature of BiOI. In our study, the lowest S_{BET} is found as 50.87 m²/g for 12.5 mol% BiOI/TiO₂ composite.

Table 1. Average crystallite size and specific surface area of photocatalysts.

	Crystallite size (nm)		
Sample	anatase TiO2	BiOI	S_{BET} (m ² /g)
	(101) plane	(012) plane	
Pure TiO ₂	25.02	-	110.24
5.00 mol% BiOI/TiO ₂	22.85	16.29	80.30
7.50 mol% BiOI/TiO ₂	22.43	16.31	74.14
10.0 mol% BiOI/TiO ₂	22.25	16.32	69.30
12.5 mol% BiOI/TiO ₂	22.20	16.34	50.87
Pure BiOI	-	23.16	7.50

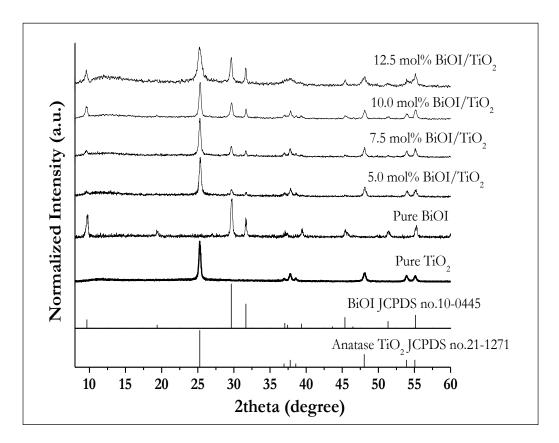


Fig. 1. XRD patterns of pure TiO₂, pure BiOI and BiOI/TiO₂ nanocomposites.

Figure 2 shows the morphology and microstructure of pure TiO₂, pure BiOI and 10.0 mol% BiOI/TiO₂ characterized by SEM-EDS. Pure TiO₂ (Fig. 2(a)) presents as aggregated spherical particles with different sizes in the range of 0.3–0.7 μm. Meanwhile, pure BiOI (Fig. 2(b)) appears as plate-like structure and agglomerations of plate building units. Figure 2(c) shows that BiOI plates are covered with several small TiO₂ particles. The EDS analysis of BiOI/TiO₂ nanocomposite (Fig. 2(d)) also confirms the presence of Ti, O, Bi and I in the composite catalyst.

TEM micrographs of TiO₂, BiOI, and 10.0 mol% BiOI/TiO₂ nanocomposite are shown in Fig. 3. The morphology of pure TiO₂ (Fig. 3(a)) reveals almost spherical shape with the average particle size of 20–30 nm, which well relates to the crystallite size calculated by Scherrer equation. Figure 3(b) shows the aggregation of plate-like structure of BiOI with a diameter of α . 50 nm. For 10.0 mol% BiOI/TiO₂ nanocomposite in Fig. 3(c), TiO₂ nanoparticles are found buried in BiOI sheets. Figure 3(d) also shows close interfacial contacts between TiO₂ nanoparticles and thin lamellar of BiOI in the composite which would lead to an efficient electron-hole transfer, and an enhanced photocatalytic activity as a consequence [19]. High resolution TEM microgaph showing lattice fringes of 10.0 mol% BiOI/TiO₂ in Fig. 3(d) reveals the crystalline nature of the particles. The lattice spacings of 0.34 nm and 0.28 nm follow the d-values of anatase TiO₂ (101) [20] and BiOI (110) planes [21], respectively.

