Integrating Plasmonic Au Nanorods with Dendritic Like α -Bi₂O₃/Bi₂O₂CO₃ Heterostructures for Superior Visible-light-driven Photocatalysis

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Abstract

To explore the relationship between semiconductor structure and plasmonic noble metal nanoparticles (NPs) property is crucial for developing highly efficient visible light driven photocatalyst. Here, dendritic $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ biphasic heterostructures were first synthesized by a facile and low-cost phase transformation method. Then, plasmonic Au NPs (including Au nanospheres (NSs, ~ 30 nm) and Au nanorods (NRs, ~ 20 , ~ 30 , and ~ 35 nm) were loaded onto the $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure. The results revealed that these $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures exhibited much higher visible-light photocatalytic activities than $\alpha\text{-Bi}_2\text{O}_3$ for dye degradation. More importantly, compared to plain $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures, loading of Au NSs brought ~ 4 times increase in activity and Au NRs 5-11 times depending on nanorods size. The significant boosting of activity is attributed to the large enhancement of charge separation by the formation of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ interface and more production of $\bullet\text{OH}$ radicals by Au NSs or Au NRs. The surface plasmon resonance (SPR) absorption of these gold NPs on the $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures could also have significant contribution to the activities due to their strong plasmonic near-fields. This work demonstrates that tailoring the semiconductor substrate structure and the plasmonic noble metal NPs properties should constitute a promising strategy for the design efficient solar energy driven photocatalytic materials.

Keywords: $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure; Au nanospheres and nanorods; Surface plasmon resonance; Photocatalysis; Visible light

1. Introduction

Photocatalysis is an environmentally friendly and promising technology in

environmental purification and converting solar energy into chemical energy ^[1-10]. Noble metal elements play an important role in enhancing photocatalytic performance. For example, noble metal oxides or sulphides (RuO_2 ^[11], IrO_2 ^[12], PdS ^[13]) can act as cocatalyst ^[14] to exert distinct synergistic effect in enhancing photocatalytic activity for water splitting. Of particular interest is the application of noble metal nanoparticles (NPs) to reduce the photo-generated e^-/h^+ recombination rate and thus enhance photocatalytic activity. This is owing to the better charge separation, i.e. the photo-generated electrons readily accumulate on the metal component, while holes remain on the photocatalyst surface ^[15-17].

More recently, noble metal NPs plasmon-induced photocatalysis has been gaining significant attention due to its high throughput and low excitation-energy requirements ^[18,19]. The major drawback of the widely used TiO_2 photocatalyst is its large band gap (~ 3.2 eV) which limits its optical absorption within the UV light region (2-4% of the entire solar spectrum). However, in plasmon-induced photocatalysis, noble metal NPs (e.g., Au, Ag) can absorb visible light *via* surface plasmon resonance (SPR). The plasmon-excited electrons in the noble metal NPs can be transferred to the conduction band of adjacent semiconductor ^[20,21] and the photogenerated charge carriers are thus efficiently separated, giving rise to enhanced photocatalytic activity ^[22]. Moreover, it was found that SPR can create intense local electromagnetic fields which in turn enhance sub-bandgap absorption in TiO_2 and thus increase the photocatalytic activity in the visible range ^[23]. The desirable plasmonic properties of noble metal NPs have promoted the concept of assembling plasmonic noble metal NPs together with certain semiconductors that can offer relatively high surface area as well as active sites to produce visible light responsive composite photocatalysts. In these composite materials, noble metal NPs and the substrates work in a cooperative way to enhance the photocatalytic activity.

At present, gold (Au) NPs have been attracting much attention because they can strongly

interact with light in the visible and near-infrared region due to their extraordinary SPR properties and also because of their remarkable photostability^[24-34]. The plasmon-induced photocatalytic performance of Au is strongly related to the properties of Au NPs (particle size, morphology, etc) and substrates (semiconductor type, crystal phase, crystallinity, morphology, etc) and the interactions between Au NPs and substrates. For example, Subramanian et al^[35] investigated the size-dependent catalytic activity of Au NPs in the TiO₂/Au composite and found that the size-dependent shift in the apparent Fermi level of the TiO₂-Au composite (20 mV for 8 nm diameter, 40 mV for 5 nm and 60 mV for 3 nm Au NPs) shows the ability of Au NPs to influence the energetics by improving the photoinduced charge separation. Seh et al^[36] reported that Janus Au-TiO₂ nanostructures with large Au NPs (50 nm) showed highly efficient visible-light hydrogen generation due to their strong localization of plasmonic near-fields close to the Au-TiO₂ interface. Moreover, Liu et al^[37] found that depositing Au NPs onto TiO₂ nanoflakes showed high efficiency and ultrastability for the degradation of the azo dye brilliant red X-3B, and the ultrafine metal particle size and strong metal-support interaction were considered as the key factors for the overall photocatalytic activity. With respect to the influence of substrate crystal phase, the photocatalytic production of H₂ over Au/TiO₂ anatase was found to be around two orders of magnitude higher than that recorded for Au/TiO₂ rutile^[38]. More interestingly, Tsukamoto et al^[39] observed that Au particles located at the interface of anatase/rutile TiO₂ particles could behave as the active sites for aerobic photocatalytic oxidation *via* plasmon activation of the Au particles by visible light followed by consecutive electron transfer in the Au/rutile/anatase contact sites. Formation of interface or heterojunction between two semiconductors is an effective strategy in enhancing the separation of photogenerated electron-hole pairs^[40]. For example, the formation of phase junction between the surfaces of anatase and rutile NPs could greatly enhance the

photocatalytic activity for H₂ production ^[41]. The above results indicate that design and fabrication of Au NPs/semiconductor heterostructures hold promise as an effective strategy to develop highly efficient visible-light-driven photocatalysts.

