In-situ growth of Au and β -Bi₂O₃ nanoparticles on flower-like Bi₂O₂CO₃: a multi-heterojunction photocatalyst with enhanced visible light responsive photocatalytic activity

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Abstract

In this work, flower-like Au/Bi₂O₂CO₃/Bi₂O₃ multi-heterojunction photocatalysts were prepared by a in-situ growth method. The as-prepared samples were characterized by different techniques including Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), UV-vis diffuse reflectance spectrometry (DRS), X-ray photoelectron spectroscopy (XPS), Photoluminescence (PL) and photo-induced current. The photocatalytic performance of the as prepared samples was evaluated by degradation of rhodamine B (RhB) under visible light ($\lambda > 400$ nm). Au/Bi₂O₂CO₃/Bi₂O₃ exhibited much higher activity than pure Bi₂O₂CO₃ or Bi₂O₂CO₃/Bi₂O₃. The rate constant of best one Au/Bi₂O₂CO₃/Bi₂O₃ sample is 100 and 14 times as that of pure Bi₂O₂CO₃ and β -Bi₂O₃/Bi₂O₂CO₃, respectively. The enhanced photocatalytic activity of Au/Bi₂O₂CO₃/Bi₂O₃ can be ascribed to the surface plasmon resonance (SPR) effects of Au nanoparticles and the formed multi-heterojunctions,

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which enhanced the absorbance of visible light and facilitated the transferring and separation of photogenerated electron-hole pairs, respectively.

Keywords: Multi-heterojunction; $\text{Bi}_2\text{O}_2\text{CO}_3$; Surface plasmon resonance; Flower-like structure; Photocatalysis

1. Introduction

Nowadays, semiconductor-based photocatalysis is considered to be one of the most promising methods for solving environmental and energy issues since it is a facile and environmental friendly way which exhibits potential on utilization of solar energy[1-3]. Recently, bismuth-based oxides with Aurivillius-layered structure, such as BiVO_4 [4-5], Bi_2WO_6 [6-7], BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [8-10], have attracted considerable attention. Bismuth subcarbonate ($\text{Bi}_2\text{O}_2\text{CO}_3$) is a typical member in Aurivillius-related oxide family. It is constructed by $(\text{Bi}_2\text{O}_2)^{2+}$ slabs interleaved with CO_3^{2-} layers, which is favorable for formation of layered nanostructures and separation of photo-generated charges [11]. However, $\text{Bi}_2\text{O}_2\text{CO}_3$ with a wide band gap (3.1-3.5 eV) can only absorb UV light, restricting its practical application under the solar light[12-14]. Constructing heterojunctions between $\text{Bi}_2\text{O}_2\text{CO}_3$ and other semiconductors with suitable band has been proved to be an effective way to extend the light absorbance range, such as $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{S}_3$ [15], $\text{MoS}_2/\text{Bi}_2\text{O}_2\text{CO}_3$ [16], $\text{Bi}_2\text{O}_2\text{CO}_3/\text{BiOCl}$ [17]. In particular, $\beta\text{-Bi}_2\text{O}_3$ is an appropriate semiconductor to capture a large part of the solar light because of its small band gap (2.4 eV) [18]. Hu's research indicated that the $\beta\text{-Bi}_2\text{O}_3$ -sensitized $\text{Bi}_2\text{O}_2\text{CO}_3$ composite photocatalyst exhibited an enhanced photocatalytic activity for the degradation of o-phenylphenol [19].

On the other hand, modification of photocatalysts with noble metal nanoparticles (NMNPs) is also an effective approach to improve their visible light activity, owing to the surface plasmon resonance (SPR) effect of NMNPs enables the supported photocatalysts to absorb visible light[20-21]. Among different noble metals, gold (Au) is considered to be one of the most promising materials due to its high photocatalytic activity, low toxicity and good biocompatibility[22]. Liu et al. reported that modification of $\text{BiOBr}_{0.2}\text{I}_{0.8}$ with Au improved the visible-light photocatalytic performance for degrading methyl orange (MO), Rhodamine B (RhB) and phenol [23]. Zhang et al. prepared Au/BaTiO_3 heterostructures with high visible light photocatalytic activity[24]. Hou's group also observed that Au-modified ZnO displays a high visible light activity[25].