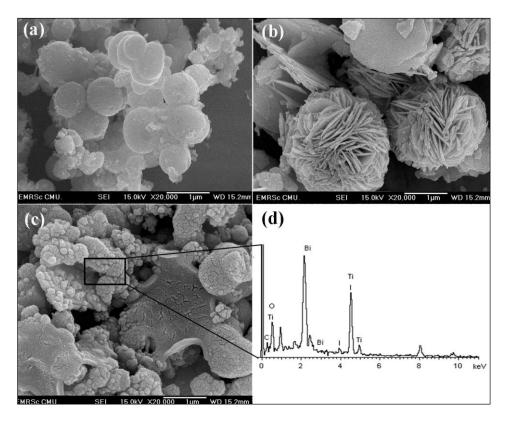


Fig. 2. FE-SEM images of (a) Pure TiO₂; (b) Pure BiOI; (c) 10.0 mol% BiOI/TiO₂ composite and (d) the EDX spectrum of (c).

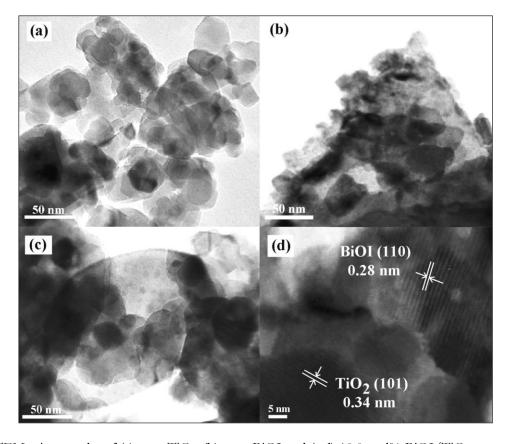


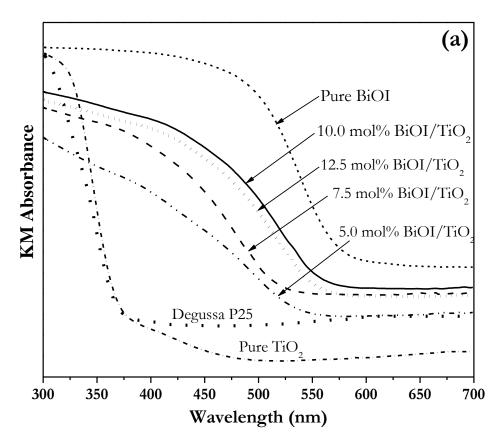
Fig. 3. TEM micrographs of (a) pure TiO₂, (b) pure BiOI and (c,d) 10.0 mol% BiOI/TiO₂ nanocomposite.

3.2. UV-vis Diffuse Reflectance Spectra

The diffuse reflectance UV-vis spectra (DR-UV-vis) of pure BiOI, pure TiO₂, Degussa P25 and BiOI/TiO₂ composite catalysts at different Bi/Ti molar ratios are presented in Fig. 4(a). From the figure, pure BiOI shows the strongest light absorbance with the absorption onset at α . 630 nm, whereas pure TiO₂ and Degussa P25 present the absorption edges at α . 385 and α . 387 nm, respectively. A significant shift of TiO₂ absorption edge into the visible light region can be clearly observed upon incorporation TiO₂ with BiOI. According to Eq. (2), optical band gap energy (E_g) of the catalysts can be obtained as illustrated in Fig. 4(b):

$$(\alpha h \upsilon)^{1/2} = A(h\upsilon - E_g) \tag{2}$$

where, $h\nu$ is the photon energy, α is the absorption coefficient, h is Planck's constant and ν is light frequency [22]. From Fig. 4(b), the band gap energies of pure TiO₂, pure BiOI, 5.0, 7.5, 10.0 and 12.5 mol% BiOI/TiO₂ composites are approximately 3.22, 1.86, 2.16, 2.20, 2.04 and 2.08 eV, respectively. The lowest band gap energy of composite photocatalyst is received from 10.0 mol% BiOI/TiO₂ (2.04 eV). The significant red-shift of the light absorption range upon increasing BiOI amount in the composite sample corresponds well with the reduced band gap energy. This suggests the high efficiency of visible-light utilization of the BiOI/TiO₂ composite which would lead to high generation of electron-hole pairs and probably an enhanced photocatalytic activity [23]. It is clear from our finding that by forming BiOI/TiO₂ composite, optical and physical properties of the materials change significantly. This also affects the phenol photodegradation activity of the materials as shown in the next section.



