Graphical Abstract

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Articles

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photocatalyst for enhanced solar-light photocatalytic conversion of nitrite

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ABSTRACT

Z-scheme structure is an effectively construction to improve the photocatalytic activity due to the excellent photo-generated electron-hole pairs separation efficiency. In this paper, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, $(\text{Au}/\text{rGO})/\text{CdS}$ and modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalysts were prepared by hydrothermal, ultrasonic dispersion, deposition-precipitation and ultrasonic-assisted methods. The prepared samples were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectra (DRS), fourier transform infrared spectra (FT-IR), raman spectra and photoluminescence (PL) spectra. The photocatalytic activity of prepared samples were evaluated via photocatalytic conversion rate of nitrite under ultraviolet-light and simulated solar-light irradiations. Due to the enhanced separation efficiency of electron-hole pairs, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ exhibited excellent performance under both ultraviolet-light and simulated solar-light irradiation, reaching 94.59% and 91.25% conversion rates, respectively. Meanwhile, the effects of simulated solar-light irradiation time and corresponding reaction kinetics on photocatalytic conversion of nitrite were studied. Subsequently, the effects of

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electron and hole scavengers were investigated to further elaborate the possible mechanism. In addition, the study of used times showed that the prepared modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ nanocomposites can be effectively recycled without an apparent inactivation on photocatalytic activity. This research may provide a potential way by utilizing solar energy efficiently for converting nitrite and other contaminants released into the environment.

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Keywords: Photocatalytic conversion, Nitrite, Up-conversion luminescence agent ($\text{Er}^{3+}:\text{YAlO}_3$), Simulated solar-light, Modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalyst.

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1. Introduction

Recently, the worldwide increasing concentration of nitrite anions in the water body caused by overusing nitrogenous fertilizer, excessive discharge of industrial effluents and incomplete abiotic denitrification process have become one of the considerably severe environmental issues [1–3]. The World Health Organization recommends a value of 3.0 mg/L as the maximum allowable concentration of NO_2^- in drinking water [4]. There are well known treatments for nitrite conversion, e.g., electron dialysis, reverse osmosis, ionic membrane, biological degradation and catalytic or electrochemical

reduction, etc [5–9]. Among all the methods, photocatalysis is regarded as a promising and efficient environmental purification technology since it offers an effortless way to deal with environment pollutions by utilizing solar energy [10–14]. However, nitrite is a contaminant of intermediate valence condition, and it can be reduced to NH_4^+ ($\text{pH} \leq 7.0$) or N_2 ($\text{pH} \geq 7.0$) and oxidized to NO_3^- . Although the photocatalysts used for the treatment of nitrite, such as TiO_2 and ZnO , have been widely investigated, they can hardly process strong oxidation-reduction ability as wide-band semiconductors [15–17].

Generally speaking, wide-band semiconductors can only utilize ultraviolet light which accounts for less than 5.0% of the entire solar spectrum. Though the narrow-band semiconductors can be stimulated under visible-light irradiation, they possess low redox ability. And they all suffer from the recombination of the photo-generated electron-hole pairs [18]. Due to the rapid recombination of photo-generated electron-hole pairs, the semiconductors can not have high photocatalytic performance. Since the Z-scheme TiO_2 -Au-CdS system was reported in 2006 as the first example of an all-solid-state PS-C-PS system, the concept of all-solid-state Z-scheme visible-light-driven photocatalyst has been paid much attention [19]. The development of the Z-scheme system could provide an excellent photocatalyst with high performance and strong oxidation-reduction ability [20–25]. It is quite suitable for the photocatalytic conversion of nitrite.

Choosing proper semiconductor components with suitable band structure and a solid electron mediator to couple the components are significant. BiPO_4 possesses a wide bandwidth of 3.83 eV and a relative more positive oxidation potential (valence band (VB)) position of 4.27 eV [26,27]. Such the band structure makes BiPO_4 applicable to form semiconductor coupling with narrow-band semiconductors. Meanwhile, in order to broaden the solar-light absorption region to strengthen

solar-light photocatalytic activity, we investigated a large amount of literatures and found that the upconversion luminescence agents can convert the low energy (long wavelength) light to high energy (short wavelength) light [28–30]. In other words, the upconversion luminescence agents can absorb visible or infrared light and then emit the ultraviolet light, to satisfy the requirements of those wide-band gap semiconductor. Therefore, we chose $\text{Er}^{3+}:\text{YAlO}_3$, as a kind of effective upconversion luminescence agent, to coat with BiPO_4 . While under the irradiation of visible light, $\text{Er}^{3+}:\text{YAlO}_3$ could transform visible light into ultraviolet light, thus stimulating BiPO_4 [31,32]. Additionally, CdS has a bandwidth of 2.4 eV. Its valence band (VB) and conduction band (CB) electric potentials are 1.88 eV and -0.52 eV, respectively [33,34]. For CdS , the relative more negative conduction band (CB) position is in a high possibility of forming Z-scheme charge transfer, as a reduction site. Owing to these photocatalytic characters, BiPO_4 and CdS were chose as semiconductor components in this study.

