Construction of 2D/0D/2D face-to-face contact g-C₃N₄@Au@Bi₄Ti₃O₁₂ heterojunction photocatalysts for promising dye degradation

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Abstract

Herein a new type of 2D/0D/2D face-to-face contact g-C₃N₄@Au@Bi₄Ti₃O₁₂ heterojunction photocatalysts have been developed. The ternary composite photocatalysts are constructed by coupling Bi₄Ti₃O₁₂ nanosheets with g-C₃N₄ nanosheets face-to-face and sandwiching Au nanoparticles between Bi₄Ti₃O₁₂ and g-C₃N₄ nanosheets. The as-prepared g-C₃N₄@Au@Bi₄Ti₃O₁₂ composite photocatalysts were systematically investigated by various characterization techniques including XRD, UV-vis DRS, FTIR, SEM, TEM and XPS. The degradation experiments were carried out by removing rhodamine B (RhB) from water under simulated sunlight. It is found that the g-C₃N₄@Au@Bi₄Ti₃O₁₂ composite photocatalysts exhibit much enhanced photodegradation performance when compared with bare Bi₄Ti₃O₁₂ and g-C₃N₄ nanosheets, and moreover they exhibit excellent photocatalytic stability in recycling dye degradation. The underlying photodegradation mechanism of the g-C₃N₄@Au@Bi₄Ti₃O₁₂ composite photocatalysts was systematically investigated and discussed.

1. Introduction

Water, being an important element of life, is getting polluted ever increasingly due to the generation of huge amount of wastewater annually from chemical industries. Organic dyes (e.g., rhodamine B (RhB)) are majorly included in the industrial effluent, which impose a potential threat to our health and survival due to their high water solubility, chemical stability, non-biodegradability and carcinogenicity. In recent years, semiconductor-based photocatalysis has gained increasing interest in water remediation [1–4]. This technology stands out due to its capability of utilizing solar radiation to decompose the harmful organic dyes. The sunlight-induced conduction band (CB) electrons (e⁻) and valence band (VB) holes (h⁺) in photocatalysts possess the reduction/oxidation capabilities are the basic reactive species, which take part in the direct or indirect redox reactions to cause the dye decomposition. Nevertheless, the photodegradation activities of most semiconductor photocatalysts are limited due to the easy recombination of photoexcited e⁻/h⁺ pairs. Efficient suppression of the photoexcited electron/hole recombination has become one of most important strategies to improve the photodegradation performances of semiconductors [5–11].

Noble metal and carbon nanomaterials, attracting extensive attention owing to their outstanding physical properties and broad application prospects [12–20], have been extensively employed to modify the photocatalysts in order to improve their photodegradation performances [21–26]. The main enhanced photocatalytic mechanism is that these nanomaterials can serve as good electron sinks to trap the photoproduced electrons, thus leading to the decreased combination of e⁻/h⁺ pairs. Furthermore, these nanomaterials can efficiently absorb and utilize visible light during the photocatalytic process benefiting from the photoluminescence up-conversion of carbon nanomaterials and localized surface plasmon resonance (LSPR) of noble metal nanoparticles [27–29]. Construction of semiconductor-semiconductor heterojunctions is another important avenue showing the capability to separate the photoexcited e⁻/h⁺ pairs [30–34]. The photoproduced carriers will transfer one semiconductor to another under the action of

the formed internal electric field at the heterojunction interface, thus resulting in the efficient e^-/h^+ separation. How to optimize the interface and realize good contact between two semiconductors is the key point facilitate the carrier transfer and separation.

