Efficient visible-light photocatalytic degradation of sulfadiazine sodium with hierarchical Bi$_7$O$_9$I$_3$ under solar irradiation

MengMeng Xu, YaLei Zhao and QiShe Yan

ABSTRACT

Bi$_7$O$_9$I$_3$, a kind of visible-light-responsive photocatalyst, with hierarchical micro/nano-architecture was successfully synthesized by oil-bath heating method, with ethylene glycol as solvent, and applied to degrade sulfonamide antibiotics. The as-prepared product was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–visible diffuse reflection spectra and scanning electron microscopy (SEM). XRD and XPS tests confirmed that the product was indeed Bi$_7$O$_9$I$_3$. The result of SEM observation shows that the as-synthesized Bi$_7$O$_9$I$_3$ consists of a large number of micro-sheets with parallel rectangle structure. The optical test exhibited strong photoabsorption in visible light irradiation, with 617 nm of absorption edges. Moreover, the difference in the photocatalytic efficiency of as-prepared Bi$_7$O$_9$I$_3$ at different seasons of a whole year was investigated in this study. The chemical oxygen demand removal efficiency and concentration of NO$_3$ and SO$_4$$^2$– of solution after reaction were also researched to confirm whether degradation of the pollutant was complete; the results indicated a high mineralization capacity of Bi$_7$O$_9$I$_3$. The as-synthesized Bi$_7$O$_9$I$_3$ exhibits an excellent oxidizing capacity of sulfadiazine sodium and favorable stability during the photocatalytic reaction.

Key words | Bi$_7$O$_9$I$_3$, solar irradiation, sulfadiazine sodium, visible-light photocatalysis

INTRODUCTION

In recent decades, applications of solar energy conversion and environmental remediation by semiconductor photocatalysts have attracted considerable attention. As one of the most widely investigated photocatalysts, TiO$_2$ can only be activated by ultraviolet light (λ < 400 nm), which only makes up about 4% of the solar spectrum (Di Paola et al. 2012). Moreover, the recombination rate of photo-induced carriers of TiO$_2$ photocatalyst is very high, which significantly decreased its photocatalytic performance. Furthermore, it is well known that the photocatalysts with nanosize are difficult to separate completely from post-treatment slurry because of their small particle size (Yu et al. 2006); hence their practical application is extremely limited. Therefore, developing an efficient visible-light-driven, excellent photocatalytic performance and easily recycled photocatalysts, in order to neutralize those apparent shortcomings, is urgent and promising.

Bismuth-based photocatalysts, an abundant novel non-TiO$_2$-based visible-light photocatalyst, with the characteristics of unique electronic structure, excellent absorption capacity of visible-light and favorable degradation efficient for organic materials, has drawn great interest from more and more researchers. Among these photocatalysts, bismuth oxyhalides (BiOX, X = F (Su et al. 2010), Cl (Zhu et al. 2010), Br (Zhang et al. 2008a), and I (Xiao & Zhang 2010)), as a new group of promising photocatalysts, have shown considerable photocatalytic activities due to the unique layered structure with an internal static electric field perpendicular to each layer, which can induce effective separation of photogenerated electron-hole pairs, and hence results in a cracking photocatalytic performance (Xiao et al. 2012). Some complex bismuth oxyhalides, e.g. yBiO(Cl$_x$Br$_{1-x}$)-(1–y)BHO (She-nawi-Khalil et al. 2012), Bi$_3$O$_5$Br (Chen et al. 2014), BiO$_x$Cl$_y$/BiO$_{2-x}$Br$_n$ (Huang et al. 2014) and Bi$_3$O$I$ (Sun et al. 2009), have been researched and show considerable visible-light photocatalytic performance for the degradation of different organic compounds. Among these photocatalysts mentioned above, BiOI has the smallest band gap (~1.8 eV) and strong absorption in the visible-light region (the absorption edge is ~ 680 nm), resulting in excellent photocatalytic
performance under sunlight irradiation. (Zhang et al. 2008b; Xiao & Zhang 2010). Besides BiOI, other bismuth oxyiodides, including Bi$_2$O$_6$I$_2$ (Liu et al. 2013), Bi$_7$O$_{11}$I$_3$ (Xiao et al. 2012) and α-Bi$_2$O$_7$I (Keller & Kraemer 2007), also have been investigated by some researchers. However, these photocatalysts lack practical applicability in the degradation of antibiotics wastewater.