In this work, dendritic α -Bi₂O₃/Bi₂O₂CO₃ heterostructures are first successfully prepared *via* a phase transformation method. Then, large plasmonic Au NPs prepared by wet chemistry methods, including Au nanospheres (NSs, 30 ± 3 nm) and single crystal Au nanorods (NRs, 20 ± 4, 30 ± 5, and 35 ± 4 nm) were loaded onto α -Bi₂O₃/Bi₂O₂CO₃ heterostructures. The as-prepared Au/ α -Bi₂O₃/Bi₂O₂CO₃ hybrid nanostructures possess interesting optical properties and highly efficient photocatalytic performance in degradation of dye under visible light irradiation. In comparison to the previously reported Au plasmonic photocatalysts, our Au/ α -Bi₂O₃/Bi₂O₂CO₃ hybrid nanostructures are superior in three aspects for plasmon-enhanced photocatalytic reactions: (1) the substrate is a unique α -Bi₂O₃/Bi₂O₂CO₃ heterostructure prepared by a facile, low-cost and one-step method. (2) Au NPs have uniform size and morphology, which benefits the understanding of the effect of Au NPs property on plasmon-enhanced performance. (3) Intimate integration of plasmonic NPs and the light-harvesting semiconductors could be effective in improving the photocatalytic performance, offering the potential of studying a wide variety of plasmonic photocatalysts with heterostructures.

2. Experimental

2.1. Preparation of Catalysts

Synthesis of dendritic like α -Bi₂O₃/Bi₂O₂CO₃ heterostructure. All chemicals were purchased from Sigma-Aldrich. 5 mmol Bi(NO₃)₃·5H₂O was dissolved in a dilute (1 M) HNO₃ solution, and then 3.75 mmol sodium citrate (Na₃C₆H₅O₇) was added to the above solution. The mixture was stirred for ~10 min until a clear solution was formed. Finally, the

pH value of the solution was adjusted to 4 using 2.0 M NaOH under stirring. The formed white-colored precursor was transferred into a Teflon-lined stainless steel autoclave and heated to 180 °C and maintained at this temperature (total time 24 h). The gray product was isolated by centrifugation, washed with distilled water and absolute ethanol for several times, then dried in vacuum at 90 °C for 5 h to give rise to Bi₂O₂CO₃ nanosquares. In air atmosphere, the as-prepared Bi₂O₂CO₃ was placed a muffle furnace at 350 °C and calcined for 10 or 20 min, then taken out immediately, which gave rise to biphasic α -Bi₂O₃/Bi₂O₂CO₃ heterostructures.

Synthesis of Au nanospheres(NSs) (~ 30 nm) and nanorods (NRs) (~ 20 nm, ~ 30 nm, ~ 35 nm). This method is similar to our previous report ^[42]. In this procedure, there are two primary steps. The first step is to prepare Au seeds. 364 mg cetyltrimethylammonium bromide (CTAB) and 1 mg HAuCl₄•3H₂O was dissolved in 10 mL nanopure water in a tri-neck 25 mL round bottom flask. After 10 min, 0.6 mL (10 mM) NaBH₄ was added to the flask under vigorous magnetic stirring. The as-obtained Au seeds were used in the growth of nanorods. The second step is to prepare Au nanorods. 364 mg CTAB, 2 mg HAuCl₄•3H₂O and different amounts of 4 mM AgNO₃ solution (10 μ L, 20 μ L, 50 μ L, 100 μ L) were mixed in 10 mL nanopure water in a tri-neck 25 mL round bottom flask. After stirring 10 min, 70 μ L (78.8 mM) ascorbic acid was added to the flask. The flask was immersed in a warm water bath at 27-30 °C, and 12 μ L of Au seed was added and the reaction was allowed to proceed for 1 h. Finally, the excess CTAB was separated by centrifugation and one obtained Au NSs and NRs with different sizes.

Synthesis of Au loaded α -Bi₂O₃/Bi₂O₂CO₃ heterostructure. Au nanocrystals were loaded onto α -Bi₂O₃/Bi₂O₂CO₃ by the impregnation method. Typically, 100 mg α -Bi₂O₃/Bi₂O₂CO₃ powders were impregnated by a Au NPs solution. After stirring for 24 h at room temperature, Au loaded α -Bi₂O₃/ Bi₂O₂CO₃ powders were collected by centrifugation and

dried at 120 °C in a vacuum oven. The final mass content of Au over α -Bi₂O₃/Bi₂O₂CO₃ is 0.85-0.90 % determined by XPS ESCALAB 250. No silver was detected.

2.2. Characterization of Catalysts

The thermogravimetric analysis (TGA) was performed with Seiko instruments TGA/SDTA 6300 at a heating rate of 10 ° C min⁻¹ from room temperature to 700 ° C under air flow. Powder X-ray diffraction data were recorded on a X' Pert PRO X-ray diffractometer at 40 kV and 40 mA for monochromatized Cu K_α (λ =1.5418 Å) radiation. The morphology of the samples was analyzed by scanning electron microscopy (SEM) on a LEO 1450VP scanning electron microscope. Transmission electron microscopy (TEM) image was recorded on a Tecnai 20 FEG microscope. The valence states of elements were analyzed by XPS using a thermo scientific ESCALAB 250 system with a monochromatic Al K_α source and a charge neutralizer. The UV-vis diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (UV-2550, Shimadzu). The absorption spectra were referenced to BaSO₄. The nitrogen adsorption-desorption isotherm was measured using a Micromeritics ASAP 2020 physisorption analyzer. The photocurrent measurement was carried out by using a standard three-electrode system with the help of CHI660D electrochemical workstation. Graphite electrode, standard calomel electrode and the as-prepared samples played a role of counter electrode, reference electrode, and working electrode, respectively. The electrolyte solution was 0.1 mol/L sodium sulfate solution. 0.01g catalyst was dispersed into 0.4 ml 0.05 wt% Nafion ethanol solution with sonication for 30min, then 20 μL slurry was dropped on fluorine-tin oxide (FTO) glass substrates to make working electrode. The light source was simulative solar light (xenon lamp, perfect light PLS-SXE300, Beijing). The light intensity is about 100 μw/ cm².

