1. Introduction

Increasing wastewater emissions from industry, in particular organic pollutants, into the river are broadly recognized to be one of the primary causes of environmental deterioration. The development of semiconductor photocatalytic materials as a green purification technique appears to be a potential way to solve this crisis, and thus various types of photocatalysts, such as TiO₂, ZnO, CdS, and g-C₃N₄, have been developed. In spite of the advantages of the photocatalysis process including electron injection, charge separation promotion, and DMPO-assisted ESR measurements. This study not only provides evidence for the feasibility of metallic Au as a SPR co-catalyst of bismuth-based materials, but also furnishes new insights into the multiple effects for enhancing the photochemical properties.

Plasmon induced Au particle and surface oxidation co-decorated BiOIO₃ heteronanostructures with highly promoted photocatalysis and photoelectrochemical properties

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Plasmon induced Au nanoparticle and surface oxidation induced co-decorated BiOIO₃ heterostructured nanocomposites have been developed via a facile in situ photosynthesis route. The structural and optical properties of the as-prepared photocatalysts were systematically characterized by XRD, XPS, TEM, SEM, UV-Vis DRS and PL. Fascinatingly, the introduction of Au nanoparticles induced not only an enhanced photoabsorption in the visible region, but also the microstructural variation of BiOIO₃. The oxidative effect of HAuCl₄ resulted in the formation of Bi⁴⁺/Bi⁵⁺, which led to the increased specific surface area of the products. The photocatalysis and photoelectrochemical properties of the samples were investigated by monitoring the photodecomposition of Rhodamine B (RhB) and photocurrent generation under UV-visible light illumination. The results revealed that Au@BiOIO₃ presents drastically enhanced photoactivity compared with the pristine BiOIO₃. The highly improved photochemical properties are ascribed to the synergic contribution of the highly promoted generation and separation of charge carriers induced by the surface plasmon resonance (SPR) effect of Au particles, surface chemical state change, as well as the significantly high surface area that provides more reactive sites. These results are corroborated by the electrochemical impedance spectra (EIS), bode-phase spectra, PL spectra, active trapping and DMPO-assisted ESR measurements. This study not only provides evidence for the feasibility of metallic Au as a SPR co-catalyst of bismuth-based materials, but also furnishes new insights into the multiple effects for enhancing the photochemical properties.

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photoabsorption to longer wavelengths. Besides, local generation of hole–electron pairs in these semiconductors is induced by the resonant energy delivery of localized plasmonic oscillations in metallic Au NPs, reinforcing the photochemical properties. Given the advantages of Au nanoparticles, the solar-energy conversion efficiency of BiIOI\textsubscript{3} might be elevated by coupling Au NPs, and thus enhanced photochemical properties may be realized.

In this study, we report the successful fabrication of Au-decorated BiIOI\textsubscript{3} (Au@BiIOI\textsubscript{3}) heteronanostructures via a facile in situ photosynthesis route. Introduction of Au NPs not only results in significantly enhanced visible-light absorption, but also induces the microstructural alteration of BiIOI\textsubscript{3}, along with the increase in specific surface area. Both factors benefit the photochemical reaction. The photochemical properties of Au@BiIOI\textsubscript{3} are investigated in terms of Rhodamine B (RhB) decomposition and photocurrent generation under simulated solar light illumination. In comparison with pristine BiIOI\textsubscript{3}, Au@BiIOI\textsubscript{3} displays a significant enhancement in photo-reactivity, which is attributed to the cooperative effect of the boosted generation of charge carriers, efficient separation of electron–hole pairs, and increased surface area. To confirm the abovementioned results, the behavior of charge carriers is surveyed in detail and the underlying photocatalysis mechanism is also proposed.

2. Experimental section

2.1 Synthesis

All the reagents were of AR grade and were used without further purification. The Au@BiIOI\textsubscript{3} composites were prepared by the following processes: first, BiIOI\textsubscript{3} precursors were prepared by a hydrothermal method according to a previous study.\textsuperscript{14} Subsequently, BiIOI\textsubscript{3} was ultrasonically dispersed in HAuCl\textsubscript{4} solution and then exposed to UV light for 30 min to obtain Au@BiIOI\textsubscript{3}. The composites with HAuCl\textsubscript{4} molar proportions of 1%, 2% and 5% are denoted as 1%, 2% and 5% Au@BiIOI\textsubscript{3}, respectively. The schematic illustration of the formation of the Au@BiIOI\textsubscript{3} composite is shown in Scheme 1.