The photo-generated electron transfer rate and electron-hole pairs recombination rate are so crucial for photocatalytic activity that a solid electron mediator to couple the components needs to be chosen seriously. The rGO, a large two-dimensional carbon-based material with a size of several micrometers and high carrier mobility, as a supporting substrate could efficiently increase active sites on the surface of material and rapidly transfer photo-generated electrons [35,36]. In addition, the decorating Au nanoparticles on the rGO material can trap the photo-generated electrons around the edges [37–39]. It provides an effective way for electron-hole pairs to promote their bonding, thus the recombination of which was restrained. Therefore, in this work, we chose Au/rGO as the electron mediator. To further investigate the effects of modification, we also prepared Au/rGO/ CdS and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, respectively. Of which, the Au/rGO was functioned as the conduction band co-catalyst and PdS functioned as the valence band co-catalyst, respectively. And

then, the photocatalytic activity of the modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalyst was investigated through the stimulated solar-light photocatalytic conversion of nitrite.

Herein, we investigated the photocatalytic performance enhancement of Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalyst, which was structured via hydrothermal, ultrasonic dispersion, deposition-precipitation and ultrasonic-assisted methods. The effects of ultraviolet-light and simulated solar-light were investigated through the photocatalytic conversion rate of nitrite. In addition, the effects of simulated solar-light time and used times were also studied. Besides, the possible mechanism for enhanced photocatalytic activity on simulated solar-light photocatalytic conversion of nitrite in the presence of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ was proposed.

2. Experimental

2.1. Materials and reagents

Cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, analytically pure, Sinopharm Chemical Reagent Co, Ltd, China) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, analytically pure, Sinopharm Chemical Reagent Co, Ltd, China) were used to prepare the cadmium sulfide (CdS). Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%, Aladdin Chemical Co., Ltd, China) and phosphoric acid (H_3PO_4 , 85%, Sinopharm Chemical Reagent Co., Ltd, China) and were used to prepare the bismuth phosphate (BiPO_4). Erbium oxide (Er_2O_3 , 99.999%, Sinopharm Chemical Reagent Co., Ltd, China), yttrium oxide (Y_2O_3 , 99.999%, Aladdin Chemical Co., Ltd, China), aluminum nitrate nonahydrate ($(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$, analytically pure, Sinopharm Chemical Reagent Co., Ltd, China), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, analytically pure, Sinopharm Chemical Reagent Co., Ltd, China) and nitric acid (HNO_3 ,

68%, guaranteed pure, Veking Company, China) were used to prepare the up-conversion luminescence agent ($\text{Er}^{3+}:\text{YAlO}_3$). Graphene oxide (GO, analytically pure, Veking Company, China), hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 85%, Sinopharm Chemical Reagent Co., Ltd, China) and Hydrogen tetrachloroaurate ($\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$, 97%, Sinopharm Chemical Reagent Co., Ltd, China) were used to obtain Au/RGO as electron mediator and conduction-band co-catalyst. Sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, 98%, Aladdin Chemical Co., Ltd, China) and palladium chloride (PdCl_2 , 99%, Sinopharm Chemical Reagent Co., Ltd, China) were used to obtain PdS as valence-band co-catalyst precursor. Silver nitrate (AgNO_3 , 99%, Sinopharm Chemical Reagent Co., Ltd, China) and Ethylenediamine tetraacetic acid (EDTA, analytically pure, Veking Company, China) were used as electron and hole scavengers. Sodium nitrite (NaNO_2 , 99%, Sinopharm Chemical Reagent Co., Ltd, China) was used to make stock and standard solution of NO_2^- . All chemicals were used without further purification.