2.3. Catalytic Performance

The photocatalytic performance of the prepared samples was evaluated by measuring the degradation of methyl orange under visible light irradiation. The light source is the same as literature [8]. A 150 Watt quartz halogen lamp (Dolan jenner Fiber-Lite MI-150 illuminator) with a cutoff filter solution jacket (HCl aqueous solution of CuSO_4 (0.5 M) and K_2CrO_4 (0.002 M)), which cuts off wavelengths shorter than 400 nm and longer than 660 nm was used as the light source. The distance from the light source to reaction solution is around 10 cm. The light intensity is around $70 \mu\text{W}/\text{cm}^2$. 0.05 g photocatalyst was suspended in 100 mL aqueous solution of methyl orange with the concentration of $C_0 = 0.020 \text{ g/L}$. Prior to light illumination, the suspension was magnetically stirred for 40 min in the dark for attaining adsorption/desorption equilibrium. The suspension was vigorously stirred during the photocatalytic reaction process. The reaction mixture was sampled at given time intervals during light illumination. After centrifugation, the dye or phenol concentration was measured on a UV-Vis spectrophotometer (Agilent, HP8453). The method of active species trapping experiment is the same as photoactivity tests.

2.4. Radicals Trapping

In photoactivity tests for $\bullet\text{OH}$ generation, coumarin (10 mM in a 10 mM FeCl_3 solution) was used as a chemical trap of $\bullet\text{OH}$ radicals because coumarin readily reacts with $\bullet\text{OH}$ to form a highly fluorescent product, 7-hydroxycoumarin (7HC). The experimental procedure was similar to the measurement of photocatalytic activity. The fluorescence emission intensity of 7-hydroxycoumarin was measured at 460 nm under the excitation at 332 nm using a Fluorolog spectrofluorometer (HORIBA, JobinYvon) after centrifugation.

3. Results and Discussions

3.1. Catalyst Characterization

3.1.1. TG

The α - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures were prepared by a calcination method *via* the partial phase transformation of $\text{Bi}_2\text{O}_2\text{CO}_3$. $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosquares were first synthesized under hydrothermal conditions. TGA measurements were carried out to determine the temperature for phase transformation of $\text{Bi}_2\text{O}_2\text{CO}_3$ during the temperature increase. Fig.1 (a) shows that there are two weight loss steps. The first weight loss of 1.46%, from 216 to 300 °C, could be caused by dehydration. From 297 to 390 °C, $\text{Bi}_2\text{O}_2\text{CO}_3$ phase began to transform to α - Bi_2O_3 , which caused the second weight loss of 8.26%, corresponding to the transformation reaction: $\text{Bi}_2\text{O}_2\text{CO}_3 \rightarrow \alpha\text{-Bi}_2\text{O}_3 + \text{CO}_2$, $\Delta m = -9.4\%$ (referenced to $\text{Bi}_2\text{O}_2\text{CO}_3$). Fig. 1 (b) suggests that by maintaining the temperature at 350 °C, the duration for transformation from $\text{Bi}_2\text{O}_2\text{CO}_3$ to $\alpha\text{-Bi}_2\text{O}_3$ is ~31 min.

Fig.1. TGA profiles of $\text{Bi}_2\text{O}_2\text{CO}_3$ powders in air. (a) Weight loss versus temperature; (b) Weight loss versus time.

3.1.2. XRD

The above data indicates that by precise control of the calcination time and temperature, biphasic α -Bi₂O₃/Bi₂O₂CO₃ heterostructures could be obtained. Thus, 0.2 g of the initially prepared Bi₂O₂CO₃ nanosquares was placed in a furnace at 350 °C and calcined for different times (10, 20, 30 min). Fig. 2 shows the XRD patterns of the as-prepared samples. The initial Bi₂O₂CO₃ (prior to calcination) shows sharp and intense diffraction peaks, which can all be indexed as a tetragonal phase of Bi₂O₂CO₃ (JCPDS card No. 41-1488, $a = 3.865$ Å, $b = 3.865$ Å, $c = 13.675$ Å). No peaks from impurities such as (BiO)₄CO₃(OH)₂ are detected in XRD pattern^[43,44]. When Bi₂O₂CO₃ was calcined at 350 °C for 10 min, new reflection peaks at 2θ of 28.29, 33.01, and 55.79° appear. These new reflection peaks are ascribed to the tetragonal phase of α -Bi₂O₃ with the lattice constants of $a = b = 7.740$ Å and $c = 5.632$ Å, which are consistent with the values from the standard JCPDS card No. 71-2274. After heat treatment at 350 °C for 30 min, the characteristic diffraction peaks of Bi₂O₂CO₃ are completely disappeared. Obviously, Bi₂O₂CO₃ calcined at 350 °C for 10 or 20 min shows the distinct diffraction peaks of both Bi₂O₂CO₃ and α -Bi₂O₃ phases, indicating the formation of α -Bi₂O₃/Bi₂O₂CO₃ composite phases.

Fig.2. XRD patterns of the initial Bi₂O₂CO₃ and samples after calcination at 350 °C for different times (10 min, 20 min, 30 min).

3.1.3. SEM and TEM

Fig.3 shows the SEM images of the initial $\text{Bi}_2\text{O}_2\text{CO}_3$ and samples calcined at 350 °C for different times. The initial $\text{Bi}_2\text{O}_2\text{CO}_3$ is composed of predominant plates with different sizes. When heated at 350 °C for 10 min, these plates aggregated together and the plate-like morphology disappeared gradually with heating time. When the calcination time was increased to 20 or 30 min, the aggregated plates were transformed to linked rod-like particles with length of 0.2-0.5 μm . The detail morphology was further analyzed by TEM.

Fig. 3. SEM images of the samples. (a) $\text{Bi}_2\text{O}_2\text{CO}_3$; (b), (c), (d) for $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350 °C for 10 min, 20 min, and 30 min, respectively.