Because of high stability and large amount, the discharged antibiotics can enter the aqueous environment from soil and sediments by surface runoff, which may be taken in by animals and mankind, and become a significant risk to the environment and human health (Mitchell et al. 2015). As a kind of artificially synthesized and traditional antibacterial medicine, sulfa drugs have been widely used as veterinary drugs in recent decades and have attracted growing attention of scientists and the public (Peng et al. 2006; Sukul & Spittel 2006). In previous work, sulfadiazine was successfully degraded by various methods, such as gamma irradiation (Guo et al. 2012), UV-activated persulfate oxidation (Gao et al. 2012), microwave-activated persulfate (Qi et al. 2014) and sonolysis (Gao et al. 2015). Sulfadiazine sodium (SD-Na) is one of the most widely used sulfonamide antibiotics and exists as a contaminant in surface and ground waters; however, apparently only a limited number of studies of SD-Na degradation have been reported. Therefore, it is necessary and significant to research the degradation of SD-Na on bismuth-based photocatalysts.

In the present work, sheet-like hierarchical hollow Bi$_7$O$_{11}$I$_3$ micro-nanoplate was synthesized in ethylene glycol solvent, and an oil-bath heating method at a relatively low temperature was used. The photodegradation of SD-Na was employed to evaluate the photocatalytic activities of as-prepared Bi$_7$O$_{11}$I$_3$ catalysts with direct solar irradiation as the light source. The morphology, structure and photo-absorption property of the as-synthesized hierarchical Bi$_7$O$_{11}$I$_3$ microsheets were characterized. The paper investigated photodegradation efficiencies of as-prepared Bi$_7$O$_{11}$I$_3$ photocatalyst at different seasons of a whole year as well as the effect of adding H$_2$O$_2$ as pro-oxidant at winter on the photodegradation efficiency. Moreover, the stability and recycling property of the Bi$_7$O$_{11}$I$_3$ photocatalyst after several photocatalytic degradation experiments were assessed.

**EXPERIMENTAL**

**Materials and methods**

All chemicals were purchased from Aladdin Chemical Co. Ltd and were of analytical grade without further purification. Distilled water was used in all experiments. The synthesis method of Xiao & Zhang (2011) was used in this study, detailed as follows. In a typical synthesis procedure, 0.728 g Bi(NO$_3$)$_3$·5H$_2$O was dissolved completely in 20 mL ethylene glycol (EG), and 0.249 g KI was dissolved in 10 mL EG by stirring at room temperature, respectively. Afterward, 30 mL EG was placed in a 150 mL three-necked round-bottom flask and pre-heated to 160 °C by an oil-bath with continuous stirring and a refluxing system carried out in a hood. Then, the above KI-EG solution was added into the heated EG and stirred for 10 min. Finally, the Bi(NO$_3$)$_3$·EG solution was added rapidly into the previous mixture and stirred continuously for 3 h at 160 °C. The precipitates were air cooled to room temperature, collected by centrifugation, washed several times with distilled water and ethanol, and dried overnight in an oven at 60 °C. For comparison, BiOI nanospheres were prepared according to Hao et al. (2012) by a hydrothermal process and their corresponding photocatalytic performance was also tested.

**Characterization**

X-ray diffraction (XRD) analysis was performed on an X-ray diffractometer (X’Pert PRO MRD, PANalytical, The Netherlands) equipped with a Cu Kα X-ray source. UV–visible (UV-vis) diffuse reflection spectra (DRS) of the samples were obtained using a UV-vis spectrophotometer (Caly 5000, Agilent, USA). The morphology of the samples was investigated by scanning electron microscopy (SEM, Quonxe-2000, Phi-lent, USA). The surface elemental component and the chemical state of the sample were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5300, Perkin Elmer) with a monochromatized Al Kα X-ray source ($hν = 1.487$ eV). The photoabsorption of SD-Na solution was evaluated by UV-vis spectrophotometry (UV-2450, Shimadzu, Japan). The band gap energy ($E_g$) of these samples was evaluated by using the following equation (Zhang et al. 2008b):

$$a(hν) = A(hν - E_g)^n/2$$

(1)

where $a$, $ν$, $E_g$ and $A$ are the absorption coefficient, light frequency, band gap energy, and a constant, respectively. Among these parameters, $n$ depends on the characteristics of the transition in a semiconductor. For BiOX, the value of $n$ is 4 for their indirect transition (Cao et al. 2012; Su et al. 2012). Then $E_g$ values of BiOX can be thus estimated from a plot of $(ahν)^{1/2}$ versus photon energy $(ahν)$. The specific surface areas were measured by using nitrogen
Adsorption of SD-Na by Bi7O9I3