In this work, we prepared visible-light-driven $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ multi-heterojunction photocatalysts by a facile calcination method. The obtained photocatalysts were characterized thoroughly by different techniques. The photocatalytic activities of the obtained photocatalysts were evaluated by RhB degradation under the irradiation of visible light. Moreover, possible mechanism for the activity enhancement was investigated and proposed in detail.

2. Experimental

2.1. Synthesis of flower-like $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ nanostructures

Flower like $\text{Bi}_2\text{O}_2\text{CO}_3$ were synthesized by a typical hydrothermal method as reported in previous work with some modification [26]. In a typical process, 0.97 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 60 mL deionized water. Then, 1.76 g sodium citrate,

0.48 g urea, 1 g polyvinyl pyrrolidone (PVP) were added and kept another 45 min vigorous stirring. The obtained mixture was transferred into a Teflon-lined autoclave with a capacity of 100 mL. Then the autoclave was placed into an oven and kept at 180 °C for 12 h [26]. After be naturally cooled down to room temperature, the obtained samples were filtrated and rinsed with ethanol and deionized water. At last, the samples are dried at 60 °C overnight.

The Au/Bi₂O₂CO₃/Bi₂O₃ composites were prepared as follows: 0.3 g Bi₂O₂CO₃ was firstly dispersed in 15 mL methanol through an ultrasonic treatment process (20 min), which was then denoted as suspension A. HAuCl₄•4H₂O (3.13, 12.54, 25.08, 50.16 mg) were dissolved in 5 mL methanol by stirring magnetically for 15 min to form solution B. Afterwards, solution B was added to suspension A dropwise under vigorous stirring before the mixtures were stirred at 60 °C to evaporate the methanol completely. The above samples were grinded and calcined at 350 °C for 1 h. The obtained samples were loaded with varied amount of Au (0.5, 2, 4, 8 wt.%) and denoted as Au/Bi₂O₂CO₃/Bi₂O₃-1, Au/Bi₂O₂CO₃/Bi₂O₃-2, Au/Bi₂O₂CO₃/Bi₂O₃-3, Au/Bi₂O₂CO₃/Bi₂O₃-4, respectively. While the sample without Au was denoted as Bi₂O₂CO₃/Bi₂O₃.

2.2. Characterization

The phase structure of the as-synthesized samples was characterized by X-ray diffractometer (XRD, Rigaku, SmartLab). The morphology was examined by a transmission electron microscopy (TEM, JEOL, JEM-2100 (HR)). The surface states of different elements of the obtained samples were studied by X-ray photoelectron

spectroscopy (XPS, Thermo ESCALAB 250Xi). The binding energy data for different elements were calibrated with the C1s signal at 284.6 eV. The UV-Vis diffuse reflectance spectra (DRS) of different samples were recorded by a UV-vis spectrophotometer (Shimadzu, UV3600). The photoluminescence (PL) spectra (excitation wavelength is 280 nm) were recorded by a fluorescence spectrophotometer (Hitachi, F-7000). Photocurrent was recorded by an electrochemical station (Chenhua Instruments, CHI660D) in a traditional three electrodes system.

2.3. Photocatalytic activity

RhB was chosen as the probe molecule to investigate the photocatalytic performance of the obtained samples. The light source was a 300 W Xe lamp (Zhong jiaojinyuan, CEL-HXF300) with a light filter which remove the light below 400 nm. 0.03 g of the as-prepared samples was dispersed in RhB solution (50 mL, 5 mg/L) by ultrasonic treatment for 2 min before it was magnetically stirred for 1 h in the dark. After the beginning of light irradiation, 1.5 mL of solution was collected at a given interval and immediately centrifuged to remove the catalys. Subsequently, the concentration of RhB was measured by a UV-vis spectrophotometer.