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BTO) with bandgap energy of ~ 3.1 eV [35], crystallizing in a layer structure constructed by an alternating stack of perovskite-like $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ blocks and $(\text{Bi}_2\text{O}_2)^{2+}$ units, has received much recent attention as an important semiconductor photocatalyst for photodegradation of organic pollutants [36–41]. Due to its special layer structure, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ exhibits a high anisotropy of photocatalytic properties. In particular, the (010) facet is expected to have a high photocatalytic activity because the photoproducted electrons and hole are readily separated and migrate to the (010) facet driving by the polarization electric field (along the [010] direction) [42]. This was confirmed by the observation of extremely high photodegradation activity of two-dimensional (2D) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets with nearly 100% exposed (010) facet [35]. Graphite-like carbon nitride ($\text{g-C}_3\text{N}_4$, CN) is famously known to be a metal-free polymeric semiconductor, showing a promising visible-light-responsive photoactivity [38]. Due to its simple preparation and excellent thermal/chemical stability, $\text{g-C}_3\text{N}_4$ is interesting for the application in organic dye photodegradation. Moreover, $\text{g-C}_3\text{N}_4$ is bonded with abundant surface groups, implying that it is suitable for hybridizing with other photocatalysts to form heterojunctions [43–47].

Herein $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets have been coupled together face-to-face via a hydrothermal route. The derived 2D/2D $\text{g-C}_3\text{N}_4@\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunctions have a maximum contact area and are beneficial to the carrier transfer and separation. Furthermore, zero-dimensional (0D) Au nanoparticles have been sandwiched between $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets to construct 2D/0D/2D $\text{g-C}_3\text{N}_4@\text{Au}@\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunctions, where Au nanoparticles serve as the conductive bridges to facilitate the charge transfer between $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. RhB was used as the model dye to evaluate the photocatalysis degradation performances of the as-prepared $\text{g-C}_3\text{N}_4@\text{Au}@\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composite photocatalysts under irradiation of simulated sunlight. It is demonstrated that the photodecomposition performances of composite photocatalysts are much higher than those of bare $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets.

2. Experimental

2.1. Synthesis of $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets

All chemical reagents (analytical grade) used in the present experiments were directly supplied by chemical industries without further purification. A simple pyrolysis of melamine was used to fabricate $\text{g-C}_3\text{N}_4$ nanosheets. Typically, 5 g of melamine was put in a corundum boat, semi-closed with a cover, and then calcinated in a tube furnace (520 °C, 4 h). The calcinated product was ground and obtained as final $\text{g-C}_3\text{N}_4$ nanosheets.

A hydrothermal method as elaborated in the literature was employed to synthesize $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets [35]. A stoichiometric amount of bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 1.9402 g) was dissolved in 10% (v/v) dilute nitric acid solution. To the $\text{Bi}(\text{NO}_3)_3$ solution was then slowly added with titanium tetrachloride solution (0.5691 g TiCl_4 + 20 mL deionized water) and sodium hydroxide solution (4.8 g NaOH + 40 mL deionized water). The resultant mixture was loaded into a Teflon-lined autoclave and subjected to the hydrothermal reaction at 200 °C for 24 h. After that, the precipitate was gathered as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets, which were washed with deionized water/absolute ethanol and drying at 60 °C for 12 h.

2.2. Fabrication of CN@BTO composites

During the above hydrothermal preparation process of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets, stoichiometric g- C_3N_4 nanosheets were uniformly dispersed in the precursor mixture solution, which results in the preparation of CN@BTO composites. The hydrothermal reaction temperature/time and sample collection/washing/drying process were performed under the same conditions. By adding different amounts of g- C_3N_4 nanosheets in the precursor mixture solution, several CN@BTO composite samples with different g- C_3N_4 mass fractions were prepared (i.e., 5%CN@BTO, 10%CN@BTO and 15%CN@BTO).