The linear correlation coefficients of the Henry model, Langmuir model and Freundlich model are 0.90, 0.98 and 0.95 (Table 1), respectively. The adsorption model of SD-Na by Bi7O9I3 is best fitted with the Langmuir model. These three models can be expressed respectively as:

\[ q_e = K_D c_e + a, \]  
\[ q_e^{-1} = K_L^{-1} q_f^{-1} c_e^{-1} + q_e^{-1}, \]  
\[ \log q_e = \log K_F + n^{-1} \log c_e \]  

where \( q_e, c_e, K_D, K_L, K_F, a \) and \( n \) are the adsorption quantity, equilibrium concentration, Henry constant, Langmuir constant, Freundlich constant, and two constants, respectively. Also, some adsorption thermodynamic parameters were obtained as the slopes and intercepts of straight lines. A 2.95 mg g\(^{-1}\) of the maximum adsorption amount indicates that Bi7O9I3 has high adsorption capacity. In addition, \( n \) larger than 1 indicates that Bi7O9I3 can adsorb SD-Na preferentially.

Photocatalytic measurement

The photocatalytic activities of the as-prepared samples were evaluated by degradation of SD-Na in aqueous solution under direct solar irradiation. The reaction was carried out under normal circumstances. Initial conditions of all photocatalytic experiments performed were identical and described as follows: 50 mL SD-Na solution (10 or 20 mg L\(^{-1}\)) was mixed with 1 g L\(^{-1}\) catalyst, under continuous magnetic stirring. Prior to irradiation, the solution was stirred for 1 h in darkness to allow the system to reach adsorption and desorption equilibrium. After the equilibrating process, 50 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \) was added into the suspension as a pro-oxidant if the experiment was performed in the wintertime. Throughout the reaction, about 3 mL of the suspension was extracted every 20 min and filtered by a 0.45 \( \mu \)m filter membrane. The concentration of SD-Na in the samples was determined by UV-vis spectroscopy (\( \lambda = 266 \) nm).

The degradation efficiency of SD-Na and residual of long-lived organic intermediates in the solutions (Zhang et al. 2013) were measured by chemical oxygen demand (COD). The COD concentration of filtrate was determined by a closed microwave digestion instrument and measured by potassium dichromate titration. Before measurement, a certain amount of \( \text{MnO}_2 \) was added into the filtrate to remove the residual \( \text{H}_2\text{O}_2 \), to eliminate the negative impact on the accuracy of the COD determination. The \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) concentrations of the degradation product of SD-Na in solution under sunlight irradiation were determined by an ion chromatograph, equipped with an anion chromatography column (AS-14), anion guard column (AG-14), chemical suppressor (AMMS 30), and 8.0 mM \( \text{Na}_2\text{CO}_3/1.0 \) mM \( \text{NaHCO}_3 \) as a leachate with 0.8 mL min\(^{-1}\) flow rate and dilute sulphuric acid as regeneration solution.

### RESULTS AND DISCUSSION

Characterization of catalysts

Crystal structure

The powder XRD pattern provides crystal structure and phase information of the as-prepared sample (Figure 1). The strong peaks indicate that the synthesized product is highly crystallized. As shown in Figure 1, in the whole range of 0–90°, the diffraction patterns of the samples are quite similar but shift slightly compared with those of the standard tetragonal structure for BiOI (JCPDS No. 10-0445), which can

<table>
<thead>
<tr>
<th>Henry constant</th>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_D )</td>
<td>( R^2 )</td>
<td>( K_L (\text{L mg}^{-1}) )</td>
</tr>
<tr>
<td>0.033</td>
<td>0.90</td>
<td>0.12</td>
</tr>
</tbody>
</table>

\( K_0, K_u, K_e, q_{\text{max}}, R^2, a \) and \( n \) are the Henry constant, Langmuir constant, Freundlich constant, the maximum adsorption quantity, linear correlation coefficient and two constants, respectively.
be attributed to the extra bismuth and oxygen in the lattice (Xiao & Zhang 2014), thus causing expansion (Zhang & Zhang 2013) and distortion compared with the standard BiOI crystal structure. Characteristic peaks of bismuth oxides, basic bismuth nitrate or any other impurities were not observed in the pattern. The diffraction angle of characteristic peaks of the obtained sample are at $2\theta = 28.6^\circ$, $31.8^\circ$, $45.8^\circ$, and $55.5^\circ$, respectively, which match well with those of Bi$_7$O$_9$I$_3$ (Li et al. 2011; Xiao & Zhang 2011).