2.2. Preparation of samples

2.2.1. Preparation of up-conversion luminescence agent ($\text{Er}^{3+}:\text{YAlO}_3$)

$\text{Er}^{3+}:\text{YAlO}_3$ as the up-conversion luminescence agent was prepared by sol-gel and calcination methods [40]. $\text{Y}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions were prepared by dissolving stoichiometric Y_2O_3 (2.7281 g) and Er_2O_3 (0.0464 g) into right quantity of hot HNO_3 aqueous solution (about 60 °C). Then, the prepared solutions were mixed with $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (9.0633 g) with magnetic stirring up to the homogeneous and transparent solution was obtained. Subsequently, added $\text{C}_6\text{H}_8\text{O}_7$ (30.4649 g) into the above mixture solution (molar ratio of citric acid: metal ion is 3:1) and further stirred and heated the solution at 50–60 °C until the transparent sol was formed. And then transferred the transparent sol into

an electrothermal blowing dry box. After heated at 80 °C for 24 h and then cooled down to the room temperature naturally, the obtained xerogel was grinded into fine homogeneous powders. Next, heated the particles at 1100 °C and keep for 2.0 h so that residual organic components and nitrate ions can be removed completely. Finally, after taking it out of the muffle furnace and cooling down in the air, grinded down the sintered substance into uniform powders. And then the desired white $\text{Er}^{3+}:\text{YAlO}_3$ particles were obtained and stored for preparing nanocomposites.

2.2.2. Preparation of BiPO_4

BiPO_4 powders were prepared through hydrothermal process [26]. Firstly, 6.00 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2.91 g) and 60 mL H_3PO_4 (12 mol/L) were put into a beaker while stirring magnetically for 1.0 h to form a homogeneous solution. Subsequently, the obtained suspension was transferred into a 100 mL polytetrafluoroethylene (PTFE) autoclave equipped with a stainless steel shell and maintained at 100 °C without shaking or stirring. After 72 h hydrothermal treatment and cooling down to room temperature in the air, the monoclinic BiPO_4 (space group: $\text{P}2_1/\text{n}$, nMBIP) was obtained, by filtering off, washing with distilled water for several times and being dried at 80 °C for 24 h [41].

2.2.3. Preparation of CdS

The CdS particles were prepared as followed as below. 6.0 mmol $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (1.368 g) was dissolved in 40 mL distilled water. And then 6.0 mmol Na_2S (0.4680 g) was added slowly under continuous stirring. Subsequently, the orange solution was stirred for 30 min and then transferred into a 50 mL polytetrafluoroethylene (PTFE) autoclave equipped with a stainless steel shell and maintained at 100 °C for 4.0 h. After cooling down to room temperature in the air, the orange precipitation was

filtered and washed several times with distilled water and ethanol subsequently, and kept under vacuum at 80 °C for 3.0 h followed by calcination in air for 3.0 h at 500 °C. Finally, grinded down the obtained CdS powders for the following experiments and characterizations.

2.2.4. Preparation of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $(\text{Au}/\text{rGO})/\text{CdS}$

The loading of PdS on $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ producing $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ was realized by deposition-precipitation method with PdS (0.13 wt%) as valence band co-catalyst [42,43]. To begin with, a PdCl_2 aqueous solution (11 mmol/L) was dropwise added into a suspension of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ powder (1.00 g, as prepared above) which dispersed in Na_2S aqueous solution (0.50 mol/L) while stirring magnetically. After centrifugation, washed completely with distilled water and dried at 60 °C for 10 h. And then the obtained powders were calcined in vacuum at 200 °C for 3.0 h. Finally, grinded down the sintered substance into uniform powders and the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ composite was obtained.

Modification of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ with Au/rGO as conduction band co-catalyst was prepared via ultrasonic-assisted method [44]. Firstly, 4.0 mL GO (3.00 mg/mL) and 0.461 mL $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (85%) were added in 16 mL of ethanol and adequately dispersed with sonication (frequency: 80 kHz and output power: 50 W) for 60 min. Subsequently, $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$ (97%) and 1.00 g $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ powder was added to the above obtained rGO solution, and then well-dispersed by ultrasound for 2.0 h. Finally, the obtained mixture was washed with ethanol several times and dried at 60 °C in a dryer for 12 h. After grinding the product into homogeneous powder and annealing in a muffle furnace at 200 °C for 2.0 h, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ powders was obtained.

The modification of CdS with Au/RGO as conduction band co-catalyst was carried out in the

same way.