2.3. Fabrication of CN@Au@BTO composites

The CN@Au@BTO composites were prepared using the following two processes. The first process was to decorate Au nanoparticles on the surface of g- C_3N_4 nanosheets via a photocatalytic reduction route. Stoichiometric ammonium oxalate (AO, 0.025 g) and g- C_3N_4 nanosheets (0.13 g) were put in deionized water (80 mL), followed by ultrasonic dispersion (30 min) and magnetic stirring (1 h). Subsequently, HAuCl_4 aqueous solution (0.029 mol L^{-1} , 1 mL) was added to the above suspension, and then irradiated by a 15 W low-pressure mercury lamp for 30 min. The product, i.e. CN@Au composite, was rinsed with deionized water/absolute ethanol and subjected to drying at 60 °C for 12 h. In the second step, the as-prepared CN@Au composite was loaded in the precursor mixture solution that was used for the preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets as described in 2.1 section. The subsequent hydrothermal treatment process followed the same procedure for the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ preparation. The composite derived according to this procedure was designated as 10%CN@4.2%Au@BTO, where g- C_3N_4 and Au occupy a mass fraction of ~ 10% and ~ 4.2%, respectively. Figure 1 depicts the preparation process of CN@BTO and CN@Au@BTO composite photocatalysts.

2.4. Sample characterization methods

X-ray powder diffraction (XRD) measurements were carried out by using a D8 Advance X-ray diffractometer ($\lambda_{\text{Cu-K}\alpha} = 0.15406 \text{ nm}$). A TU-1901 double beam spectrophotometer was applied for the analysis of ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS). Fourier transform infrared (FTIR) spectra were collected on a Spectrum Two FTIR spectrophotometer. A JSM-6701F field-emission scanning electron microscope was employed for the scanning electron microscopy (SEM) observations.

Transmission electron microscopy (TEM) investigations were carried out by means of a JEM-1200EX field-emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 multi-functional X-ray photoelectron spectrometer.

2.5. Photocatalytic testing process

Simulated-sunlight driven photodecomposition of RhB was used to evaluate the photoactivities of the as-prepared photocatalysts. The initial RhB concentration was $C_0 = 5 \text{ mg L}^{-1}$ and the photocatalyst dosage was $C_{\text{photocatalyst}} = 1000 \text{ mg L}^{-1}$. The photoreactor (capacity: 200 mL) was filled with 100 mL of RhB solution together with 100 mg of the photocatalyst. The adsorption experiment was performed by placing the photoreactor in the dark for 30 min, during which a magnetic stirring was applied. After that, turn on the light (a 200-W xenon lamp emitting simulated sunlight) to start the photocatalytic experiment. The change of the RhB concentration during the photocatalysis was determined by testing its absorbance at $\lambda_{\text{RhB}} = 554 \text{ nm}$ by using a UV-vis spectrophotometer. The photocatalyst was removed from the reaction solution by centrifugation testing the absorbance of the reaction solution. According to the initial concentration (C_0) and residual concentration (C_t) of RhB, the degradation percentage (η) of RhB was derived as: $\eta = (C_0 - C_t)/C_0 \times 100\%$.

3. Results And Discussion

XRD patterns of $\text{g-C}_3\text{N}_4$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $10\%\text{CN}@4.2\%\text{Au}@ \text{BTO}$ were recorded to determine their crystalline structures, as displayed in Fig. 2. On the XRD pattern of $\text{g-C}_3\text{N}_4$, two diffraction peaks are observed at 13.17° and 27.40° , which correspond to the in-plane structural packing motif of tri-s-triazine units (i.e., (100) facet) and the inter-layer stacking of conjugated aromatic system (i.e., (002) facet), respectively [47]. This diffraction feature suggests that $\text{g-C}_3\text{N}_4$ nanosheets are obtained. The diffraction peaks of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, matching well with the diffraction data of PDF#35-0795, imply the formation of pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ orthorhombic phase (cell: $0.545 \times 3.282 \times 0.541 \text{ nm}^3$). The XRD pattern of $10\%\text{CN}@4.2\%\text{Au}@ \text{BTO}$ is very similar to that of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, indicating no structural change of the orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the composite. The XRD pattern of the composite presents no diffraction peaks assignable to $\text{g-C}_3\text{N}_4$ nanosheets and Au nanoparticles, which is possibly due to the low diffraction intensities of $\text{g-C}_3\text{N}_4$ and low content of Au.