Further information of the evaluation of the surface elemental composition and purity of the product can be provided by the XPS measurements. The binding energy obtained in the XPS analysis was modified for specimen charging by referencing C 1s to 284.80 eV. Figure 2(a) shows a typical XPS survey spectrum of the prepared sample. No peaks of other elements except Bi, C, O and I are observed in the spectrum, indicating the high purity of this product. Figure 2(b), 2(c) and 2(d) show the high-resolution XPS spectra of Bi 4f, I 3d and O 1s, respectively. The binding energies of two strong peaks at the Bi region (Figure 2(b)) are 158.8 and 164.1 eV, which are corresponding to Bi 4f 7/2 and Bi 4f 5/2, respectively, and are characteristic of Bi$^{3+}$ (Xiao et al. 2013). The peaks with binding energies of 618.9 eV and 631.5 eV are I 3d spin-orbital doublets, I 3d 5/2 and I 3d 3/2, respectively (Figure 2(c)), indicating −1 valance state of the I in the sample. (Fujishima et al. 2000; Xiao et al. 2013) Similarly, the O 1s core level spectrum (Figure 2(d)) can be fitted well with the peak, with the characteristic of a bismuth–oxygen bond in BiOX at 529.8 eV (Xiao & Zhang 2011).

**Photoabsorption property**

The UV-vis absorption spectra of the as-synthesized BiOI and Bi$_7$O$_9$I$_3$ are shown in Figure 5. Both samples exhibited strong
photoabsorption in the UV to visible light range, where the optical absorption edges were found to be 617 nm for Bi$_7$O$_9$I$_3$ and 653 nm for BiOI. The absorption spectrum of Bi$_7$O$_9$I$_3$ is shifted markedly to red compared with that of TiO$_2$, but smaller to blue compared with that of BiOI. By using Equation (1), the estimated band gap energies for P25, Bi$_7$O$_9$I$_3$ and BiOI were calculated to be approximately 3.17 eV, 2.01 eV and 1.90 eV, respectively. The band gap energy of as-prepared Bi$_7$O$_9$I$_3$ is higher than that of BiOI, which can contribute to the decrease of the stoichiometric proportion of iodine (Huang & Zhu 2013). As shown in Table 2, the valence band potential and conduction band potential of Bi$_7$O$_9$I$_3$ are 2.44 eV and 0.43 eV respectively, and those of BiOI are 2.38 eV and 0.48 eV; both the oxidant capacity of the valence band and reduction capacity of the conduction band of Bi$_7$O$_9$I$_3$ are stronger than those of BiOI, leading to the higher photocatalytic activity of the former, while the visible-light absorption range is slightly narrowed.

### Surface morphology

The crystal morphologies of the Bi$_7$O$_9$I$_3$ and BiOI by SEM are shown in Figure 4, in which the as-synthesized Bi$_7$O$_9$I$_3$ consists of a large number of micro-sheets with parallel rectangle structure. The sheet size of the entire structure ranges from 2 to 10 μm, and the thickness ranges from 1 to 2 μm. the BiOI is composed of many microspheres with the maximum diameter of 2 μm. Comparing to obtained BiOI, the three-dimensional (3D) hierarchical structure of Bi$_7$O$_9$I$_3$ is more difficult to agglomerate and its surface to volume ratio is relatively high. Moreover, the 3D structure contains plenty of 3D tunnels, in which the pollutants and their intermediates can be transported internally; thus the degradation efficiency of the organic pollutants is higher within the as-synthesized Bi$_7$O$_9$I$_3$.

### Specific surface area and pore size distribution of Bi$_7$O$_9$I$_3$

The specific surface area and porosity of the as-synthesized Bi$_7$O$_9$I$_3$ were investigated by using nitrogen adsorption and desorption isotherms. As shown in Figure 5(a), the isotherms present the features of type-IV curves with the characteristic of mesoporous material. Figure 5(b) displays the pore size distribution of Bi$_7$O$_9$I$_3$; it can be that the major proportion is mesoporous, along with a small part of macroporous structure. As is presented in Table 2, the specific surface area and total pore volume of Bi$_7$O$_9$I$_3$ are 66.6 eV and 0.3708 cm$^3$ g$^{-1}$, which are apparently higher than those of BiOI, 18.0 eV and 0.0746 cm$^3$ g$^{-1}$. The average pore diameters of BiOI and Bi$_7$O$_9$I$_3$ are 14.4 nm and 16.8 nm, respectively, both belonging to the mesoporous materials. The existence of amounts of mesoporous material in obtained Bi$_7$O$_9$I$_3$ can efficiently enhance the adsorption of target molecules on the surface of the photocatalyst particle. It can be assumed that the Bi$_7$O$_9$I$_3$ with higher BET surface area may have the improved photocatalytic activity.