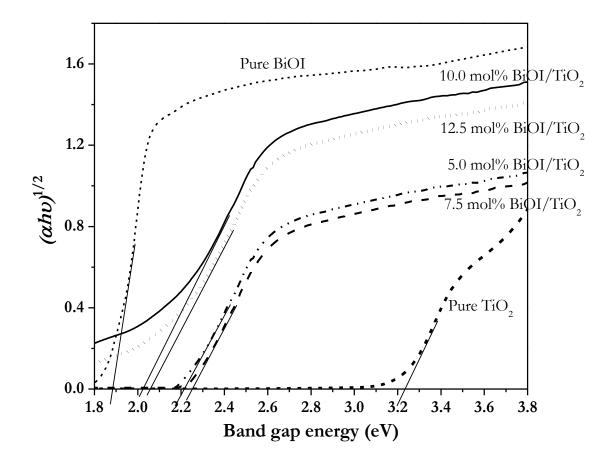


Fig. 4. (a) KM absorption spectra and (b) band gap energy of different Bi/Ti mole ratios.

3.3. Photocatalytic Activities and PL Properties of the Photocatalyst

The performance of phenol degradation over the entire catalysts is shown in Fig. 5. The photocatalytic activity in case of Degussa P25 is only 5.7%; whereas pure TiO₂ and pure BiOI synthesized in this work exhibit slightly higher efficiencies of 9.1% and 8.4%, respectively. However, all BiOI/TiO₂ nanocomposite photocatalysts show remarkably better degradation performance than pure TiO₂, pure BiOI and Degussa P25. A drastic reduction of electron-hole recombination rate as observed from PL analysis (Fig. 6) also confirms an excellent electron-hole separation efficiency of the composite materials, hence enhanced photocatalytic performance can be acquired in this work [24]. Additionally, simultaneous agglomeration of TiO₂ and BiOI and the close interfacial connection between BiOI and TiO₂ in the composite material as clearly observed from SEM and TEM results also suggest a better electron-hole transfer. Thus, more electrons would be available for the generation of OH radical [25], resulting in the enhancement of the photocatalytic performance as observed in this study. The results clearly show that the phenol degradation activity is improved as the BiOI amount in the composite increases. However, further increasing the BiOI to 12.5 mol% instead leads to a decrease of photocatalytic efficiency. This is probably due to its lower S_{BET} compared to the 10 mol% as evidenced from BET results in Table 1.

In order to explain the kinetic rate constant, a plot between $-\ln(Ct/C_0)$ versus irradiation time (Fig. 7) was performed according to Eq. (3) [26]:

$$-\ln(C_t/C_0) = kK_t \tag{3}$$

where k is the true rate constant and K_t is the Langmuir adsorption equilibrium constant. Pseudo-first order degradation rate constants (k) and correlation coefficient (R^2) of photocatalytic degradation of phenol over all synthesized photocatalysts are shown in Fig. 7 and Table 2. The high correlation coefficient obtained in this work suggests that the phenol photodegradation over BiOI/TiO₂ nanocomposite follows

pseudo-first order kinetic and the highest rate constant of 3.7×10^{-3} min⁻¹ is obtained from 10.0 mol% BiOI/TiO₂, the best catalyst in this work.

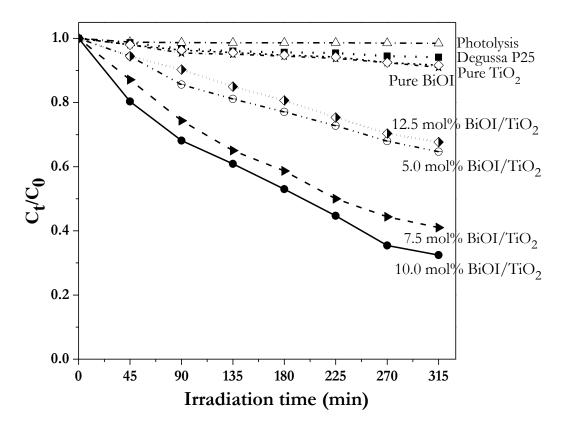


Fig. 5. Phenol photodegradation efficiencies over synthesized catalysts.