It is necessary to characterize the light-absorption characteristics of nanomaterials because they are highly related to their physical properties [48–50]. UV-vis DRS measurements were carried out to determine the optical absorption properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{g-C}_3\text{N}_4$, $10\%\text{CN}@ \text{BTO}$ and $10\%\text{CN}@4.2\%\text{Au}@ \text{BTO}$. As shown in Fig. 3(a), $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{g-C}_3\text{N}_4$ and $10\%\text{CN}@ \text{BTO}$ have a poor visible-light absorption in the wavelength region $\lambda > 450 \text{ nm}$. In contrast, the $10\%\text{CN}@4.2\%\text{Au}@ \text{BTO}$ composite with the introduction of Au nanoparticles manifests a relatively higher visible-light absorption, which is attributed to the strong light absorption of Au nanoparticles in the visible-light region. The absorption peak observed at around 550 nm for the $10\%\text{CN}@4.2\%\text{Au}@ \text{BTO}$ composite can be characterized as the

plasmon resonance peak of Au nanoparticles [35]. Figure 3(c) shows the apparent colors of the samples, further confirming their visible-light absorption properties. It is observed that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{g-C}_3\text{N}_4$ and 10%CN@BTO present a white or faint yellow color, implying a weak visible-light absorption of these samples. In contrast, a gray color is observed for 10%CN@4.2%Au@BTO, suggesting a relatively stronger visible-light absorption of the ternary composite photocatalyst. Figure 3(b) depicts the differential curves of UV-vis DRS spectra, from which the wavelength of absorption edge (λ_{abs}) can be derived [51]). The bandgap of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ is obtained as 3.13 and 2.83 eV, respectively. For the 10%CN@BTO and 10%CN@4.2%Au@BTO composites, the bandgap of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ undergoes a slight change possibly due to their interactions.

FTIR analysis was employed to reveal the possible presence of functional groups in the samples, as illustrated in Fig. 4. Figure 4(a) presents the FTIR spectrum of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, where the absorption peaks located at 571 and 472 cm^{-1} originate from the stretching vibration of Ti–O, and the peak at 825 cm^{-1} is ascribed to the Bi–O stretching vibration, which confirms the crystallization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure [35]. The peaks at 1096 and 1403 cm^{-1} could originate from the symmetric and anti-symmetric stretching vibrations of CO_3^{2-} groups introduced on the surface of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ during the hydrothermal synthesis process, respectively [52]. The absorption peak located at 1642 cm^{-1} is induced by the H–O bending vibration of water molecules [53]. On the FTIR spectrum of $\text{g-C}_3\text{N}_4$ (Fig. 4(b)), the characteristic absorption peaks of $\text{g-C}_3\text{N}_4$ nanosheets are observed at 807 cm^{-1} (breathing mode of the tri-s-triazine units), 1247/1324 cm^{-1} (stretching vibrations of C–NH–C bridges), and 1410–1640 cm^{-1} (C–N heterocycles skeletal vibrations of aromatic rings) [47]. For the 10%CN@BTO and 10%CN@4.2%Au@BTO composites, the absorption peaks of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ are detected on their FTIR spectra (Fig. 4(c) and (d)), indicating that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ are included in the composites without structural change. No characteristic peaks from Au nanoparticles are detected for 10%CN@4.2%Au@BTO possible due to infrared inactivity of Au nanoparticles. For all the samples, the presence of CO_3^{2-} groups and water molecules on their surface is confirmed by the observation of the infrared-absorption peaks 1403 and 1642 cm^{-1} .

SEM observation was carried out to reveal the morphologies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and 10%CN@4.2%Au@BTO. Figure 5(a) shows the SEM image of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, implying that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is crystallized into nanosheets with thickness of 45–80 nm (average thickness: ~60 nm). The surface of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets appears smooth and clean. Figure 5(b) shows the SEM image of 10%CN@4.2%Au@BTO, demonstrating the formation of composite nanosheets with thickness of 150–210 nm (average thickness: ~170 nm). Compared to that of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets, the thickness of the composite nanosheets becomes much increased, suggesting that they are constructed by $\text{g-C}_3\text{N}_4$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets with face-to-face contact. Moreover, the surface of the composite nanosheets becomes rough possibly due to the decoration of Au nanoparticles.