### Photocatalytic properties of Bi$_7$O$_9$I$_3$

#### Evaluation of the photocatalytic activity

The time dependence of degradation efficiency of SD-Na on the Bi$_7$O$_9$I$_3$ microsheets was investigated and compared with as-prepared BiOI, which was carried out in the sunny days during summer. The degradation efficiencies of

### Table 2 | Specific surface area, pore volume, pore diameter, band gap energy, valence band potential and conduction band potential of BiOI and Bi$_7$O$_9$I$_3$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>Average pore diameter (nm)</th>
<th>Band gap energy (eV)</th>
<th>Valence band potential (eV)</th>
<th>Conduction band potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOI</td>
<td>18.0</td>
<td>0.0746</td>
<td>14.4</td>
<td>1.90</td>
<td>2.38</td>
<td>0.48</td>
</tr>
<tr>
<td>Bi$_7$O$_9$I$_3$</td>
<td>66.6</td>
<td>0.3708</td>
<td>16.8</td>
<td>2.01</td>
<td>2.44</td>
<td>0.43</td>
</tr>
</tbody>
</table>

$S_{BET}$ is specific surface area measured by BET method.
SD-Na on Bi$_7$O$_9$I$_3$ were 96% with H$_2$O$_2$ as pro-oxidant and 81% without H$_2$O$_2$ under solar irradiation (Figure 6), and those of SD-Na on BiOI were 87% with H$_2$O$_2$ and 53% without it. The result indicates the solar responsiveness and photocatalytic efficiency of Bi$_7$O$_9$I$_3$ are much higher than that of BiOI. Also, the photocatalytic efficiency of SD-Na on Bi$_7$O$_9$I$_3$ without H$_2$O$_2$ is in close proximity to that on BiOI with H$_2$O$_2$, which shows the degradation performance of Bi$_7$O$_9$I$_3$ is higher than that of BiOI. In addition, the degradation experiment with H$_2$O$_2$ in darkness indicates that the solar irradiation is crucial to ensuring the proceeding of the photocatalytic reaction, while the aim of adding H$_2$O$_2$ is to promote the oxidant reaction, in order to increase the photocatalytic efficiency.

Effect of illumination intensity on degradation of SD-Na

In the present work, the effect of illumination intensity of four seasons on photocatalytic efficiency has been investigated. The research results show the degradation efficiencies are 69, 82, 70 and 60% from spring to winter at ambient condition without adding H$_2$O$_2$. The low temperature and weak intensity of solar illumination are adverse to the contamination adsorption of catalyst and degradation efficiency in winter. The degradation efficiency in winter was raised to 82% with adding H$_2$O$_2$ as extra pro-oxidant while the other experiment conditions were kept the same, and this is highly similar to that in summer without adding H$_2$O$_2$. Moreover, adding extra light source also can improve degradation efficiency on account of the illumination intensity as the main influence factor.

Figure 7 shows the effect of illumination intensity of four seasons on photocatalytic efficiency of Bi$_7$O$_9$I$_3$. The illumination intensity in summer ranges from 66,100 lux to 120,000 lux, from 8:00 to 10:00. Actually, the illumination intensity is always higher than 55,000 lux from 8:00 to 18:00, even in the cloudy weather. The autumn experiments were carried out from 9:00 to 11:00, with the intensity from 21,600 to 65,000 lux, which is much lower than that in summer and results in the low photocatalytic efficiency of autumn. Also, the illumination intensity of winter is comparable to that of summer, which is from 61,800 to 100,100 lux at 10:50 to 12:50. The period of time with high illumination intensity is concentrated in 10:00 to 14:00, less than that of
summer. Moreover, the low temperature of winter may have adverse impact on photocatalytic efficiency.