The TEM image in Fig.4 (a) indicates that the $\text{Bi}_2\text{O}_2\text{CO}_3$ particles show nanosquare morphology with length of ~100 nm and width of ~50 nm. Fig. 4 (b)-(d) indicate that when calcined at 350 °C, the dispersed nanosquares were fused together, forming dendritic

particles. The morphology change was caused by the transformation of $\text{Bi}_2\text{O}_2\text{CO}_3 \rightarrow \alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3 \rightarrow \alpha\text{-Bi}_2\text{O}_3$. These results show that the unique dendritic $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ nanoheterostructures can be obtained *via* calcination of $\text{Bi}_2\text{O}_2\text{CO}_3$. Thermal decomposition reaction of $\text{Bi}_2\text{O}_2\text{CO}_3$ could be a complex kinetic process. Fig. 5 illustrates the characteristic and formation mechanism of the produced dendritic like $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ nanoheterostructures. $\text{Bi}_2\text{O}_2\text{CO}_3$ is thermally unstable and when heating temperature is over 350 °C, partial decomposition of $\text{Bi}_2\text{O}_2\text{CO}_3$ to $\alpha\text{-Bi}_2\text{O}_3$ occurs. The formation of $\alpha\text{-Bi}_2\text{O}_3$ is a solid reaction process. The grain size of the reactant substrate decreases gradually due to the transition of $\text{Bi}_2\text{O}_2\text{CO}_3$, as detected by TEM. The as-produced grain boundary is a reactive site for thermal decomposition. Because of the reaction at the grain boundary, the respective grains of the internal $\text{Bi}_2\text{O}_2\text{CO}_3$ are coated by $\alpha\text{-Bi}_2\text{O}_3$. Therefore, in the limited calcination time, $\text{Bi}_2\text{O}_2\text{CO}_3$ particles could be coated by a surface product layer of $\alpha\text{-Bi}_2\text{O}_3$ and formed $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure with well contacted interface. The formation of a surface $\alpha\text{-Bi}_2\text{O}_3$ layer over $\text{Bi}_2\text{O}_2\text{CO}_3$ at the beginning of thermal decomposition could cause the later slow reaction by blocking the diffusion of CO_2 . At the same time, the surface morphology of $\alpha\text{-Bi}_2\text{O}_3$ crystal depends on the extent of deviation of the formation conditions from the thermodynamic equilibrium or the driving force for crystallization. Specifically, dendrites will form when the formation conditions are far from the thermodynamic equilibrium because of the increasing contribution of mass diffusion ^[45,46]. In other words, when the $\alpha\text{-Bi}_2\text{O}_3$ growth rate is larger than that of the mass transport of ions that feed the growing crystals, the dendrite growth will be promoted. The formation of a surface $\alpha\text{-Bi}_2\text{O}_3$ layer over $\text{Bi}_2\text{O}_2\text{CO}_3$ could block the diffusion of CO_2 and hinder the mass transport, which could contribute to thermodynamic unequilibrium state of $\alpha\text{-Bi}_2\text{O}_3$ growth. The as-produced $\alpha\text{-Bi}_2\text{O}_3$ particles are fused together and finally produce dendritic like $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ nanostructure. The color

changes sequentially from gray → shallow yellow → deep yellow over the phase transformations.

Fig.4. TEM images of the samples. (a) Bi₂O₂CO₃; (b), (c), (d) for Bi₂O₂CO₃ samples calcined at 350 °C for 10 min, 20 min, and 30 min, respectively.

Fig.5. Schematic model of the formation dendritic α-Bi₂O₃/Bi₂O₂CO₃ heterostructure during the course of Bi₂O₂CO₃ calcination in air atmosphere.

Au nanospheres (NSs) and Au nanorods (NRs) with different size were prepared by a wet chemistry method ^[42]. Fig. 6 shows the photograph of the prepared Au NPs aqueous solutions (colloids). The prepared Au NSs (~ 30 nm) and Au NRs (~ 20 nm) colloids show the brilliant ruby-red color. Au NRs colloids (~ 30 nm and ~ 35 nm) exhibit the deep red color. The difference in color was caused by the different optical properties (e.g., absorption and scattering) of Au colloids, which were determined by the shape and size of Au NPs^[47].

Fig.6. Photographs of the prepared Au NSs (~ 30 nm) and Au NRs with different size (~ 20 , ~ 30 and ~ 35 nm) aqueous solutions. The concentration of Au NPs is 0.5 m M L^{-1} . Nanospheres: NSs, Au nanorods: NRs.

Fig.7 show the TEM images of the Au NPs. Figure 7(a) shows the Au NPs with diameter of 30 ± 3 nm. Fig.7 (b)-(d) shows the Au NRs with different length and diameter. Fig. 7 (b) shows Au NRs of 20 ± 4 nm in length and 15 ± 1 nm diameter. Fig. 7 (c) shows Au NRs of 15 ± 2 nm diameter and length of 30 ± 5 nm. Figure 7 (d) shows Au NRs of 13 ± 1 nm diameter and length of 35 ± 4 nm. According to previous research ^[42], these Au NRs are fcc crystalline with $[110]$ as the growth direction (i.e. the long axis). The structural model for the nanorod is shown in Fig.7 (e), in which the side faces consist of four $\{111\}$ facets and two $\{100\}$ facets; note that the two $\{100\}$ facets are formed due to longitudinal truncation

of the $\{111\}$ (otherwise, the four $\{111\}$ planes form a parallelogonal radial cross section of the rod); this truncation is better observed from the end view of the rod. The typical high resolution (HRTEM) TEM image of Au NRs (30 nm)/ α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ sample is shown in Fig.7 (f). As observed in the HRTEM image, a single crystalline Au NR is deposited over the surface of the crystalline α - Bi_2O_3 . The measured lattice spacing of the crystalline substrate α - Bi_2O_3 ($d = 0.33$ nm) corresponds to the (120) spacing of α - Bi_2O_3 phase ^[48]. Some particles with no obvious lattice spacing could be the undecomposed $\text{Bi}_2\text{O}_2\text{CO}_3$ particles. The single-crystalline Au nanorod shows lattice fringe of 0.203 nm, matching the crystallographic planes of metallic cubic-phase Au (200). The HRTEM result suggests that the Au/ α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ sample manifests as the heterostructures with well contacted interfaces.

