Controllable fabrication of heterostructured Au/Bi₂O₃ with plasmon effect for efficient photodegradation of rhodamine 6G

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ABSTRACT
Three-dimensional (BiO)₂CO₃ (BSC) nanostructures were synthesised by a hydrothermal reaction, and Bi₂O₃ nanoparticles were then obtained by calcining BSC precursor at different temperatures. BSC and Bi₂O₃ samples were then sputtering coated with Au to get the resultant Au/BSC and Au/Bi₂O₃ for the investigation of the effect of the Au coating on the photocatalytic performance of the samples. The phase structure, morphology and composition of the samples were characterised by X-ray diffraction, scanning electron microscopy and energy-dispersive spectroscopy (EDS). UV–vis diffuse reflectance spectra were used to measure the response of different catalysts to UV–vis light. The photocatalytic activity was investigated for the degradation of rhodamine 6G at room temperature and the light intensity was 1 sun. Bi₂O₃ exhibited better photocatalytic performance than BSC due to the narrow band gap of Bi₂O₃, and the coating of Au also endowed the samples with higher photocatalytic capability as compared to the bare one.

KEYWORDS
Bismuth oxide; gold; plasmon effect; photodegradation; dye

1. Introduction
Problems with water are expected to grow worse with the society development and have attracted worldwide attention. Serious environmental water pollution is caused by the discharge of the industrial dye wastewater [1]. Specifically, a great quantity of dyes are used in the manufacturing processes of the textile industries and dyeing industries, which will lead to the discharging of the dye wastewater with high concentration (~50 wt%) into the environment. Of note, such toxic dye wastewater is normally non-biodegradable and potentially carcinogenic and gives rise to various environmental crises [2].

Many treatment technologies have been utilised for the treatment of dye wastewater, from physico-chemical to biological processes [3–8]. Physical techniques such as adsorption, reverse osmosis, ultrafiltration and ion exchange on synthetic adsorbent resins can
efficiently decolourise the dye wastewater [9–12]. However, they will lead to secondary pollution since physical process just transfers organic compounds from aqueous phase to other phases [13]. In terms of biotechnologies which shows relatively better degradation efficiency of the dye waste water, however, [14–17], it is still difficult for most of the microorganisms to decompose the present dyes containing various structures [18]. By contrast, the use of heterogeneous photocatalytic degradation methods is an alternative option, as the catalysts can be regenerated and reused. The solar energy-driven photocatalysis has been extensively studied to solve growing environment problems and the global energy shortage, as the times require, plenty of new-type photocatalysts are emerging to drive photocatalytic reactions [19–27].

Recently, bismuth-based compounds like (BiO)₂CO₃ (BSC) and Bi₂O₃ with remarkable properties have received considerable attention as potential candidates of photocatalysts [28–36]. Self-assembly of nanocrystals into complex or three-dimensional (3D) nanostructures has received much attention particularly for applications in energy, electronics, environment science and biomedical fields [37,38]. Hierarchical or shape controlled bismuth sub-carbonate is fabricated and studied by various research groups [39–43]. 3D BSC nanocrystals have been synthesised for selective adsorption and separation of dyes [44]. However, BSC showed poor photocatalytic efficiency and its application in the dye degradation is then limited. As an important p-type semiconductor, Bi₂O₃ nanomaterials have also attracted considerable attention in recent years for photocatalysis [36,45].

In recent years, plasmon-induced hot-electron generation at nanoparticle/metal oxide interface has attracted much interest for photovoltaic and photocatalytic devices. It has been proved that the synergy of plasmonic nanostructure and semiconductor can significantly enhance the photocatalytic activity. Bi₂O₃ with low band gaps (< 2.58 eV) has shown promise in the photodegradation of the dye wastewater [31–33,41,46,47]. However, the usage of Bi₂O₃ with Au coating has not been investigated until now; considering the positive effect of Au coating on the photodegradation, it is valuable to investigate the Au/Bi₂O₃ catalysts for the photodegradation. In this work, a mild and low cost approach was developed for the fabrication of 3D BSC nanoflowers. Through the thermal decomposition of BSC precursor, Bi₂O₃ or Bi₂O₃/BSC mixture was obtained. To improve their response to visible light, BSC and Bi₂O₃ were coated with transition metal Au by sputtering coating. The photocatalytic activity was examined for the degradation of rhodamine 6G (R6G) as typical dye.