To reveal the microstructure of the 10%CN@4.2%Au@BTO composite, TEM investigation was further performed. Figure 6(a) and (b) show the TEM images of the composite, demonstrating that g-C₃N₄ nanosheets and Bi₄Ti₃O₁₂ nanosheets are coupled face-to-face and Au nanoparticles are possibly sandwiched between g-C₃N₄ and Bi₄Ti₃O₁₂ nanosheets. On the selected area electron diffraction (SAED) pattern (Fig. 6(c)), one can see that the diffraction spots are periodically arranged and can be indexed into the [010] zone axis of Bi₄Ti₃O₁₂ orthorhombic phase. This implies that Bi₄Ti₃O₁₂ nanosheets are featured by a single-crystalline nature with highly exposed (010) facet. No diffraction spots or rings from g-C₃N₄ nanosheets and Au nanoparticles are detected on the SAED pattern, which is possibly due to the amorphous feature of g-C₃N₄ nanosheets and absence of Au nanoparticles in the selected area. Figure 6(d) and (e) illustrate the high-resolution TEM (HRTEM) images of the composite, further elucidating the construction of 2D-g-C₃N₄@0D-Au@2D-Bi₄Ti₃O₁₂ heterojunctions with face-to-face contact. The clear lattice fringes with $2d = 0.384$ nm, corresponding to the (202) facet of the orthorhombic Bi₄Ti₃O₁₂, confirm the single-crystalline nature of Bi₄Ti₃O₁₂ nanosheets with highly exposed (010) facet.

Energy-dispersive X-ray spectroscopy (EDS) spectrum was collected from the 10%CN@4.2%Au@BTO composite (Fig. 7(a)), which clearly shows the inclusion of C/N/O/Bi/Ti/O/Au species in the composite. Except for the Cu signals, possibly induced by the TEM microgrid holder [54], no other impurity elements are detected on the EDS spectrum. Figure 7(b) displays the dark-field scanning TEM (DF-STEM) image recorded from 10%CN@4.2%Au@BTO, and the corresponding EDS elemental mapping images of the area are presented in Fig. 7(c)–(h). It is obvious that the composite nanosheets manifest the uniform distribution of the C/N/O/Bi/Ti/O elements, whereas Au element is dispersedly decorated on the composite nanosheets. The elemental mapping analysis gives support to the construction of 2D/0D/2D face-to-face contact g-C₃N₄@Au@Bi₄Ti₃O₁₂ heterojunctions.

The 10%CN@4.2%Au@BTO composite was analyzed by XPS to reveal the chemical states of the elements Bi, Ti, O, C, N and Au in the composite, as shown in Fig. 8. Two peaks separately with binding energies of 159.1 (Bi-4f_{7/2}) and 164.4 eV (Bi-4f_{5/2}) are detected from the XPS spectrum of Bi-4f core level (Fig. 8(a)), implying the presence of Bi³⁺ oxidation state [35, 55]. By deconvoluting the Ti-2p XPS core-level spectrum (Fig. 8(b)), three peaks at 458.1, 463.6 and 466.0 eV are recognized. The former two peaks correspond to the binding energies of Ti⁴⁺-2p_{3/2} and Ti⁴⁺-2p_{1/2}, respectively, whereas the third peak can be ascribed to Bi-4d_{3/2} binding energy [35, 56]. The O-1 s XPS spectrum (Fig. 8(c)) reveals two kinds of oxygen species, i.e., the crystal lattice oxygen of Bi₄Ti₃O₁₂ (529.9 eV) and chemisorbed oxygen species on the sample (531.9 eV) [35, 57, 58]. The C-1 s XPS spectrum (Fig. 8(d)) presents three peaks located at 284.8, 288.0 and 282.6 eV, which are characterized as the carbon existing in the instrument, sp²-hybridized carbon in g-C₃N₄, and metal carbides, respectively [47]. On the N-1 s XPS spectrum (Fig. 8(e)), the binding energy peak at 397.5 eV is ascribed to sp²-hybridized nitrogen (C = N – C) resulting from g-C₃N₄ [47]. The strong peak at 392.2 eV could be ascribed to the formation of metal nitrides. The observed binding energies at 84.1 (Au-4f_{7/2}) and 87.8 eV (Au-4f_{5/2}) on the Au-4f XPS spectrum (Fig. 8(f)) are indicative of the existence of metallic Au nanoparticles in the composite [35].