Fig. 7. (a) TEM images of the Au NSs (~30 nm), (b)-(d) Au NRs with different sizes (~20, ~30 and ~35 nm), (e) Structural model of single crystalline Au nanorods, (f) High resolution TEM image of Au NRs (~30 nm)/ α -Bi₂O₃/Bi₂O₂CO₃. Nanospheres: NSs, Au nanorods: NRs.

3.1.3. SEM and TEM

Fig. 8 (a) shows the UV-Vis spectra of the Au colloids. It can be seen that the shape and structural anisotropy of Au NPs substantially influence their SPR absorption. Au NSs show a distinct peak at 530 nm due to the SPR extinction ^[49]. The three Au NR colloids display different SPR peaks. Au NRs (~20 nm) give rise to the peak at 532 nm, and the longitudinal SPR peak of Au NRs (~30 nm) shifts to 608 nm and a shoulder peak (i.e. transverse SPR) at around 530 nm was also observed. The Au NRs (~35 nm) show the major SPR peak at 697 nm and a shoulder peak at ~515 nm. The change in the major peak wavelength is mainly due to the variation in the anisotropy of Au NRs (aspect ratio). Here, the aspect ratio is defined as the ratio of the nanorod length to its diameter. The values of aspect ratio of Au NRs (~20 nm), Au NRs (~30 nm) and Au NRs (~35 nm) are estimated to be 1.3, 2.0, and 3.5, respectively. The increase in structural anisotropy shifts the SPR to the longer wavelength direction.

Fig.8 (b) shows the UV-Vis diffuse reflectance spectra of the as-prepared Bi₂O₂CO₃ and Bi₂O₂CO₃ calcined at 350 °C for different times. The absorption edge of Bi₂O₂CO₃ is estimated to be at 370 nm (Fig.8b). The calcination treatment makes the absorption edges shift from 370 nm to 537, 545, and 548 nm, corresponding to Bi₂O₂CO₃ calcined at 350 °C for 10, 20, and 30 min, respectively. The produced α -Bi₂O₃/Bi₂O₂CO₃ heterostructures and α -Bi₂O₃ exhibit intense absorption in the visible light region. The band gap energies of the produced samples were estimated from the intercept of the tangents to the plots of $(\alpha h\nu)^{1/2}$

vs photon energy^[50] (see supporting Fig. S1(a)-(b)). The estimated band gap energies were approximately 3.18 eV for $\text{Bi}_2\text{O}_2\text{CO}_3$, 2.17 eV for $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (220 °C, 10 min), 2.08 eV for $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (220 °C, 20 min), and 2.12 eV for $\alpha\text{-Bi}_2\text{O}_3$.

Fig.8 (c) shows the UV-Vis diffuse reflectance spectra of the Au loaded $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (220 °C, 20 min) composites. Integrating plasmonic Au NSs (~30 nm) or NRs (~20 nm) onto $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ slightly increases its absorption in the visible light region. However, no obvious plasmonic resonance peaks of Au NSs (530 nm) and NRs (~20 nm) (532 nm) was detected, which should be caused by the ~530 nm SPR band of Au NPs being shorter than the bandgap (2.1 eV = 590 nm) of the $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ substrate. When Au NRs (~30 nm) were loaded on $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, an obvious absorption band at ~606 nm appeared. This absorption band was ascribed to the SPR of Au NRs since this peak is similar to that of Au NRs (~30 nm) colloids. A similar absorption band from 600 to 670 nm was observed after loading Au NRs (~35 nm). This result indicates that integrating plasmonic Au NRs with $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure could substantially increase the visible light absorption by the hybrid material.

Fig.8. (a) UV-Vis spectra of the prepared Au colloids; (b) UV-Vis diffuse reflectance spectra of Bi₂O₂CO₃ and Bi₂O₂CO₃ samples calcined at 350 °C for 10 min, 20 min, and 30 min; (c) UV-Vis diffuse reflectance spectra of the Au/ α -Bi₂O₃-Bi₂O₂CO₃ (NRs: nanorods, NSs: nanospheres).

3.1.4. XPS

XPS was used to investigate the valence state of elements in Au NRs (~30 nm) supported on α -Bi₂O₃-Bi₂O₂CO₃. Fig. 9 (a) shows the high resolution XPS spectrum of O 1s. Obviously, the O 1s region can be deconvoluted into three peaks at 531.6, 529.9 and

528.6 eV, indicating the co-existence of three distinguishable chemical states of oxygen on this surface. The peak at 529.9 eV is ascribed to the oxygen attached to the Bi–O bond ^[51] and the peak around 531.1 eV can be assigned to carbonate species ^[50]. The affiliation of the peak at 528.6 eV is not clear because the characteristic peak of adsorbed H₂O (or surface hydroxyl groups) is 532.2 eV ^[42,50]. Fig.9 (b) shows the high-resolution XPS spectrum of Bi 4f. The Bi 4f spectrum can be deconvoluted into two peaks. The binding energy of 163.1 eV is for the Bi 4f_{5/2} and 157.8 eV for Bi 4f_{7/2}. The dominant chemical state of Bi in the sample is +3 ^[52]. In Fig. 9 (c), the binding energies of Au 4f_{5/2} and Au 4f_{7/2} are at 87.7 and 83.8 eV, respectively, which are attributed to metallic Au ^[53].

Fig. 9. High resolution XPS spectra of O 1s, Bi 4f and Au 4f of the Au NRs (~ 30 nm)/ α -Bi₂O₃/Bi₂O₂CO₃.