2.2.5. Preparation of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$

The $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ was prepared via ultrasonic-assisted method. Firstly, 1.00 g $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and 1.00 g $(\text{Au}/\text{rGO})/\text{CdS}$ were added in 50 mL of ethanol and well-dispersed with sonication (frequency: 80 kHz and output power: 50 W) for 2.0 h. And then, the obtained mixture was filtered and washed with ethanol several times and dried at 60 °C for 12 h. After grinding the product into uniform powder and annealing in a muffle furnace at 200 °C for 2.0 h, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ composite was prepared.

2.3. Characterization of prepared samples

The prepared samples were characterized by X-ray diffraction (XRD, D-8, Bruker-axs, Germany), scanning electron microscope (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan), energy dispersive X-ray spectroscopy (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan), X-ray photoelectron spectroscopy (XPS, XSAM800, Shimadzu-Kratos, Japan), UV-vis diffuse reflectance spectra (DRS, UV-3600, SHIMADZU, Japan), fourier transform infrared spectra (FT-IR, Nicolet 5700, Beckman Coulter, America), raman spectra (JY HR800, Horiba, Japan) and photoluminescence spectra (PL, F4500, Hitachi Corporation, Japan). Experiment operations were conducted in a photochemical reaction instrument (TL-GHX-V, Xujiang Electrome Chanical Plant, China). Concentration of nitrite was determined in ion chromatograph (IC, ICS 200, Dionex, China).

2.4. Experiment of stimulated solar-light photocatalytic conversion of nitrite

The stimulated solar-light photocatalytic conversion experiment of nitrite was conducted by using

a photochemical reaction instrument, in which nitrite aqueous solution (50 mL and 10 ppm) and an assigned amount of samples (50 mg) were put in a glass tube. To reach adsorption-desorption equilibrium, the suspension was magnetically and constantly stirred in the dark for 30 min before light irradiation. Then the suspension was irradiated for 8.0 h by using a 1000 W xenon lamp as simulated solar source. At interval of 2.0 h, 3.00 mL solution was sampled and filtered to remove the photocatalysts. The photocatalytic conversion rate of nitrite was determined using the following formula:

$$\text{Stimulated solar-light photocatalytic conversion rate (\%)} = (1 - C_t/C_0) \times 100$$

Where C_0 and C_t were the initial concentration of nitrite and the instant concentration of nitrite, respectively, at irradiation time (t).

3. Results and discussion

3.1. XRD, SEM, TEM, EDX, XPS, DRS, FT-IR, Raman and PL of prepared samples

The phase structures and crystallite sizes of the prepared samples are investigated via XRD. As shown in Fig. 1(a), the $\text{Er}^{3+}:\text{YAlO}_3$ could be indexed to JCPDS #33-0040 of YAlO_3 at $2\theta = 17.95^\circ$ (211), 34.50° (400), 42.11° (422), 45.98° (521) and 56.12° (532) [45]. It displays that the YAlO_3 has formed, in which the Er^{3+} ions enter the crystal lattice replacing the partial Y^{3+} ions. In Fig. 1(b), the $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ exhibits characteristic peaks at $2\theta = 18.13^\circ$, 22.32° and 34.82° attributed to the planes (-101), (-111) and (-202) of nMBIP (monoclinic BiPO_4 (space group: P21/n, nMBIP)). And they are consistent with the standard data JCPDS #80-0209 [41]. Also, it can be found that the characteristic diffraction peaks of $\text{Er}^{3+}:\text{YAlO}_3$ also appear in Fig. 1(b). As depicted in Fig. 1(c and d), the XRD patterns of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ are very

similar to that of $\text{Er}^{3+}:\text{YAlO}_3@ \text{BiPO}_4$. And the characteristic diffraction peaks of PdS and Au/rGO are difficult to be found due to the small proportion of them. Fig. 1(e and f) show the main peak positions appear at $2\theta = 24.91^\circ, 26.52^\circ, 28.34^\circ, 37.01^\circ, 43.85^\circ, 48.17^\circ$ and 52.3° corresponding to the (100), (002), (101), (102), (110), (103) and (112) planes, which are successfully indexed to hexagonal wurtzite phase of CdS and consistent with JCPDS #41–1069 [32]. In Fig. 1(g), the XRD pattern of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ is given. The main characteristic diffraction peaks of $\text{Er}^{3+}:\text{YAlO}_3$, BiPO_4 and CdS can be clearly found, which demonstrates that the sample has been successfully composited.

Fig. 1.