Figure 9(a) shows the time-dependent degradation curves of RhB photocatalyzed by $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{g-C}_3\text{N}_4$, CN@BTO composites and $10\%\text{CN@4.2\%Au@BTO}$ composite. Before photocatalysis, the dye adsorption onto the samples is determined to be 5.4%–9.9%. The blank (photolysis) experiment shows that RhB exhibits good stability under simulated sunlight irradiation in the absence of photocatalysts [59]. Under irradiation for 120 min, bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ photocatalyze 71.0% and 44.8% degradation of RhB, respectively. When $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets and $\text{g-C}_3\text{N}_4$ nanosheets are coupled face-to-face together, the constructed CN@BTO composite nanosheets exhibit improved photodecomposition performances. The $10\%\text{CN@BTO}$ composite with a $\text{g-C}_3\text{N}_4$ mass fraction of 10% is demonstrated to be the optimal composite photocatalyst, over which the degradation percentage of RhB reaches 85.3% after 120 min photoreaction. Furthermore, by sandwiching Au nanoparticles between $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ nanosheets, a more promising ternary $10\%\text{CN@4.2\%Au@BTO}$ composite photocatalyst is achieved, which causes 94.4% of RhB to be photodegraded. As organic dyes are generally “tricky” in their photocatalytic degradation process, the exact photodegradation mechanism needs to be further investigated [60].

The photodegradation performances of the samples are further elucidated from the kinetic viewpoint. As displayed in Fig. 9(b), the degradation kinetic plots of RhB conform perfectly to the pseudo-first-order kinetic equation $\ln(C_t/C_0) = -k_{\text{app}}t$ [61] due to their good linear behavior with R^2 larger than 0.99. The apparent first-order reaction rate constant k_{app} can be employed for the quantitative comparison between the photodegradation performances of the photocatalysts. According to the values of k_{app} as displayed in Fig. 9(b), it is concluded that the $10\%\text{CN@BTO}$ composite possesses a photodegradation activity ~ 1.8 and ~ 3.9 times over that of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$, respectively; whereas the photodegradation activity of the ternary $10\%\text{CN@4.2\%Au@BTO}$ is increased by 2.3 and 5.0 times compared with that of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$, respectively.

To examine the reusability of $10\%\text{CN@4.2\%Au@BTO}$ for photocatalytic degradation of RhB, the photocatalyst was collected by centrifugation after the photodegradation experiment and recovered with deionized water rinsing. The next photodegradation experiment was carried out under the same procedure by loading the recovered $10\%\text{CN@4.2\%Au@BTO}$ in fresh RhB solution. To balance the minor loss of the photocatalyst after each run, fresh photocatalyst was added. As seen in Fig. 9(c), the photodegradation percentage of RhB within 120 min reaction slightly decreases from 94.4% at the 1st cycle to 90.1% at the 4th cycle, implying the degradation percentage of RhB undergoes only a minor loss (3.3%). The recycling photocatalytic experiment clearly demonstrates an excellent stability of the $10\%\text{CN@4.2\%Au@BTO}$ composite photocatalyst for repeatedly degrading organic dyes.