2. Experimental

2.1. Synthesis of flower-like BSC nanocrystals and heterostructured Bi₂O₃

Three-dimensional and flower-like BSC nanocrystals were synthesised through the hydrothermal method. The reaction solution was prepared by dissolving 0.5 mol NaOH, 10 mmol bismuth nitrate (Bi(NO₃)₃), 2.5 g urea (CO(NH₂)₂) and 20 mmol of sodium citrate (Na₃C₆H₅O₇) in 30 mL distillate water. The reaction solution was magnetic stirred at 600 rpm for 1 hour to ensure the homogeneity. Subsequently, the reactant solution was transferred into a 40-mL Teflon-lined stainless steel autoclave. The auto-calve was then sealed and placed in an oven at a temperature of 140 °C for 6 h. After the hydrothermal treatment, the auto-clave was cooled down to room temperature naturally. The precipitate was collected by centrifugation and washed with copious distilled water and absolute
ethanol to remove possible residues. Finally, the obtained sample was dried in an oven at 80 °C overnight. For the synthesis of heterostructured Bi$_2$O$_3$, the obtained BSC precursor was calcined at various temperatures from 200 °C up to 500 °C for 3 h to optimise the synthetic condition.

2.2. Synthesis of Au/BSC and Au/Bi$_2$O$_3$

Au/BSC and Au/Bi$_2$O$_3$ were obtained by sputtering Au particles on BSC and Bi$_2$O$_3$. The Au is used because its Fermi level is lower than that of BSC and Bi$_2$O$_3$, where photoexcited electrons can be transferred from conduction band to Au particles, and photogenerated valence band holes remain on the BSC or Bi$_2$O$_3$ surface [48].

2.3. Characterisation

The structure of the as-prepared samples were investigated by X-ray diffraction (XRD, D8 ADVANCE) with Cu Kα radiation (25 mA and 40 kV) in the 2θ range from 10° to 90° with a scanning step size of 0.01°. The morphology of the samples was determined by the scanning electron microscope (SEM, JEOL JSM-7001F). Transmission electron microscopic images were recorded by a FEI Tecnai G2 T20 working at 200 kV. The samples were prepared by drop-casting the sample/ethanol solution on a copper grip. The chemical composition was characterised by energy-dispersive spectrometer (EDS) that is attached to JEOL JSM-7001F. UV–vis diffuse reflectance spectra were scanned by a spectrophotometer in the range of 200–800 nm (UV–VIS, SHIMADZU UV-2600).

2.4. Photocatalytic test for dye degradation

Rhodamine 6G (R6G) is chemically stable and poorly biodegradable dye contaminants in waste water. In this work, we use the typical dye, rhodamine 6G (R6G) as model reactions to evaluate the photocatalytic activity [49–51]. Figure 1 shows the molecule structure of R6G. The concentration of the dye aqueous solution was 25 mg L$^{-1}$. A total of 10 mg of the catalyst powder was added into 25 ml of dye solution and the muddy solution was dispersed with an ultrasonic instrument for 30 min. The initial concentration of R6G was measured.

![Figure 1. The molecular structure of rhodamine 6G (R6G).](image)
after ultrasonic dispersing to eliminate the adsorption effect of catalysts. A CHF-XM-
500WXe lamp positioned 25 cm from reaction tube was used as light source and the sunlight
intensity was 1 sun. The photodegradation was carried out at room temperature with mag-
nenic stirring for 1 hour and pH was adjusted to 2.5–11.5 with 0.1 mol L\(^{-1}\) HCl aqueous solu-
tion. The concentration change of the dye solution after photodegradation was recorded by a
Cary 60 UV–Vis spectrophotometer by comparing the light absorption intensity.