The SEM images of prepared samples are all given in Fig. 2. As shown in Fig. 2(a), it can be seen that there are numerous particles with an average size of approximately 80 nm, which are identified as the $\text{Er}^{3+}:\text{YAlO}_3$ particles. From the image depicted in Fig. 2(b), it can be found that $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 have been combined together to form a coated structure. The prepared monoclinic BiPO_4 (space group: P21/n, nMBIP) are some cuboid nanoparticles with length about 300 nm. Fig. 2(c) demonstrates that the surfaces of BiPO_4 are loaded with some small particles with diameter of nearly 30 nm. These particles were attributed to PdS nanoparticles. In Fig. 2(d), it can be clearly seen that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ is covered with rGO sheet and some Au particles are dispersed on it. It displays that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/\text{rGO}$ has been prepared. It can be seen that in Fig. 2(e) there are irregular spherical particles with diameters in the range of 40–60 nm, which should attribute to the typical crystal form of nano-sized CdS particles. From Fig. 2(f), the CdS particles were loaded on the rGO sheet and some Au particles dispersed on it. It indicates that the $(\text{Au}/\text{rGO})/\text{CdS}$ has

successfully prepared. Fig. 2(g) showed the overall morphology of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$, which was composed of different size nanospheres. Obviously, many irregular spherical nanospheres CdS and Au are loaded on surface of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$. The rGO is transparent and hard to be found. And the sample exhibits obvious agglomeration.

Fig. 2.

An in-depth observation is further performed by TEM shown in Fig. 3. As can be seen in Fig. 3(a, b and c), the rGO sheets are transparent and plicate, which illustrates that the rGO sheets are quite thin and in disorder. In addition, CdS and Au nanoparticles are distributed randomly on the surface of sheetlike reduced graphene. From Fig. 3(d), it can be noticed that the darker parts are $\text{Er}^{3+}:\text{YAlO}_3$ nanoparticles coated into the BiPO_4 . Of which the PdS nanoparticles are dispersed on the surface. Besides, rGO attached with Au of smaller particle size are also dispersed. As can be observed for $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ in Fig. 5(e), the TEM image reveals the morphology of Z-scheme photocatalyst. It can be found clearly that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{BiPO}_4)$ and CdS particles are linked by the Au particles layed on the surface of rGO sheets. Meanwhile, both PdS and Au/rGO, as valence band co-catalyst and conduction band co-catalyst, are presented.

Fig. 3.

To investigate the chemical composition and state, the EDX spectra of prepared $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ are shown in Fig. 4. The result displays the peaks of Er, Y, Al and O elements, which demonstrated the composition of $\text{Er}^{3+}:\text{YAlO}_3$ as up-conversion luminescence agent. Besides, the peaks of Bi, P, Cd and S elements can be clearly observed, which

belong to the BiPO_4 and CdS , separately. The EDX data also shows the peaks of Pd, Au and C elements, displaying the existence of PdS and Au/rGO . The result is close to the stoichiometric ratio simultaneously.

Fig. 4.

Elementary composition and valence bond structure of the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS/BiPO}_4)/(\text{Au/rGO})/\text{CdS}$ is characterized by XPS, shown in Fig. 5. It indicates that the nanocomposite contains Er, Y, Al, O, Pd, S, Bi, P, Au, C and Cd elements and the corresponding peaks are plotted carefully. Thereinto, Fig. 5(o) showed the fully XPS scanned spectra of the prepared $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS/BiPO}_4)/(\text{Au/rGO})/\text{CdS}$. The presented peaks at 173 eV (Er 4d), 150 eV (Y 3d), 101 eV (Al 2s) and 531 eV (O 1s) are closely agreed with the composition of $\text{Er}^{3+}:\text{YAlO}_3$ [46]. The characteristic peaks of Bi (165 eV 4f and 24 eV 5d) and S (163 eV 2p) can be clearly observed in the wide scan spectrum as shown in Fig. 5(o) and the binding energy peaks located at 405 eV, 412 eV, 337 eV, 340 eV and 133 eV are well matched with the values of Cd $3d_{5/2}$, Cd $3d_{3/2}$, Pd $5_{5/2}$, Pd $3_{3/2}$ and P 2p, shown in Fig. 5(a, b and c) [47–49]. These implied that BiPO_4 , CdS and PdS are successfully composited. Besides these characteristic peaks, there are three peaks at 286 eV, 88 eV and 84 eV, which belonged to C (1s), Au ($4f_{7/2}$) and Au ($4f_{7/2}$), respectively, indicating the existence of Au/rGO .

Fig. 5.