In the $10\%\text{CN@4.2\%Au@BTO}$ photodegradation system, the active species including hydroxyl ($\cdot\text{OH}$) radicals, superoxide ($\cdot\text{O}_2^-$) radicals and photoexcited holes were determined by active species trapping experiments as described in the literature [62]. Ethanol (scavenger for $\cdot\text{OH}$, 5 mL), benzoquinone (BQ, scavenger for $\cdot\text{O}_2^-$, 0.1 mmol) and ammonium oxalate (AO, scavenger for h^+ , 0.1 mmol) were separately added in the photoreaction solution to examine their effects on the RhB degradation. As shown in Fig. 9(d), the addition of ethanol has a minor effect on the photodegradation of RhB, suggesting a very

small role of $\cdot\text{OH}$ in the photodegradation process. The dye degradation is obviously inhibited by the introduction of BQ or AO, confirming that $\cdot\text{O}_2^-$ and h^+ are the main reactive species causing the dye degradation. In particular, the photoexcited h^+ plays the largest role in the photocatalysis due to the highest suppression efficiency by AO. To quantitatively determine the role of the reactive species in the photodegradation process, the trapping experiments using more quenchers are necessary [63].

It is noted that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an intrinsic n-type semiconductor ($E_g = 3.13$ eV) and g- C_3N_4 behaves as an intrinsic p-type semiconductor ($E_g = 2.83$ eV) [35]. The CB/VB potentials of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and g- C_3N_4 are theoretically estimated, by using the method elaborated in the literature [64, 65], to be $-0.19/+2.94$ and $-1.19/+1.64$ V vs NHE (normal hydrogen electrode), respectively, as schematically depicted in Fig. 10. When $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets, Au nanoparticles and g- C_3N_4 nanosheets are coupled to form 2D/0D/2D face-to-face contact CN@Au@BTO heterojunctions, electrons will diffuse from n-type $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to p-type g- C_3N_4 , and conversely, holes will diffuse from p-type g- C_3N_4 to n-type $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The role of Au nanoparticles sandwiched between $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and g- C_3N_4 nanosheets is to act as the “bridge” to facilitate the transfer of photoexcited carriers. This carrier diffusion process leads to the creation of negative charge centers at the g- C_3N_4 interface and positive charge centers at the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ interface, and simultaneous formation of internal electric field (pointing from $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to g- C_3N_4). The created internal electric field will prevent the continuous diffusion of the charge carriers, and finally a thermal equilibrium state is reached in the CN@Au@BTO heterojunctions. Under irradiated from simulated sunlight, both $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and g- C_3N_4 are photoexcited to generate CB electrons and VB holes. The internal electric field drives the electron migration from the g- C_3N_4 CB to the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ CB and conversely the hole migration from the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ VB to the g- C_3N_4 VB by using Au nanoparticles as the “bridge”. Consequently it results in the efficient separation of the photoproduced electrons and holes, which is confirmed by the photocurrent and photoelectrochemical impedance spectroscopy (EIS) analyses (Fig. S1 and S2). As a result, more electrons accumulated in the CB of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and holes accumulated in the VB of g- C_3N_4 are expected to participate in the photoreactions. This is the major factor resulting in the enhanced photocatalysis capacities of the ternary CN@Au@BTO heterojunction composite photocatalysts. Moreover, other secondary factors could also cause the dye degradation. For example, the LSPR of Au nanoparticles could cause the local electromagnetic field enhancement and thus stimulate the production of additional electrons/holes in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and g- C_3N_4 , and the LSPR-induced electrons in Au nanoparticles could also take part in the photoreactions.

As the main reactive species confirmed in the CN@Au@BTO photocatalytic system, $\cdot\text{O}_2^-$ radicals can be thermodynamically generated via the reaction between the CB electrons in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with adsorbed O_2 species since the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ CB potential (-0.19 V vs NHE) is negative to the $\text{O}_2/\cdot\text{O}_2^-$ redox potential (-0.13 V vs NHE [66]). From the thermodynamic viewpoint, the holes in the g- C_3N_4 VB cannot combine with OH^- or H_2O species to form $\cdot\text{OH}$ radicals, because the g- C_3N_4 VB potential ($+1.64$ V vs NHE) is not sufficiently positive when compared with $E^0(\text{OH}^-/\cdot\text{OH}) = +1.99$ V and $E^0(\text{H}_2\text{O}/\cdot\text{OH}) = +2.38$ V vs NHE [66].