3. Results and discussion

3.1 Characterization of different samples

The XRD patterns of Au/Bi₂O₂CO₃/Bi₂O₃ nanocomposites, Bi₂O₂CO₃/Bi₂O₃ and pure Bi₂O₂CO₃ are presented in Fig. 1. From the plot of pure Bi₂O₂CO₃, it can be noted that the main diffraction peaks were perfectly coincident with (002), (011), (013), (110), (112), (114), (020), (116) and (123) crystallographic planes of the

tetragonal $\text{Bi}_2\text{O}_2\text{CO}_3$ (PDF card No. 41-1488)[27-29] and no secondary phase is detected. In the plot of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites, besides of the diffraction peaks of $\text{Bi}_2\text{O}_2\text{CO}_3$, several newly formed peaks were detected at 27.94° , 31.76° , 46.22° , 55.65° and 57.75° , which correspond to the $\beta\text{-Bi}_2\text{O}_3$ (PDF card No. 27-0050, $a = b = 7.735 \text{ \AA}$, $c=5.628\text{\AA}$)[30-32]. The crystallite size of $\beta\text{-Bi}_2\text{O}_3$ in the obtained samples can be calculated using the Scherrer equation [33]. The obtained data are 38.5, 37.6, 36.8, 36.7, 36.5 nm for $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$, $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3\text{-1}$, $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3\text{-2}$, $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3\text{-3}$, $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3\text{-4}$, respectively. The results indicate that the addition of Au has no apparent effect on the formation of Bi_2O_3 . In the XRD patterns of $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites, additional diffraction peaks appear at 38.18° and 44.39° , which correspond to the (111) and (200) reflection planes of Au (PDF card No. 04-0784, $a = b = c=4.079\text{\AA}$)[34-35]. Hence, it can be inferred the presence of $\text{Bi}_2\text{O}_2\text{CO}_3$, Bi_2O_3 and Au in the as-prepared composites.

The morphologies of the as-obtained photocatalysts were investigated by SEM and TEM, and the results are shown in Fig. 2. It can be seen from Fig. 2a that the pure $\text{Bi}_2\text{O}_2\text{CO}_3$ sample exhibits flower-like sphere structure which formed by self assembly of 2D thin nanoplates. The spheres are uniform and present an average diameter of about 1.5 μm . The morphology of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites (Fig. 2b) is similar to that of pure $\text{Bi}_2\text{O}_2\text{CO}_3$, which indicated that the flower-like morphology unchanged after calcining process. However, no obvious Bi_2O_3 are detected in the image. It may be ascribed to the fact that Bi_2O_3 are formed by an in-situ decomposition process from $\text{Bi}_2\text{O}_2\text{CO}_3$. Therefore, there is no apparent boundary

between the formed Bi_2O_3 and initial $\text{Bi}_2\text{O}_2\text{CO}_3$. The SEM and TEM images of $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites are shown in Fig. 2c-2g. It can be seen that Au nanoparticles sized in about 3-8 nm attached on the surface of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoplates. Therefore, it is thought to be form multi-heterojunctions between the three components of Au nanoparticles, $\text{Bi}_2\text{O}_2\text{CO}_3$ and Bi_2O_3 [36-37].

XPS analyses were conducted to further investigate the chemical states and composition of $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites (Fig. 3). From the survey spectra (Fig. 3a), the peaks of Bi 4f, C 1s, O 1s, and Au 4f are clearly observed, illustrating the presence of Bi, C, O, and Au elements in the as-prepared samples. The high-resolution XPS spectrum of O is displayed in Fig. 3b. The O 1s peak can be divided into three different peaks at about 531.1 eV, 529.9 eV and 528.9 eV, indicating the co-existence of three chemical states of oxygen on this surface. The peaks at 531.1 eV could be ascribed to carbonate species[38] and the peaks at 529.9 eV were attributed to the Bi-O bond[39]. The Bi 4f spectrum, as shown in Fig. 3c, has two peaks at 164.3 eV and 159.0 eV, corresponding to the binding energies of Bi 4f_{5/2} and Bi 4f_{7/2} of Bi^{3+} , respectively[40]. Fig. 3d displays the high-resolution XPS spectrum of Au 4f. Two peaks at 87.7 eV and 83.7 eV can be seen, being assigned to the Au 4f_{5/2} and Au 4f_{7/2} binding energies, indicating that Au is existing in the state of Au^0 species in $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ nanocomposites[41].