2.2 Characterization

The as-prepared samples were characterized by X-ray diffraction (XRD) with monochromatized Cu K\textalpha\ (λ = 1.5406 nm). The X-ray photoelectron spectroscopy (XPS) operating at 150 W irradiation of Al K\textbeta\ X-ray was employed to investigate the surface chemical properties of the samples. The scanning electron microscopy (SEM) was conducted on an S-4800 scanning electron microscope (Hitachi) to examine the general morphology of the photocatalysts. Transmission electron microscopy (TEM and HRTEM; H-800 Hitachi) was used to specify the microstructure of the samples. Specific surface area was measured by the BET nitrogen adsorption method with a 3020 Micromeritics instrument. UV-Vis diffuse reflectance spectra (DRS) were recorded on a Cary 5000 (America Varian) spectrophotometer. The photoluminescence (PL) emission spectra were obtained using a Hitachi F-4600 fluorescence spectrophotometer. Paramagnetic species were spin trapped by electron spin resonance (ESR) on a Bruker A300E spectrometer with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as trapping agent, and a quanta-Ray Nd:YAG laser system was used as the light source (λ = 420 nm).

2.3 Photodegradation test

The photocatalytic properties were studied by the degradation of Rhodamine B (RhB) in an aqueous solution (50 mL, 1 × 10\textsuperscript{-5} mol L\textsuperscript{-1}) under UV-visible light irradiation using a 500 W Xe lamp. To exclude the adsorption effect, an adsorption–desorption equilibrium between the photocatalyst (50 mg) and RhB was allowed to be achieved in darkness by stirring the abovementioned suspensions for 30 min. After the photoreaction, about 3 mL supernatants were sampled at 20 min interval and analyzed by recording the variation of the absorption spectra on a Cary 5000 UV-Vis spectrophotometer.

2.4 Active species trapping experiment

As scavengers of the hole (h\textsuperscript{+}), hydroxyl radical (‘OH) and superoxide radical (‘O\textsuperscript{2–}), respectively, disodium ethylenediaminetetraacetate (EDTA), isopropyl alcohol (IPA) and 1,4-benzoquinone (BQ) were added to the RhB solution to study the function of the active species. Generally, 50 mg photocatalyst with different scavengers (1 mmol) were dispersed in the RhB aqueous solution, and the following processes are similar to those in the abovementioned RhB photodegradation experiment.

2.5 Photoelectrochemical experiments

Photoelectrochemical measurements were performed on an electrochemical analyzer (CHI 660E, Shanghai) in a standard three-electrode system with a Pt wire as the counter electrode and a Hg/Hg\textsubscript{2}Cl\textsubscript{2} (in saturated KCl solution) electrode as the reference electrode. The photocatalysts coated onto the ITO glass served as the working electrode, and an aqueous solution of Na\textsubscript{2}SO\textsubscript{4} (0.1 M) was used as the electrolyte. Irradiation was conducted with a Xe arc lamp. The working electrodes were prepared via a dip-coating method: briefly, 15 mg of photocatalyst were suspended in 1 mL ethanol to obtain a slurry. Subsequently, the mixture was dip-coated on a 20 mm × 40 mm indium-tin oxide (ITO) glass. Then, the electrodes were exposed to air for 1 day to remove ethanol, and subsequently dried at 80 °C for 1 day.

![Scheme 1 Schematic illustration of the formation of the Au@BiIOI\textsubscript{3} composite.](Image)
3. Results and discussion

3.1 Phase structure

The XRD patterns of the pure BiOIO₃, 1% Au@BiOIO₃, 2% Au@BiOIO₃ and 5% Au@BiOIO₃ samples are shown in Fig. 1. All the samples show similar diffraction peaks that correspond to the orthorhombic BiOIO₃ (ICSD # 262019), and the strongest peak was assigned to the (121) plane of BiOIO₃. There were no obvious peaks of Au that can be indexed, which may be due to its low content. The XRD results demonstrate that the introduction of Au did not significantly change the crystalline phase and growth orientation of BiOIO₃.