The UV-vis diffuse reflectance spectra (DRS) of prepared $\text{Er}^{3+}:\text{YAlO}_3$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS/BiPO}_4)$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS/BiPO}_4)/(\text{Au/rGO})$, CdS , $(\text{Au/rGO})/\text{CdS}$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS/BiPO}_4)/(\text{Au/rGO})/\text{CdS}$ are shown in Fig. 6. It is depicted in Fig. 6(a) that the $\text{Er}^{3+}:\text{YAlO}_3$ has apparent absorption in both visible-light and infrared-light regions, which indicates

that, as up-conversion luminescence agent, the $\text{Er}^{3+}:\text{YAlO}_3$ could utilize most visible-light and infrared-light of solar spectrum and convert them into high-energy ultraviolet-light. From Fig. 6(b) it can be confirmed that, due to the presence of $\text{Er}^{3+}:\text{YAlO}_3$, the $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ still displays the absorption in visible-light and infrared-light regions. Though the absorption values are relatively low on account of the small proportion of $\text{Er}^{3+}:\text{YAlO}_3$, it maybe plays a significant role in the stimulated solar-light photocatalytic conversion of nitrite, so that the wide-band semiconductor can utilize the visible-light and infrared-light of solar spectrum constantly. Due to the existence of Au/rGO, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ shows enhanced absorption intensity in the range of 300–800 nm observed in Fig. 6(c). As can be seen from Fig. 6(d), due to the addition of Au/rGO, the (Au/rGO)/CdS shows the stronger intensity than CdS. It is demonstrated in Fig. 6(e) that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ shows a apparently enhanced absorption intensity comparing with $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and (Au/rGO)/CdS, suggesting that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ may absorb solar spectrum more efficiently, and would probably exhibit good simulated solar-light photocatalytic activity.

Fig. 6.

According to Fig. 7(a and c), the bandwidths of $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ and pure CdS are estimated to be 3.83 eV and 2.36 eV, respectively, which are close to the results in the previously reported literatures [49,50]. And due to the addition of co-catalyst, the bandwidths of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and (Au/rGO)/CdS display slight decreases, estimated to be about 3.77 eV and 2.32 eV, respectively.

Fig. 7.

To provide chemical information about the bonding structure in the samples, the FT-IR spectra of prepared $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, $(\text{Au}/\text{rGO})/\text{CdS}$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ are shown in Fig. 8. From Fig. 8(a) it can be confirmed that the peak at about 3431 cm^{-1} is probably attributed to $\nu(\text{O}-\text{H})$ of the coordinated water to the bismuth atoms in the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ [51]. The peak locates around 1009 cm^{-1} is resulting from the ν_3 anti-symmetry stretching vibration of the P-O bond [52]. The bending vibration of the O-P-O linkages appear around 607 cm^{-1} and 521 cm^{-1} [53]. As can be seen in Fig. 8(b), the peaks center around 3438 cm^{-1} and 3295 cm^{-1} are due to the $\nu(\text{O}-\text{H})$ stretching vibrations. The peak locates at 1601 cm^{-1} is assigned to the C=C skeletal vibration of graphene sheets [54]. The sharp peak at 1147 cm^{-1} can be attributed to the Cd-S bond and other peaks around 613 cm^{-1} and 517 cm^{-1} assigned to Cd-S stretching vibrations are also observed [55–57]. Fig. 8(c) shows the characteristic peak of O-H stretching vibrations around 3422 cm^{-1} , the C=C skeletal vibration of graphene sheets around 1631 cm^{-1} , ν_3 anti-symmetry stretching vibration of the P-O bond around 1087 cm^{-1} and 1085 cm^{-1} and Cd-S stretching vibrations around 607 cm^{-1} and 520 cm^{-1} , respectively.

Fig. 8.

In order to investigate the valance bond interaction, the characteristic Raman spectra of samples are tested. In Fig. 9(a), $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ has the intense band observed at 530 cm^{-1} , which can be ascribed to the ν_4 bending mode of PO_4 unit [58]. The peaks centered at 970 cm^{-1} and 1038 cm^{-1} are due to the ν_3 asymmetric and ν_1 symmetric stretching vibrations of the PO_4 unit, respectively. As shown in Fig. 9(b), $(\text{Au}/\text{rGO})/\text{CdS}$ has the two characteristic peaks of 298 cm^{-1} and 598 cm^{-1} , which are corresponded to the 1st and 2nd longitudinal optical-phonon (LO) modes in CdS

[59]. As depicted in Fig. 9(c), the crystal structure of the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ is not changed, and the all characteristic peaks of BiPO_4 and CdS are appeared.