The DRS of $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ samples are shown in Fig. 4. The pure $\text{Bi}_2\text{O}_2\text{CO}_3$ displays no visible-light absorption. Comparing with pure $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites exhibit wider optical response

range and can absorb visible light. In addition, $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ shows an enhanced absorption in visible light region compared to $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$, which can be ascribed to the factor that the existence of Au nanoparticles on the surface of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$. Furthermore, it can be seen that a visible light SPR absorption peak arises around 663 nm in the spectra of $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ due to the SPR effect of Au nanoparticles[42]. From above results, it can be predicted that $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ would show better visible light-activated photocatalytic activity because of the enhanced absorbance properties for visible light.

3.2 Photocatalytic activity

The photocatalytic activity of as-obtained samples was evaluated by the degradation of RhB dye under the irradiation of visible light, and the results are shown in Fig. 5. It can be seen that pure $\text{Bi}_2\text{O}_2\text{CO}_3$ exhibits neglectable photocatalytic activity under visible-light because of its wide band gap. However, the removal percent of RhB reaches to 41% by $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ heterojunction within 30 min, suggesting that the photocatalytic activity enhances when Bi_2O_3 is introduced. As Au nanoparticles was introduced into $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ sample, the photocatalytic activity further enhances. Among these $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ composites, $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -3 displays the highest activity. The RhB can be decomposed completely within 10 min by $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -3. The results illustrate that the multi-heterojunctions between $\text{Bi}_2\text{O}_2\text{CO}_3$, Bi_2O_3 and Au nanoparticles significantly improve the photocatalytic activity.

The kinetic for RhB degradation was investigated to get better comparison of the

photocatalytic efficiency of the obtained different samples. The apparent rate constant (k_{app}) can be obtained through the kinetic fitting,. The k_{app} is independent on the RhB amount of adsorbed and remaining in the solution. The k_{app} follows the apparent first-order kinetic equation[43-44]:

$$\ln(C/C_0) = k_{app}t$$

where C_0 is the RhB concentration after dark adsorption process (mg/L), C is the concentration of RhB remaining in the solution (mg/L) , and k_{app} is the apparent rate constant (min^{-1}), t is the irradiation time (min). The calculated data of apparent rate constants (k_{app}) for different samples are displayed in Fig. 6. The order of photocatalytic activity for the samples can be summarized as follows: Au/Bi₂O₂CO₃/Bi₂O₃-3 ($0.20 \pm 0.013 \text{ min}^{-1}$) > Au/Bi₂O₂CO₃/Bi₂O₃-4 ($0.12 \pm 0.0082 \text{ min}^{-1}$) > Au/Bi₂O₂CO₃/Bi₂O₃-2 ($0.10 \pm 0.0075 \text{ min}^{-1}$) > Au/Bi₂O₂CO₃/Bi₂O₃-1 ($0.021 \pm 0.00081 \text{ min}^{-1}$) > Bi₂O₂CO₃/Bi₂O₃ ($0.014 \pm 0.00088 \text{ min}^{-1}$) > Bi₂O₂CO₃ ($0.0018 \pm 0.00016 \text{ min}^{-1}$). The results show that the photocatalytic activity boosts with the growth of Bi₂O₃ and Au nanoparticles, which can be ascribed to the formed multi-heterojunction structure and the SPR effect of Au nanoparticles.

3.3. Possible photocatalytic mechanism

The photoluminescence (PL) spectrum reflects the recombination rate of photo-generated electron-hole pairs, which is very important for the photocatalytic performance [45-46]. The lower of PL intensity means lower recombination rate of photo-induced holes and electrons [47]. The PL spectra of as-obtained samples display a emission peak at around 370 nm (Fig. 7). Clearly, one can see that the PL

intensity of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ is lower than that of pure $\text{Bi}_2\text{O}_2\text{CO}_3$, indicating $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ heterojunctions can effectively hinder the recombination of the excited electrons and holes. When Au nanoparticles growing onto the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$, the PL intensity decreases significantly, indicating further decreasing of recombination rate of electrons and holes. The decreasing recombination rate of photo-generated charges can be ascribed to the formation of multi-heterojunctions between the three components.