3.2 XPS analysis

XPS was conducted to examine the surface chemical composition and oxidation state of pristine BiOIO₃ and 2% Au@BiOIO₃. Both survey spectra contain the peaks of I 3p, I 3d, O 1s, Bi 4s, Bi 4p, Bi 4d, Bi 4f and C 1s. Besides, an obvious Au 4f peak was observed in the spectra of Au@BiOIO₃ (Fig. 2a). Fig. 2b shows the high-resolution XPS of I 3d. A shift in the binding energy of I 3d occurred in Au@BiOIO₃, which indicates that the coordination environment of I⁵⁺ in Au@BiOIO₃ may have changed. The two samples show almost the same O 1s spectra (Fig. 2c), which are composed of the peaks of lattice O at 530.34 eV and hydroxyl groups (–OH) adsorbed on the surface (531.21 eV). The Bi 4f high-resolution XPS is displayed in Fig. 2d. The pristine BiOIO₃ shows the characteristic peaks of Bi³⁺4f₅/₂ at 164.01 eV and Bi³⁺4f₇/₂ at 158.70 eV. In contrast to pristine BiOIO₃, two sets of new peaks appeared at 164.84/159.58 eV and 165.61/160.27 eV, which correspond to the characteristic states of Bi⁴⁺ and Bi⁵⁺. This implies that some Bi³⁺ ions were oxidized to Bi⁴⁺ and Bi⁵⁺ due to the strong oxidation ability of HAuCl₄, consistent with the change in binding energy of I 3d. Fig. 2e shows the high-resolution Au XPS with binding energies of 87.49 and 83.83 eV, which can be assigned to the spin–orbit splitting of Au 4f and Au 0 states, respectively, confirming the existence of Au nanoparticles in the Au@BiOIO₃ composite.

3.3 Morphological investigation

The morphological properties of the samples were investigated by SEM. The pure BiOIO₃ consists of slabs or particles with sizes ranging from 500 nm to 2 μm, and their surfaces were very smooth (Fig. 3a and b). With the introduction of Au, it is obvious that Au nanoparticles were deposited on the surface of BiOIO₃, and the amount of Au particles assembled on BiOIO₃ gradually increased from 1% to 5% Au@BiOIO₃ (Fig. 3c–f). Interestingly, the surfaces of the BiOIO₃ crystals became rough after the deposition of metallic Au, which indicates that the surface structures of BiOIO₃ were destroyed because of the oxidative effect of HAuCl₄. This is in accordance with the presence of Bi⁴⁺/Bi⁵⁺ observed from the XPS results. Specific surface area measurements confirmed this result. The surface areas of BiOIO₃, 1% Au@BiOIO₃, 2% Au@BiOIO₃ and 5% Au@BiOIO₃ were measured to be 2.6, 2.9 and 3.4 and 3.6 m² g⁻¹, respectively, indicating that the surface area of BiOIO₃ increased after the oxidation reaction. This enhancement is considered to be favorable for photocatalytic process.

The TEM images of the pure BiOIO₃, 1%, 2% and 5% Au@BiOIO₃ samples are shown in Fig. 4. It can be seen from Fig. 4a that the pristine BiOIO₃ samples are composed of nanocrystals of good quality with neat edges. Fig. 4b–f show the morphologies of the 1%, 2% and 5% Au@BiOIO₃. After Au deposition, uniform black dots with an average size of 10 nm were homogeneously dispersed on the surface of BiOIO₃. With increasing HAuCl₄ concentration, more and more Au particles were assembled on BiOIO₃, indicating the successful synthesis of Au@BiOIO₃ samples. Moreover, a change in morphology of BiOIO₃ was also observed, confirming that BiOIO₃ was oxidized by HAuCl₄. These results correspond well to those of XPS and SEM.

3.4 Optical properties

Fig. 5 displays the DRS spectra of the pure BiOIO₃ and Au@BiOIO₃ samples. The bare BiOIO₃ crystals exhibit an absorption edge around 400 nm. For the as-obtained Au@BiOIO₃ composites, their photoabsorption in the visible region is greatly enhanced with the increased amounts of Au. Moreover, all the Au@BiOIO₃ samples show SPR peaks at approximately 556 nm as a result of the Au plasmonic oscillation. The band gap energies of BiOIO₃ were obtained by the following equation:25,36

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \(E_g\), \(\alpha\), \(h\), and \(\nu\) indicate band gap energy, absorbance, Planck’s constant and photon frequency, respectively. Because BiOIO₃ is reported to be an indirect-allowed semiconductor,12,14 the optical transitions for the BiOIO₃ are directly allowed, and its \(n\) value is 2. The band gap of BiOIO₃ was determined to be 3.05 eV (Fig. 5b).