Fig. 9.

The PL spectra is a significant method to confirm the recombination of the photo-generated electron-hole pairs in semiconductor [60,61]. Generally, the lower intensity signal in PL spectra indicates lower recombination of electron-hole pairs. Conversely, the higher intensity of PL shows higher recombination of electron-hole pairs [62]. Fig. 10(a) shows the PL spectra of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. It can be clearly found that the PL intensity of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ is the lowest one, which reveals that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ possess the lowest recombination of electron-hole pairs. This may be the reason that the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ could display the best photocatalytic activity. The sequence based on the intensities is essentially $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4) > \text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO}) > \text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. As shown in Fig. 10(b), the $(\text{Au}/\text{rGO})/\text{CdS}$ shows weaker PL signal, indicating that the separation of photo-generated electron-hole pairs has been improved greatly. Furthermore, the photo-generated electron-hole pairs will transfer to the surface of CdS more efficiently. Overall, it was confirmed that the adding of co-catalysts can promote the separation of electron-hole pairs to some extent. Moreover, Z-scheme structure can retard the recombination of electron-hole pairs apparently due to the electron mediator, in which electrons and holes are bonding. Consequently, the modified Z-scheme photocatalyst probably has an excellent photocatalytic

performance.

Fig. 10.

3.2. Effects of ultraviolet-light and simulated solar-light on photocatalytic conversion rates of nitrite

Fig. 11 shows the effects of ultraviolet-light and simulated solar-light on the photocatalytic conversions of nitrite over $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, $(\text{Au}/\text{rGO})/\text{CdS}$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. In addition, for CdS , $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ the photocatalytic conversions of nitrite were also investigated for comparison. After 8.00 h irradiation, nitrite ions for different photocatalysts and light sources were converted in varying degrees. At first, under ultraviolet-light irradiation, for all used photocatalysts they displayed relatively high photocatalytic activities in the conversions of nitrite. Among them, the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ caused 94.59 % photocatalytic conversion rate of nitrite, displaying the highest photocatalytic activity. And the conversion rate of 83.33% was obtained over the $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$. Overall, these prepared photocatalysts with or without the up-conversion luminescence agent, $\text{Er}^{3+}:\text{YAlO}_3$, all displayed good photocatalytic activity under ultraviolet-light irradiation. Secondly, under simulated solar-light irradiation, the sequence based on the photocatalytic conversion rates was essentially $\text{CdS} < (\text{Au}/\text{rGO})/\text{CdS} < \text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4) < \text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO}) < \text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. It is found that, due to the presence of $\text{Er}^{3+}:\text{YAlO}_3$, the irradiated simulated solar-light can be converted into ultraviolet-light, which can effectively stimulate the wide-band semiconductor BiPO_4 . And the enhancement of photocatalytic activity can be attributed

to the higher separation efficiency of the photo-generated electron-hole pairs and lower recombination rate, which resulted from the modified Z-scheme structure photocatalysts. Particularly, the reasons why $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ exhibited the best photocatalytic activity were that not only the functions as valence band co-catalyst and conduction band co-catalyst for Au/RGO and PdS, but also the rGO, which served as a good two-dimensional layered conductor, could greatly match with layered semiconductors and enhance their conductivity, facilitating fast charge transfer. Additionally, it is worth pointing out that the metallic Au species are excellent solid state electron mediator as well.

Fig. 11.

3.3. Effects of simulated solar-light irradiation time and corresponding reaction kinetics on photocatalytic conversion rate of nitrite

The stimulated solar-light photocatalytic conversion of nitrite caused by three prepared nanocomposites, $(\text{Au}/\text{rGO})/\text{CdS}$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$, were conducted under simulated solar-light irradiation. Before light irradiation, the solutions were stirred in the dark for 30 min magnetically and constantly to reach the adsorption-desorption equilibrium. Then, the solution samples were taken out every 2.0 h for examining the conversion rates of nitrite by ion chromatograph. From Fig. 12, it can be seen that, the stimulated solar-light photocatalytic conversion rate in the presence of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ increased faster with the increase of simulated solar-light irradiation time than other two photocatalysts ($\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$) under the same conditions. Within 8.00 h irradiation, the

stimulated solar-light photocatalytic conversion rates of nitrite reached 77.59%, 86.73% and 91.25%, respectively, for (Au/rGO)/CdS, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. Therefore, it was concluded that the strategy of adding up-conversion luminescence agent ($\text{Er}^{3+}:\text{YAlO}_3$) to acquire high photocatalytic activity under simulated solar-light irradiation can be applied in the photocatalytic conversion reaction of nitrite by using other wide-band semiconductor. Meanwhile, the modification of Z-scheme structure photocatalyst could be used widely to enhance the photocatalytic activity.