3.2. Catalytic Performances

The photocatalytic activities of the as-prepared samples were evaluated by photodegradation of dye, methyl orange (MO), under visible light irradiation. As shown in Fig. 10 (a), Bi₂O₂CO₃ exhibited almost no photocatalytic activity in the MO degradation reaction due to its poor visible light absorption. Among them, α -Bi₂O₃/Bi₂O₂CO₃ heterostructure prepared by calcination of Bi₂O₂CO₃ at 350 °C for 20 min exhibited the highest photocatalytic activity. The pseudo-first-order rate constants (see Table 1 and supporting Figure S2) for α -Bi₂O₃/Bi₂O₂CO₃ (350 °C, 10 min), α -Bi₂O₃/Bi₂O₂CO₃ (350 °C, 20 min) and α -Bi₂O₃ are 0.0019, 0.0078 and 0.0036 min⁻¹, respectively. Although the surface area of the three samples is similar, the photocatalytic decomposition rate of MO over the α -Bi₂O₃/Bi₂O₂CO₃ (350 °C, 20 min) is 4.1 times the activity of α -Bi₂O₃/Bi₂O₂CO₃ (350 °C, 10 min), and 2.1 times that of α -Bi₂O₃, respectively.

The effects of integrating plasmonic Au NSs or NRs with α -Bi₂O₃/Bi₂O₂CO₃ (350 °C, 20 min) on the photocatalytic activity are shown in Fig. 10 (b). Notably, loading Au NSs or NRs on α -Bi₂O₃/Bi₂O₂CO₃ heterostructures could further substantially increases the photocatalytic efficiency. MO dye was completely degraded in 40 min over Au NRs (~ 30 nm)/ α -Bi₂O₃/Bi₂O₂CO₃ under visible light irradiation, whereas the degradation rate of MO

over $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ was only $\sim 27\%$ at the same light irradiation time. The degradation rate constant (0.0940 min^{-1}) over Au NRs ($\sim 30 \text{ nm}$)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ is 12 times that over $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (0.0078 min^{-1}). Moreover, we found that Au NRs exhibit more distinct effects on promoting activity than Au NSs. To test the stability of the best composite photocatalyst (Au NRs ($\sim 30 \text{ nm}$)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$), we carried out the recycle test. The obtained results are shown in Table S1. From Table S1, we can see that the activity of the composite photocatalyst only shows a slight decrease with the increase of recycling times, which indicates that the composite photocatalyst has good stability. The SEM and TEM images of the composite photocatalyst after cycling three times are shown in Figure S3 (a)-(b). From Figure S3 (a)-(b), we can see that compared with the fresh photocatalyst, the morphology of the reacted photocatalyst did not appear obvious variation.

Fig. 10. Photocatalytic activity comparison of the prepared samples in degradation of methyl orange. (a) Performance of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350°C for 10, 20, and 30 min, respectively; the effects of loading Au NSs and Au NRs with different size on photocatalytic activity. Nanospheres: NSs, nanorods: NRs.

Table 1. Textural properties, band gap of the materials, and photocatalysis rate constants in degradation of MO.

Material	S [m^2/g]	E_g (eV)	k (min^{-1})
	[a]	[b]	[c]
$\text{Bi}_2\text{O}_2\text{CO}_3$	6.3	3.18	0
$\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (350°C , 10 min)	4.4	2.17	0.0019
$\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ (350°C , 20 min)	3.8	2.08	0.0078
$\alpha\text{-Bi}_2\text{O}_3$	3.2	2.12	0.0036
Au NSs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ [d]	3.5	-	0.0410
Au NRs (~ 20 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ [d]	3.2	-	0.0562

Au NRs (~ 30 nm)- α -Bi ₂ O ₃ /Bi ₂ O ₂ CO ₃ [d]	3.4	-	0.0940
Au NRs (~ 35 nm)- α -Bi ₂ O ₃ /Bi ₂ O ₂ CO ₃ [d]	3.1	-	0.0520

[a] BET surface area [b] Band gap [c] The pseudo-first-order rate constant in degradation of MO and phenol, respectively.[d] α -Bi₂O₃/Bi₂O₂CO₃ was obtained by calcination of Bi₂O₂CO₃ at 350 °C for 20 min. NSs: nanospheres, NRs: nanorods.

3.3. Discussion

To understand the role of Au NPs and the electron transport paths in the efficient photocatalysis of the Au/ α -Bi₂O₃/Bi₂O₂CO₃ heterostructured catalyst, we first calculated the electronic band structures of α -Bi₂O₃/Bi₂O₂CO₃ (see supporting information for details), then the generation of the hydroxyl radicals ($\bullet$ OH) in the visible light irradiated suspensions of the photocatalysts was studied ^[54]. The top of the valence band (VB) and the bottom of the conduction band (CB) of Bi₂O₂CO₃ are calculated to be 3.56 and 0.276 eV, respectively. Accordingly, the VB and CB of α -Bi₂O₃ are estimated to be 2.33 and 0.11 eV, respectively. The supporting Fig.S3 shows the detail electronic band structure of α -Bi₂O₃/Bi₂O₂CO₃. Therefore, on the α -Bi₂O₃/Bi₂O₂CO₃ heterostructure, the CB level of α -Bi₂O₃ (0.11 eV) is slightly more negative than that of Bi₂O₂CO₃ (0.28 eV). Under visible light irradiation, the excited electrons in α -Bi₂O₃ could transfer to the VB of Bi₂O₂CO₃, which promotes the separation of the electron and hole pairs photogenerated on the α -Bi₂O₃. The generation of $\bullet$ OH radicals on the photo-illuminated α -Bi₂O₃, α -Bi₂O₃/Bi₂O₂CO₃, Au NSs (~ 30 nm)/ α -Bi₂O₃/Bi₂O₂CO₃ and NRs (~ 30 nm)/ α -Bi₂O₃/Bi₂O₂CO₃ in the presence of Fe³⁺ was detected by a fluorescence technique using coumarin as a chemical trap of $\bullet$ OH radicals ^[54,55]. Coumarin readily reacts with $\bullet$ OH to form a highly fluorescent product, 7-hydroxycoumarin. Fig.11 displayed the fluorescence emission intensities of the coumarin $\bullet$ OH adduct (7-hydroxycoumarin) produced in suspensions of the four samples after the visible light irradiation for 40 min. It can be clearly observed that the intensity