3.5 Photocatalytic and photoelectrochemical properties

Fig. 6a displays the photocatalytic activities of the pure BiOIO₃ and Au@BiOIO₃ samples in the degradation of RhB on
illumination with UV-visible light. Pristine BiOIO$_3$ presents relatively poor photocatalytic activity, and about 60% of RhB was degraded within 60 min. All the Au@BiOIO$_3$ composites exhibit largely enhanced photocatalytic activities compared to the pure BiOIO$_3$, revealing the positive effect of Au nanoparticles in promoting photocatalytic activity. Although UV-visible light is the light source used in this study, the degradation efficiency of Au@BiOIO$_3$ is considerably higher than the literature data of similar photocatalysts.\textsuperscript{14,15} With an increase in the Au content from 1% to 5%, the photocatalytic activity of Au@BiOIO$_3$ first increases, reaching a maximum at 2% Au content, and then decreases with further increase in the Au content. This may be explained as follows: owing to the SPR effect of Au particles and the significantly high surface area providing more reactive sites, the photocatalytic activity of Au@BiOIO$_3$ for degrading RhB first increases with increasing Au content. However, excessive Au loading amounts may favor the formation of recombination centers of electrons and holes, reducing the photoreactivity. As depicted in Fig. 6a and c, almost 100% of RhB can be decomposed by 2% Au@BiOIO$_3$, with the absorption spectra vanishing after 60 min of illumination. Fig. 6b shows that the apparent rate constant $k$ for 2% Au@BiOIO$_3$ is as high as 4.3 times that of pristine BiOIO$_3$ (0.109 min$^{-1}$).

The photoelectrochemical properties of BiOIO$_3$ and Au@BiOIO$_3$ electrodes were disclosed by monitoring the transient photocurrent response.\textsuperscript{37} As shown in Fig. 6d, both BiOIO$_3$ and Au@BiOIO$_3$ present obvious current switches with good reproducibility via on–off cycles and immediate response once the light is on, demonstrating that the photoresponse is reversible and the electrodes are stable. In contrast to pristine BiOIO$_3$ with a photocurrent density of 2.03 $\mu$A, Au@BiOIO$_3$ presents an improved photoelectrochemical property, where the current response (4.66 $\mu$A) is about 2.3 times higher than that of BiOIO$_3$. The highly strengthened photocurrent intensity also bodes efficient separation of photo-induced electron–hole pairs.

### 3.6 Photocatalytic mechanism

Electrochemical impedance spectroscopy (EIS) was utilized to indicate the interfacial charge transfer efficiency.\textsuperscript{38,39} The EIS
Nyquist plots of the pure BiOIO$_3$ and 2% Au@BiOIO$_3$ samples are shown in Fig. 7a. The overall semicircle radius of the 2% Au@BiOIO$_3$ appears to be smaller compared with that of pure BiOIO$_3$, revealing that a lower interfacial resistance occurred in the charge transfer process of Au@BiOIO$_3$. This could be attributed to the SPR effect of Au, which greatly facilitates the charge transfer process and contributes to the enhanced photochemical properties. Moreover, compared with the pristine BiOIO$_3$, the shift of the characteristic frequency peak to a lower frequency was observed for the 2% Au@BiOIO$_3$ electrode, as shown in Fig. 7b. The peak shift from high frequency to low frequency indicates a more swift electron transport process, because the frequency ($f$) is closely related to the lifetime ($\tau$) of the injected electrons according to the equation: $\tau = 1/(2\pi f)$. The minimum inverse frequencies of Au@BiOIO$_3$ and BiOIO$_3$ were determined to be 1546 and 3016 Hz, respectively. The electron lifetime of the 2% Au@BiOIO$_3$ (103 $\mu$s) is estimated to be about 2 times higher than that of the pure BiOIO$_3$ (52.8 $\mu$s). The rapid charge transfer could effectively suppress the charge recombination and enhance the photoconversion efficiency.

To further understand the fate of photoexcited electrons and holes, PL emission spectra were used to investigate the separation efficiency of charge carriers. Fig. 8 shows the PL spectra of the as-prepared BiOIO$_3$ and Au@BiOIO$_3$ samples. They all present emission peaks between 400 and 500 nm, corresponding to the characteristic peaks of bismuth compounds. Compared with pure BiOIO$_3$, Au deposition results in obviously decreased emission intensities, suggesting that the SPR effect of Au plays an important role in hindering the charge recombination. This is consistent with the results of RhB degradation and photoelectrochemical measurements.

Because the photocatalytic mechanism is mainly determined by the types of reactive species, we used radical trapping experiments and ESR to detect the main active species produced in the photocatalytic process. As illustrated in Fig. 9a, the degradation efficiency of RhB is significantly affected by adding benzoquinone (BQ, 1 mM) as a scavenger of $\cdot$O$_2^-$, demonstrating that $\cdot$O$_2^-$ is the most crucial reactive species for degrading RhB. It appears that h$^+$ and $\cdot$OH does not play any part in RhB degradation, because the degradation efficiencies were not reduced by the addition of isopropyl alcohol (IPA, a scavenger of $\cdot$OH) and...
ethylenediaminetetraacetate (EDTA, a scavenger of h⁺). With the addition of EDTA to the degradation system, holes can be trapped; at the same time, it also leads to an efficient separation of electrons and holes. Because O₂⁻ radicals are the most crucial active species, the photocatalytic activity is supposed to be drastically promoted by the generation of O₂⁻ radicals. Nonetheless, as revealed by the results of the active species trapping experiments (Fig. 9a), the degradation rate of RhB is only slightly improved by adding EDTA, and the difference can be neglected. This observation may suggest that holes also participate in the degradation reaction, but the influence on the degradation rate is far smaller than that of O₂⁻. The DMPO assisted ESR spin-