3. Results and discussion

Figure 2 shows the wide-angle XRD patterns of the synthesised Bi\(_2\)O\(_2\)CO\(_3\) (BSC) and the
resultant Bi\(_2\)O\(_3\) calcined at different temperatures. The tetragonal phase of BSC (JCPDS:
41-1488) can be clearly identified and no other impurities can be observed. The XRD pat-
tern obtained with sample calcinated at 200 °C is identical to that of the BSC, suggesting
no new phase was formed herein. However, the intensity of the characteristic peak (002) of
BSC decreases. For the sample calcinated at 300 °C, a series of new diffraction peaks can be
observed at \(2\theta = 16.7°, 19.7°, 28.6°, 33.2°, 46.3°\) and \(58.4°\), which can be ascribed to the
monocline \(\beta\)-Bi\(_2\)O\(_3\) (JCPDS 78-1793). Meanwhile, the newly formed peaks located at 35.1°,
42.0° and 52.3° are corresponding to \(\alpha\)-phase Bi\(_2\)O\(_3\) (JCPDS 71-2274). Besides, a majority
of the original BSC diffraction peaks disappeared or significantly become decreased. When
the sample was further calcinated at 350 °C, no BSC diffraction peaks can be detected, indicat-
ing the completely conversion of BSC to \(\alpha\)-phase and \(\beta\)-phase Bi\(_2\)O\(_3\). Furthermore, the
sample was further calcinated at higher temperatures (400 °C and 500 °C) and character-
ised by XRD technique to study the thermal stability of the obtained sample. It is noted
that \(\alpha\)-Bi\(_2\)O\(_3\) and \(\beta\)-Bi\(_2\)O\(_3\) are still coexisting even the calcined temperature is as high as
500 °C, although decrease in \(\beta\)-phase Bi\(_2\)O\(_3\) can be observed. According to previous report
[46], the \(\beta\)-phase Bi\(_2\)O\(_3\) is not stable and can be totally converted to \(\alpha\)-phase at high tem-
perature over 400 °C, resulting in significant decrease in the photocatalytic activity. Com-
pared with earlier reports, the above-obtained heterostructured Bi\(_2\)O\(_3\) can retain most of

![Figure 2. X-ray diffraction patterns of BSC and Bi\(_2\)O\(_3\) calcined at different temperatures.](image-url)
the photoactive $\beta$-phase, suggesting its remarkable photocatalytic activity and stability. The excellent thermal stability of the obtained Bi$_2$O$_3$ can be contributed from the unique nanostructure of the Bi$_2$O$_3$ and its high crystallinity. The excellent thermal stability is mainly owing to the unique nanostructure of the obtained Bi$_2$O$_3$. In this work, sample calcined at 350 °C was chosen for the photodegradation study, because most of the $\beta$-phase Bi$_2$O$_3$ can be obtained at this calcination temperature.

The morphology of the samples was investigated by SEM. As shown in Figure 3(a) and (b), BSC has a 3D nanoflower morphology, and its size is about 2–3.5 μm. The sodium

Figure 3. SEM images of flower-like BSC nanocrystals (a, b) and heterostructured Bi$_2$O$_3$ calcined at 350 °C (c, d), TEM images of Bi$_2$O$_3$ calcined at 350 °C (e, f).
citrate as a shape modifier and controller played an important roles in fabricating 3D BSC. COO- and –OH groups released from citrate could bind to certain crystal faces of the particles [52]. SEM images of BSC calcined at 350 °C (Figure 3(c) and (d)) show a lot of interconnected particles, which are completely different in the structure from BSC. The HR-TEM images of BSC calcined at 350 °C are displayed in Figure 3(e) and (f), where a clear β-Bi2O3 (201) atomic plane with the respective spacing of 0.319 nm is visible. All the above characteristic results indicate BSC crystals are completely decomposed into β-Bi2O3 with a small amount of α-Bi2O3 phase after heat treatment at 350 °C.

As mentioned earlier, Au was coated onto BSC and Bi2O3 to improve the visible light response. Figures 4 and 5 show the element analyses of Au/BSC and Au/Bi2O3, respectively. The EDS elemental mappings of Bi, C, O and Au are displayed in Figures 4(c)–(f) and 5(c)–(f), respectively. The results show that all elements including Au are uniformly distributed on the samples.

The photodegradation condition was optimised by using synthesised BSC as a function of pH. Figure 6 displayed the degradation of R6G catalysed by BSC at different pH from 2.5 up to 11. The results show that the degradation rate increases gradually along with the increase of illumination time at different pH. But with the increase of pH, the activity of catalyst decreases sharply. The degradation rate is 95.6% at pH 2.5, and reduces to only 19.6% at pH 7.5 after 75 min illumination. As reported in our previous work [44], BSC surfaces are negatively charged with a zeta potential of about −40 mV. R6G is positively charged, neutral and negatively charged in the pH range of below 6.0, 6.0−10.8 and above 10.8, respectively. Therefore, different binding force between R6G and BSC is presented at various pH values. The mechanism between BSC and R6G in different pH is shown in Figure 7. The suitable adsorption pH is below 6.0. Therefore, the photodegradation conditions were selected at room temperature and pH of 2.5. From Figure 8, it can be seen that the degradation rate of R6G increases with the reaction time increasing from 0 to 50 min.

Figure 4. SEM-EDS images of Au/BSC: SEM images (a), EDS data (b) and the EDS elemental mappings of Bi (c), C (d), O (e) and Au (f).
The blank test was studied without catalyst and the result showed that there was little degradation of R6G only under irradiation. Bi$_2$O$_3$ exhibits higher activity than pure BSC that could be attributed to the $\beta$-Bi$_2$O$_3$ with a narrower band gap [33,46,47]. The degradation rate of R6G reaches 92.53% for Bi$_2$O$_3$ in the reaction time of 50 min, while it is 84.73% for BSC.