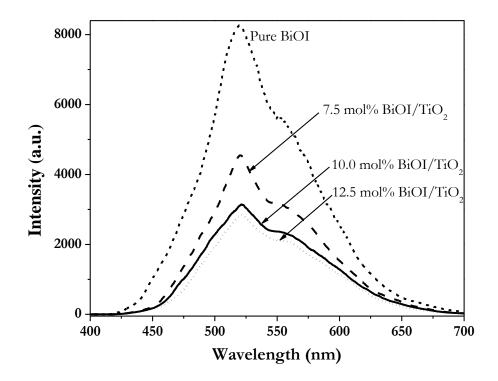


Fig. 6. Photoluminescence (PL) spectra of pure BiOI, 7.5 mol% BiOI/TiO₂; 10.0 mol% BiOI/TiO₂ and 12.5 mol% BiOI/TiO₂, repectively.

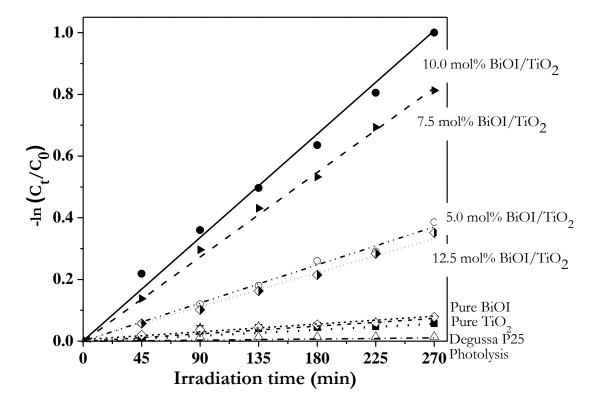


Fig. 7. Pseudo-first order degradation rate of photocatalytic degradation of phenol over the catalysts.

Table 2. Pseudo-first order degradation rate constants (k) and correlation coefficient (R^2) of photocatalytic degradation of phenol over all synthesized photocatalysts.

Sample	k (min-1)	R ²
Direct photolysis	7.0×10^{-5}	0.9908
Pure TiO ₂	3.1×10^{-4}	0.9942
Pure BiOI	3.3×10^{-4}	0.9904
5.0 mol% BiOI/TiO ₂	1.4×10^{-3}	0.9930
7.5 mol% BiOI/TiO ₂	3.1×10^{-3}	0.9975
10.0 mol% BiOI/TiO ₂	3.7×10^{-3}	0.9901
12.5 mol% BiOI/TiO ₂	1.3×10^{-3}	0.9953

4. Conclusions

The BiOI/TiO₂ nanocomposites are successfully synthesized by a two-step co precipitation/solvothermal method. XRD patterns exhibit characterization peaks of both BiOI and anatase TiO₂ phase. The nanocomposites have the average particle size in the range of 15–30 nm. Phenol degradation performance of the prepared composites is investigated under visible light irradiation. The maximum phenol degradation of 68% with the highest pseudo-first order degradation rate is found in the case of 10.0 mol% BiOI/TiO₂. The enhanced catalytic performance observed from the BiOI/TiO₂ composite might be ascribed to the significant reduction of band gap energy from 3.22 eV of pure TiO₂ to 2.04 eV of the 10.0 mol% BiOI/TiO₂ sample. A drastic reduction of electron-hole recombination rate from PL analysis also suggests an excellent electron-hole separation efficiency of this material, hence enahnced photocatalytic performance can be achieved in this work.

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