![Fig. 4 TEM images of (a) BiOIO₃; (b) 1% Au@BiOIO₃; (c and d) 2% Au@BiOIO₃; and (e and f) 5% Au@BiOIO₃.](image)

![Fig. 5 (a) UV-Vis diffuse reflectance spectra of the pure BiOIO₃ and Au@BiOIO₃ and (b) band gap of BiOIO₃.](image)
trapping method was also utilized to capture the reactive species over BiOIO₃ and Au@BiOIO₃ under illumination of visible light, as shown in Fig. 9b. For BiOIO₃, no obvious signals were generated under visible light. However, on exposure to irradiation, Au@BiOIO₃ exhibited obvious signal peaks, which were the characteristic peaks of the DMPO-·O₂⁻ adducts. These results demonstrate that much more ·O₂⁻ as active species were generated in Au@BiOIO₃, contributing to its enhanced photocatalytic properties.

On the basis of the abovementioned experimental results, the tentative reaction mechanism of the highly enhanced photocatalysis and photoelectrochemical properties of Au@BiOIO₃ was postulated as follows (Scheme 2): our previous study demonstrated that the bottom of the CB of BiOIO₃ consists of O 2p, Bi 6p and I 5p orbitals, and the top of the VB is mainly composed of O 2p orbitals. On excitation with UV-Vis light,
only a few e\textsuperscript{−}–h\textsuperscript{+} pairs were generated over the pure BiOIO\textsubscript{3}, and thereby its as-exhibited photocatalytic activity was moderate. After the introduction of Au nanoparticles (NPs), the photocactivity of BiOIO\textsubscript{3} was greatly improved. First, the photo-generated electrons of Au metal NPs can be excited from the Fermi level (0.94 eV) to about \(-1.29\) eV by its characteristic absorption at 556 nm (\(-2.23\) eV), \textsuperscript{47} and then transferred to the CB of BiOIO\textsubscript{3} through Schottky energy potential. This process induces more electrons to produce abundant superoxide radicals (\(\cdot\)O\textsubscript{2}\textsuperscript{−}), which are beneficial for the enhanced photocatalysis activity. Second, the near-field resonant energy transfer, resulting from the SPR effect of Au NPs, can greatly boost the steady-state population of energetic charge carriers in adjacent BiOIO\textsubscript{3}, and simultaneously strengthen the electric field in the BiOIO\textsubscript{3} crystal, making charge separation more efficient.\textsuperscript{23,34}

Furthermore, the Au deposition process enables a largely increased specific surface area on BiOIO\textsubscript{3} and alters the surface chemical state by modifying the microstructure, which favors the formation of more reactive sites; this further propels the enhancement of photocatalysis and photoelectrochemical properties of BiOIO\textsubscript{3}.

### 4. Conclusion
In summary, we have deposited metallic Au particles on BiOIO\textsubscript{3} to fabricate heterostructured Au@BiOIO\textsubscript{3} hybrid photocatalysts by a simple \textit{in situ} UV-light reduction method. It is interesting to find that HAuCl\textsubscript{4} as a Au source not only provides the SPR of Au to enhance the photoabsorption in the visible region, but also leads to the enlarged specific surface area of the products by modifying the microstructure of BiOIO\textsubscript{3} due to the strong oxidative ability of HAuCl\textsubscript{4}, which was confirmed by the appearance of Bi\textsuperscript{4+}/Bi\textsuperscript{3+}. In contrast to the pristine BiOIO\textsubscript{3}, Au@BiOIO\textsubscript{3} exhibits significantly boosted photoreactivity pertaining to RhB degradation and photocurrent response. The results from the measurements of charge separation and transfer behavior revealed that the synergic contributions from the SPR effect induced efficient separation of electron–hole pairs, boosted the generation of charge carriers and increased surface area, and thus are responsible for highly promoted photocatalysis and photoelectrochemical properties. This study has furnished new perspectives on the \textit{in situ} construction of Au@semiconductor hybrid materials with multiple contributions to enhancing the photochemical properties.

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## Notes and references