The transient photocurrent for different samples were also measured to compare the separation efficiency of photogenerated hole-electron pairs. The photocurrents were obtained under the intermittent visible light irradiation of 20 s in 50 mL of Na_2SO_4 solution without any applied potential. As shown in Fig. 8, the photocurrent of $\text{Bi}_2\text{O}_2\text{CO}_3$ is very low due to its large band gap. By comparison, the photocurrents of $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ are higher than both of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3$. The value of photocurrent for $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ is about 15 times as that of pure $\text{Bi}_2\text{O}_2\text{CO}_3$ and 2 times as that of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$. The orders of the photocurrents are in good agreement with the trend of photocatalytic activity, demonstrating that the high performance of $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ multi-heterojunctions may be ascribed to its high separation efficiency of photo-generated charges.

In the photocatalytic process, several kinds of active radicals including $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and hole are generated [48-49]. To further determine which kind of radical plays a main role for RhB degradation. Tert-butanol, p-benzoquinone and EDTA-Na_2 were chosen as the scavengers of $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and hole, respectively. As presented in Fig. 9,

the removal percentages of RhB decreased significantly in the presence of EDTA-Na₂ or p-benzoquinone, while no obvious change was observed when tert-butanol was added. These results confirm that h⁺ and •O²⁻ are main species for RhB degradation by the multi-heterojunction photocatalysts.

Based on the above results, we can propose the following possible mechanism (as shown in Fig. 10) for the enhanced photocatalytic activity of Au/Bi₂O₂CO₃/Bi₂O₃ multi-heterojunctions. Bi₂O₂CO₃ cannot be excited by visible light. However, β-Bi₂O₃ can be excited easily to generate electron-hole pairs under the irradiation of visible light due to its small band gap of 2.4 eV. Furthermore, Au nanoparticles can also be excited to generate electrons and holes due to its SPR effect under the irradiation of visible light. The photogenerated electrons in the CB of β-Bi₂O₃ (0.19 eV) will easily transfer to the CB of Bi₂O₂CO₃ (0.21 eV). On the other hand, the holes in the VB of β-Bi₂O₃ can directly oxidize RhB to the final products [50]. Furthermore, the photogenerated electrons in the CB of β-Bi₂O₃ can also probably transfer to Au nanoparticles since the Fermi level of metallic Au (0.5 eV vs. NHE) is lower than the CB of β-Bi₂O₃ (0.19 eV)[51]. The electrons in the CB of Bi₂O₂CO₃ and in the Au nanoparticles can be trapped by dissolved O₂ to generate •O₂⁻, which can further oxidize RhB dye. The SPR effect of Au nanoparticles and multi-junction structures are beneficial for the separation of the photogenerated charges, leading to superior visible-light photocatalytic performance.

4. Conclusion

Flower-like Au/Bi₂O₂CO₃/Bi₂O₃ multi-heterojunction photocatalysts were

synthesized by a in-situ growth method. The $\text{Au/Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ heterojunctions exhibited higher visible-light-responsive photocatalytic activity for RhB degradation than $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$. The enhanced photocatalytic performance was attributed to the formed multi-heterojunctions and the SPR effect of Au nanoparticles, which can suppress the recombination of electron-hole pairs.

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Figure Captions

Fig.1 XRD patterns of pure $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$

Fig.2 SEM images of (a) $\text{Bi}_2\text{O}_2\text{CO}_3$, (b) $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$, (c) $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -1, (d) $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -2, (e) $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -3, (f) $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -4, (g) TEM image of $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$

Fig.3 XPS spectra of $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ samples (a) survey spectrum; (b) O 1s; (c) Bi 4f; (d) Au 4f

Fig.4 Diffuse reflectance UV-vis spectra of different samples

Fig.5 Photocatalytic degradation curves of RhB in the presence of as-prepared samples under visible light irradiation

Fig.6 The apparent rate constants for pure $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$

Fig.7 Photoluminescence spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ -3 composites

Fig.8 Photocurrent of as-prepared samples under visible light irradiation

Fig.9 Effect of scavengers on the photocatalytic degradation of RhB by $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ under visible light irradiation

Fig.10 Schematic diagram of the possible photocatalytic degradation mechanism over $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ heterojunction under visible light irradiation

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

Graphical abstract:

A novel multi-heterojunction photocatalyst $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ was prepared by a one-pot in-situ growth method for the first time. The as-obtained photocatalysts show much higher activity under visible light irradiation for the degradation of organic pollutants. The rate constant of the best one $\text{Au}/\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ sample is 100 and 14 times as that of pure $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, respectively.