followed the order: $\alpha\text{-Bi}_2\text{O}_3 < \alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3 < \text{Au NSs } (\sim 30 \text{ nm})/\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3 < \text{Au NRs } (\sim 30 \text{ nm})/\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, which indicates that the produced $\bullet\text{OH}$ radical concentration could follow the same order. More $\bullet\text{OH}$ radicals were generated by Au NRs $(\sim 30 \text{ nm})/\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ under the same photocatalytic condition. The detected $\bullet\text{OH}$ radicals are produced directly through the reaction of H_2O with the hole generated on the valence band of the photo-excited $\alpha\text{-Bi}_2\text{O}_3$. The formation of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure and loading of Au NPs on $\alpha\text{-Bi}_2\text{O}_3$ favor the production of more $\bullet\text{OH}$, which reveals an efficient separation of the electron and hole pairs in the photo-excited $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Au}/\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ systems.

Fig. 11. Fluorescence emission intensities of the coumarin-OH adduct (7-hydroxycoumarin) produced in the suspensions of $\alpha\text{-Bi}_2\text{O}_3$, $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, Au NSs ($\sim 30 \text{ nm}$)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ and AuNRs ($\sim 30 \text{ nm}$)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ after the visible light irradiation for 40 min. Nanospheres: NSs, nanorods: NRs.

To further demonstrate the influence of heterostructure and AuNRs on the separation efficiency on photogenerated electrons and holes, we carried out the photocurrent test. The

obtained results of the typical samples ($\text{Bi}_2\text{O}_2\text{CO}_3$ (b) $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, $\alpha\text{-Bi}_2\text{O}_3$, Au NRs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$) are shown in following Fig.12. As shown in Fig.12, the intensity of the photocurrent follows the order of Au NRs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3 > \alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3 > \text{Bi}_2\text{O}_2\text{CO}_3 > \alpha\text{-Bi}_2\text{O}_3$. Au NRs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ shows the strongest photocurrent. According to the literatures, the higher the optical response signal, the higher the separation efficiency of the photo generated electron hole pairs ^[56]. The photocurrent measurement results demonstrated that the loading of Au NRs largely facilitate the charge carriers separation and transfer, which is consistent with the photocatalytic performance.

Fig.12. The produced photocurrent density under simulative solar light irradiation (xenon

lamp) for different samples. (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ (b) $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$; (c) $\alpha\text{-Bi}_2\text{O}_3$; (d) Au NRs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$.

Based on the above results, we proposed the following possible reasons to explain the significantly enhanced photocatalytic activity of the $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure and Au/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ photocatalyst. In $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure, the potential of the CB: 0.11 eV of $\alpha\text{-Bi}_2\text{O}_3$ is slightly more negative than that of $\text{Bi}_2\text{O}_2\text{CO}_3$ (CB: 0.26 eV) (as shown in supporting Fig. S3). Therefore, the photogenerated electrons in the $\alpha\text{-Bi}_2\text{O}_3$ layer can be transferred to the CB of the $\text{Bi}_2\text{O}_2\text{CO}_3$, leaving the holes on the BV of $\alpha\text{-Bi}_2\text{O}_3$. The good interface charge transfer process, as indicated in Fig. 13, promotes the effective separation of photoexcited electrons and holes, and hence decreases the probability of electron–hole recombination, enhancing the photocatalytic activity of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure.

Over Au/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ systems, three reasons could contribute their high photocatalytic efficiency. The first one is that the interface charge transfer process between $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ also plays the role. But, two more important reasons are the role of the loaded Au NPs. First, the integrated plasmonic Au NSs or NRs on $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ surfaces may act as electron sinks to retard the recombination of the photogenerated electrons and holes in $\alpha\text{-Bi}_2\text{O}_3$ so as to improve the charge separation on its surfaces. It is known that the Fermi level of gold is 0.5 V (versus NHE)^[57], which is more positive than the CB edge of $\alpha\text{-Bi}_2\text{O}_3$ (0.11 eV). At the Au- $\alpha\text{-Bi}_2\text{O}_3$ heterojunction, photogenerated electrons in the $\alpha\text{-Bi}_2\text{O}_3$ could fast transfer to Au particles. The accumulated electrons on Au could reduce the surface O_2 to form H_2O_2 because the CB level of $\alpha\text{-Bi}_2\text{O}_3$ (0.11 eV vs. NHE) is more positive than that of the reaction (1): $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$ (0.33 V vs. NHE), but more negative than that (+0.695 V vs. NHE) of reaction (2): $\text{e}_{\text{CB}}^- + \text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$. The

produced H_2O_2 can be further reduced to $\bullet\text{OH}$ radicals as reaction (3): $\text{e}_{\text{CB}}^- + \text{H}_2\text{O}_2 \rightarrow \bullet\text{OH} + \text{OH}^-$. This speculation was supported by the direct evidence of the in situ photoproduction of H_2O_2 in the visible light irradiated suspension of the pure $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Au}/\alpha\text{-Bi}_2\text{O}_3$ [54]. Second, the SPR of gold NPs attached on $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ surfaces could enhance visible light absorption and photocatalytic efficiency. It has been extensively demonstrated that the plasmon-exciton coupling can result in significant enhancement of charge separation [58]. According to She et al [24], under visible-light irradiation, large gold NPs (>30 nm) in Au/TiO_2 could induce plasmonic near-fields by strong localized-surface-plasmon-resonance (LSPR). The plasmonic near-fields are localized close to the Au-TiO_2 interface. The strong localization of plasmonic near-fields could enhance optical absorption and generate electron-hole pairs for photocatalysis via optical transitions between the localized electronic states in the band gap of the TiO_2 . In our case, the average sizes of Au NSs and Au NRs are close to 30 nm. Therefore, LSPR could take place in $\text{Au-}\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ interface, which further enhances the photocatalytic performance. The difference in the shape and structural anisotropy of NSs and Au NRs caused the different SPR, such as plasmonic resonance absorption wavelength, the intensity of LSPR. Activity test showed that effects of Au NPs on promoting the activity follow the order: Au NSs (~30 nm, 0.0410 min^{-1}) < Au NRs (~20 nm, 0.0562 min^{-1}) < Au NRs (~35 nm, 0.0520 min^{-1}) < Au NRs (~30 nm, 0.0940 min^{-1}). It sees that plasmonic Au NPs with moderate aspect ratio, such as Au NRs (~30 nm, aspect ratio: 2) gives the largest ability to increase visible photocatalytic activity, which could be related to its suitable plasmonic resonance absorption wavelength and strong LSPR. $\bullet\text{OH}$ production tests confirmed that more $\bullet\text{OH}$ radicals were generated by Au NRs (~30 nm)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ under the same photocatalytic condition, which suggests its high capacity to inhibit electron-hole recombination to a large extent.