Direct oxidation by the photoexcited h^+ is suggested to be another important mechanism causing the dye degradation, which agrees with the active species trapping experiment results.

Conclusions

By coupling $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ nanosheets face-to-face and sandwiching Au nanoparticles between them, 2D/0D/2D face-to-face contact $\text{g-C}_3\text{N}_4@\text{Au}@\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction photocatalysts have been prepared. Photocatalytic experiments suggest a good activity of the as-prepared ternary composite photocatalysts for photocatalytically degrading RhB under simulated sunlight irradiation. At 120 min of photoreaction, the 10%CN@4.2%Au@BTO composite photocatalyst is demonstrated to photocatalyze 94.4% degradation of RhB. Its photodegradation activity is determined by the degradation kinetic analysis to be about 2.3 and 5.0 times larger than that of bare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ nanosheets, respectively. The enhanced photodegradation mechanism of the ternary composite photocatalysts is dominantly attributed to the photoexcited electron/hole transfer between $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ nanosheets and efficient spatial separation of the electron/hole pairs. The role of Au nanoparticles sandwiched between $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{g-C}_3\text{N}_4$ nanosheets is to act as the “bridge” to facilitate the carrier transfer.

Abbreviations

RhB: rhodamine B; CB: conduction band; VB: valence band; e^- : electrons; h^+ : holes; LSPR: localized surface plasmon resonance; BTO: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$; 2D: two-dimensional; CN: $\text{g-C}_3\text{N}_4$; XRD: X-ray powder diffraction; u UV-vis DRS: Ultraviolet-visible diffuse reflectance spectroscopy; FTIR: Fourier transform infrared; SEM: scanning electron microscopy; TEM: Transmission electron microscopy; XPS: X-ray photoelectron spectroscopy; SAED: selected area electron diffraction; HRTEM: high-resolution scanning electron microscopy; EDS: Energy-dispersive X-ray spectroscopy; DF-STEM: dark-field scanning transmission electron microscopy; $\bullet\text{OH}$: hydroxyl; $\bullet\text{O}_2^-$: superoxide; BQ: benzoquinone; AO: ammonium oxalate

Declarations

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Figures

Figure 1

Schematic illustration of the preparation process of CN@BTO and CN@Au@BTO composite photocatalysts.

Figure 2

XRD patterns of g-C₃N₄, Bi₄Ti₃O₁₂ and 10%CN@4.2%Au@BTO.

Figure 3

UV-vis DRS spectra (a), differential curves of the DRS spectra (b) and apparent colors (c) of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{g-C}_3\text{N}_4$, 10%CN@BTO and 10%CN@4.2%Au@BTO.

Figure 4

FTIR spectra of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (a), $\text{g-C}_3\text{N}_4$ (b), 10%CN@BTO (c) and 10%CN@4.2%Au@BTO (d).

Figure 5

SEM images of (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and (b) $10\%\text{CN}@4.2\%\text{Au}@\text{BTO}$.

Figure 6

TEM images (a,b), SAED pattern (c) and HRTEM images (d,e) of $10\%\text{CN}@4.2\%\text{Au}@\text{BTO}$.

Figure 7

EDS spectrum (a), DF-STEM image (b) and EDS elemental mapping images (c–h) of 10%CN@4.2%Au@BTO.

Figure 8

High-resolution XPS spectra of (a) Bi-4f, (b) Ti-2p, (c) O-1s, (d) C-1s, (e) N-1s and (f) Au-4f of 10%CN@4.2%Au@BTO.

Figure 9

(a) Photodegradation plots of RhB photocatalyzed by all the samples. (b) RhB degradation kinetic plots. (c) Photodegradation percentage of RhB over repeatedly used 10%CN@4.2%Au@BTO. (d) Effects of ethanol, BQ and AO on the RhB degradation percentage over 10%CN@4.2%Au@BTO.

Figure 10

Schematic illustration of the photocatalytic mechanism of the $\text{g-C}_3\text{N}_4@\text{Au}@\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction photocatalysts.

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