By using Au/BSC and Au/Bi$_2$O$_3$ with 2 times sputtering Au particles, the degradation rates of R6G are higher than those of BSC and Bi$_2$O$_3$, respectively. At 10 min irradiation, the degradation rate of R6G on BSC, Bi$_2$O$_3$, Au/BSC and Au/Bi$_2$O$_3$ are 0.48%, 5.1%, 13.24% and 30.22%, respectively. When the reaction time is 30 min, the degradation rate...
on BSC, Bi$_2$O$_3$, Au/BSC and Au/Bi$_2$O$_3$ increases to 57.52%, 68.13%, 73.61% and 86.58%, respectively. The highest degradation of R6G reaches 100% on Au/Bi$_2$O$_3$ after 40 min illumination. Therefore, Bi$_2$O$_3$ exhibits better photocatalytic performance than the un-calcined BSC, and the Au coating also increases the photocatalytic performance as compared to the bare one. The recycling performance of Au/Bi$_2$O$_3$ was carried out after 50 min irradiation. The excellent photocatalytic activity performance of Au/Bi$_2$O$_3$ can be summarised as the following: (i) the plasmonic Au nanoparticles can dramatically enhance the light absorption, thereby improving the utilisation efficiency of solar energy. (ii) The coated Au can also act as electron collector to prevent the hole and electron recombination. (iii) The interaction between Au and Bi$_2$O$_3$ can facilitate the electron transport through the entire Au/Bi$_2$O$_3$ catalyst, and carried out reduction and oxidation reactions, respectively. The mechanism of photodegradation of R6G was investigated by previous studies [53–55]. The recycling performance of Au/Bi$_2$O$_3$ was carried out after 50 min irradiation and no significant photoreactivity decrease is observed as compared with the fresh Au/Bi$_2$O$_3$, indicating the photostability of Au/Bi$_2$O$_3$ for the visible light R6G degradation. The degradation rate reaches 93.36% on recycling sample of Au/ Bi$_2$O$_3$ at 50 min.

**Figure 7.** Adsorption mechanism of BSC and R6G at various pH: pH below 6.0 (a), 6.0–10.8 (b) and above 10.8 (c).

**Figure 8.** Photodegradation of R6G catalysed by Au/Bi$_2$O$_3$, Bi$_2$O$_3$, Au/BSC and BSC in pH = 2.5 aqueous solution at room temperature.
To further explain the enhanced photocatalytic of Au-coated Bi$_2$O$_3$, UV–vis spectra were performed to compare the light absorbance. Figure 9 shows UV–vis diffuse reflectance spectra of different photocatalysts BCS, Au/BCS, Bi$_2$O$_3$ and Au/Bi$_2$O$_3$. The results indicate that BSC has the UV absorption band edge of 375 nm with a corresponding band gap of 3.30 eV. After coating Au, the Au/Bi$_2$O$_3$ exhibit enhanced light absorption performance [56]. Thus, the Au/Bi$_2$O$_3$ exhibits better photocatalytic performance. The Bi$_2$O$_3$ are composed of both α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$, the absorption band shifts to right with a band edge extending to 500 nm (2.48 eV). The UV–vis diffuse reflectance spectra confirm that Bi$_2$O$_3$ exhibits higher activity than BSC due to the shift of band gap, whilst the Au nanoparticles improve the photocatalytic activity through its plasmonic effect.

4. Conclusion

Three-dimensional BSC nanostructures were prepared by a hydrothermal method. After being calcined at 350 °C for 3 h, BSC phase can be transferred into β-Bi$_2$O$_3$ phase with a small amount of α-Bi$_2$O$_3$ phase. The EDS analysis reveals that Au nanoparticles were homogeneously coated on the BSC and Bi$_2$O$_3$ by the sputtering coating method. The photodegradation results show that Bi$_2$O$_3$ prepared by 350 °C calcination exhibits the higher activity than BSC. The enhanced photocatalytic activity can be attributed to the narrow band gap of β-Bi$_2$O$_3$. Moreover, the introduction of Au nanoparticles onto the surface of Bi$_2$O$_3$ gives a further increase in the photocatalytic performance. As a result, the Au/Bi$_2$O$_3$ heterostructures exhibit a remarkable photocatalytic activity towards degradation of R6G, which has the potential for sun light driven environmental remediation.

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