Fig.13. Schematic photocatalytic reaction process and charge transfer of the Au NRs / α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructured catalyst under visible-light irradiation. Nanorods: NRs.

4. Conclusions

In summary, dendritic-like α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures have been first successfully prepared by using a phase transformation strategy. Then, plasmonic Au NPs including Au NSs (~30 nm) and Au NRs (~20, ~30, and ~35 nm), were loaded onto the α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures. The α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ and Au- α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructured photocatalysts exhibit highly efficient visible-light-driven photocatalytic activities for dye degradation compared to pure α - Bi_2O_3 and α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$. As for the α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures, the improved photocatalytic efficiency is attributed to the enhanced charge separation by interfacial charge transfer. Moreover, the loading of Au NSs or Au NRs gives rise to 4 or 5~11 times increase in activity compared to α - Bi_2O_3 / $\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures. The effects of Au NPs on promoting the activity follow the increasing order of Au NSs (30 nm) < Au NRs (20 nm) < Au NRs (35 nm) < Au NRs (30 nm). The presence of Au NSs or Au NRs greatly promote the $\cdot\text{OH}$ radical production, which is attributed to the significant enhancement of charge separation.

Furthermore, the SPR absorption of these large Au NPs on the α -Bi₂O₃/Bi₂O₂CO₃ nanostructures could have significant contribution to the visible light photocatalytic activities due to their strong plasmonic near-fields. The strategy of the heterostructure synthesis involving Au NPs on the semiconductor inter-surface may have considerable impact on the future development of highly efficient visible light photocatalysts. This work also provides insight on the mechanism behind efficient visible-light plasmonic photocatalysis.

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Fig.1. TGA profiles of $\text{Bi}_2\text{O}_2\text{CO}_3$ powders in air. (a) Weight loss versus temperature; (b) Weight loss versus time.

Fig.2. XRD patterns of the initial $\text{Bi}_2\text{O}_2\text{CO}_3$ and samples after calcination at 350°C for different times (10 min, 20 min, 30 min).

Fig.3. SEM images of the samples. (a) $\text{Bi}_2\text{O}_2\text{CO}_3$; (b), (c), (d) for $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350°C for 10 min, 20 min, and 30 min, respectively.

Fig.4. TEM images of the samples. (a) $\text{Bi}_2\text{O}_2\text{CO}_3$; (b), (c), (d) for $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350°C for 10 min, 20 min, and 30 min, respectively.

Fig.5. Schematic model of the formation dendritic $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructure during the course of $\text{Bi}_2\text{O}_2\text{CO}_3$ calcination in air atmosphere.

Fig.6. Photographs of the prepared Au NSs (~ 30 nm) and Au NRs with different size (~ 20 , ~ 30 and ~ 35 nm) aqueous solutions. The concentration of Au NPs is 0.5 m M L^{-1} . Nanospheres: NSs, Au nanorods: NRs.

Fig. 7. (a) TEM images of the Au NSs (~ 30 nm), (b)-(d) Au NRs with different sizes (~ 20 , ~ 30 and ~ 35 nm), (e) Structural model of single crystalline Au nanorods, (f) High resolution TEM image of Au NRs (~ 30 nm)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$. Nanospheres: NSs, Au nanorods: NRs.

Fig.8. (a) UV-Vis spectra of the prepared Au colloids; (b) UV-Vis diffuse reflectance spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350°C for 10 min, 20 min, and 30 min; (c) UV-Vis diffuse reflectance spectra of the Au/ $\alpha\text{-Bi}_2\text{O}_3\text{-Bi}_2\text{O}_2\text{CO}_3$ (NRs: nanorods, NSs: nanospheres).

Fig. 9. High resolution XPS spectra of O 1s, Bi 4f and Au 4f of the Au NRs (~ 30 nm)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$.

Fig. 10. Photocatalytic activity comparison of the prepared samples in degradation of

methyl orange. (a) Performance of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ samples calcined at 350 °C for 10, 20, and 30 min, respectively; the effects of loading Au NSs and Au NRs with different size on photocatalytic activity. Nanospheres: NSs, nanorods: NRs.

Fig. 11. Fluorescence emission intensities of the coumarin-OH adduct (7-hydroxycoumarin) produced in the suspensions of $\alpha\text{-Bi}_2\text{O}_3$, $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$, Au NSs (~ 30 nm)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ and AuNRs (~ 30 nm)/ $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ after the visible light irradiation for 40 min. Nanospheres: NSs, nanorods: NRs.

Fig.12. The produced photocurrent density under simulative solar light irradiation (xenon lamp) for different samples. (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ (b) $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$; (c) $\alpha\text{-Bi}_2\text{O}_3$; (d) Au NRs (~ 30 nm)- $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$.

Fig.13. Schematic photocatalytic reaction process and charge transfer of the Au NRs / $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructured catalyst under visible-light irradiation. Nanorods: NRs.

Integrating Plasmonic Au Nanorods with Dendritic Like α - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ Heterostructures for Superior Visible-light-driven Photocatalysis

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Graphical abstract