Evaluation of the mineralization of SD-Na

From evaluation of the mineralization of SD-Na, the COD removal efficiency, and SO$_4^{2-}$ and NO$_3^{-}$ concentration with and without H$_2$O$_2$ were observed. The initial concentrations of H$_2$O$_2$, catalyst and SD-Na are 50 mg L$^{-1}$, 1 g L$^{-1}$ and 20 mg L$^{-1}$, respectively. As shown in Figure 8(a), COD removal is 70% without H$_2$O$_2$ under ambient conditions in the sunlight irradiation and increases to 80% with H$_2$O$_2$ at the same condition. Compared with the 40% COD removal after irradiation time of 60 h from literature (Stylidi et al. 2004), 70% of COD removal efficiency without H$_2$O$_2$ after 2 h irradiation indicates efficient degradation and favorable mineralization of SD-Na by Bi$_7$O$_9$I$_3$, suggesting its potential applicability in wastewater treatment. The SO$_4^{2-}$ and NO$_3^{-}$ concentrations of SD-Na solution after photodegradation were measured by ion chromatography. Generated ion concentrations with H$_2$O$_2$ are slightly higher than those without H$_2$O$_2$ (Figure 8(b)); this implies that adding H$_2$O$_2$ has little effect on the ion concentration. The SO$_4^{2-}$ concentration in solution is obviously lower than the NO$_3^{-}$ concentration, indicating the degradation of elemental sulfur was incomplete. This may relate to pH of the solution after the reaction, where
SO$_4^{2-}$, HSO$_3^-$, SO$_3^{2-}$ and S$_2$O$_5^{2-}$ are coexistent. In comparison, the degradation of elemental nitrogen was complete, which is different from the research literature (Calza et al. 2004) and may be attributed to the difference in reaction condition and catalyst used; hence the specific mechanism needs further research. The above phenomenon indicates that a part of sulfur-containing organics may still exist.

**Recycle of Bi$_7$O$_9$I$_3$**

It is generally well known that photocatalysts with smaller size present a superior activity due to the higher efficiency of electron-hole pairs generated inside the crystal transferring to the surface (Hao et al. 2012). However, in a particular photocatalytic process, these small particles are not readily collected for the recycle from suspended solution after reaction. Due to the relatively larger size, the photocatalyst of Bi$_7$O$_9$I$_3$ micro/nano-architecture with parallel rectangle structure has an overwhelming advantage compared with other nanostructure catalysts, as it can be separated by a simple filtration step or even a natural sedimentation.

To test the stability and recoverability of Bi$_7$O$_9$I$_3$, the sample powder was collected after photocatalytic reaction and reused for photodegradation of SD-Na for three times with the same conditions and catalyst dosage. The photocatalytic efficiencies of Bi$_7$O$_9$I$_3$ were 82, 81 and 79% for one reuse cycle, which indicates that Bi$_7$O$_9$I$_3$ sample is very stable. The slight decrement in photocatalytic performance of the sample may be due to gradual decay in adsorptive capacity of the catalyst. In addition, H$_2$O$_2$ was not added into the solution of SD-Na during the degradation by Bi$_7$O$_9$I$_3$, whose surface was not adsorbing the excessive amounts of hydroxyl radical, which may lead to the low reduction of photocatalytic efficiency. The results indicate that the hierarchical Bi$_7$O$_9$I$_3$ prepared by this facile method is stable for the photodegradation of pollutants in the wastewater; this is important for its practical application.

**CONCLUSION**

In conclusion, a novel Bi$_7$O$_9$I$_3$ hierarchical micro/nano-architecture with parallel rectangle structure has been synthesized by an easy, temple-free oil-bath heated method under atmospheric pressure. The COD removal efficiency and SO$_4^{2-}$ and NO$_3^-$ concentration of SD-Na solution indicate that the pollutant is degraded thoroughly after photodegradation reaction, except for a little residual of sulfur-containing organics. Effects of illumination and climate of different seasons on degradation efficiency were investigated. Moreover adding H$_2$O$_2$ as pro-oxidant can increase the photocatalytic activity of Bi$_7$O$_9$I$_3$. The as-synthesized Bi$_7$O$_9$I$_3$ demonstrated an excellent visible-light-induced photocatalytic activity, high mineralization capacity and good stability for the degradation of SD-Na in aqueous solution.

**REFERENCES**


photocatalytic properties. Journal of the Taiwan Institute of Chemical Engineers 45, 1892–1909.


First received 15 April 2015; accepted in revised form 3 August 2015. Available online 17 August 2015