In order to infer the stimulated solar-light photocatalytic conversion rates of nitrite caused by these photocatalysts, the reaction kinetics were investigated as shown in Fig. 8. It can be seen that all $-\ln(C_t/C_0)$ data for first-order reaction and irradiation time (t) were able to be considered as approximately linear relationships. The reaction kinetic equations corresponding to $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, (Au/rGO)/CdS and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ were found to be $-\ln(C_t/C_0) = 0.2528t - 0.0687$ ($R^2 = 0.9941$), $-\ln(C_t/C_0) = 0.1883t + 0.0449$ ($R^2 = 0.9938$) and $-\ln(C_t/C_0) = 0.3007t - 0.0839$ ($R^2 = 0.9888$), respectively. The rate constants were 0.2528 min^{-1} , 0.21883 min^{-1} , 0.3007 min^{-1} , respectively, for $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$, (Au/rGO)/CdS and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. Thus, the order of stimulated solar-light photocatalytic conversion rates of nitrite for these photocatalysts can be judged as (Au/rGO)/CdS < $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ < $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$.

Fig. 12.

3.4. Effects of electron and hole scavengers on stimulated solar-light photocatalytic conversion of nitrite

To further investigate the process and mechanism of the stimulated solar-light photocatalytic conversion of nitrite under simulated solar-light irradiation caused by $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$, Ag^+ and EDTA were used as electron and hole scavengers, respectively. As depicted in Fig. 13(a), the stimulated solar-light photocatalytic conversion rates of nitrite displayed an apparent decline and reached 56.92%, 59.80% and 62.67%, respectively, over $(\text{Au}/\text{rGO})/\text{CdS}$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ in the presence of Ag^+ . And stimulated solar-light photocatalytic conversion rate that based on NO_3^- was a little bit higher than that based on NH_4^+ and N_2 . This demonstrated that Ag^+ , which was acted as an electron scavenger, competed with nitrite ions on the conduction band (CB). Meanwhile, Ag^+ was effectively oxidized, causing a decreased conversion of NO_2^- to NH_4^+ or N_2 , but an increased conversion of NO_2^- to NO_3^- . As shown in Fig. 13(b), in the presence of EDTA, the stimulated solar-light photocatalytic conversion rates of nitrite were also decreased and reached 65.59%, 59.03% and 77.34%, respectively, over $(\text{Au}/\text{rGO})/\text{CdS}$, $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$. Conversely, the stimulated solar-light photocatalytic conversion rates that based on NH_4^+ and N_2 were much higher than that based on NO_3^- , which showed that EDTA had acted as an electron scavenger and competed with nitrite ions on the valence band (VB). Moreover, EDTA was availably reduced causing a decreased conversion of NO_2^- to NH_4^+ or N_2 , but an increased conversion of NO_2^- to NO_3^- . It can be clearly seen that the oxidation and reduction reactions of the NO_2^- ions should occur on the conduction band (CB) and valence band (VB), respectively, producing the NH_4^+ , N_2 and NO_3^- . Additionally, it was found that the use of electron scavenger could facilitate the reaction on valence band and the use of hole scavenger could accelerate the reaction on conduction band as well.

Fig. 13.

3.5. Effects of used times on stimulated solar-light photocatalytic conversion rate of nitrite over $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$

The stability of photocatalytic activity of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ was evaluated by repeating experiments on the stimulated solar-light photocatalytic conversion of nitrite under simulated solar-light irradiation as shown in Fig. 14. It can be obviously found that, for $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$, the stimulated solar-light photocatalytic conversion rates of nitrite decreased only slightly along with the increase of used times. The stimulated solar-light photocatalytic conversion rate still reached 85.15% after five cycles, indicating that the photocatalytic activity of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ can be maintained for long time to highly effectively convert nitrite under simulated solar light irradiation.

Fig. 14.

3.6. Possible mechanism on simulated solar-light photocatalytic conversion of nitrite in the presence of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$

The possible mechanism on stimulated solar-light photocatalytic conversion of nitrite for the prepared $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ under simulated solar-light is proposed in Fig. 15. Firstly, the $\text{Er}^{3+}:\text{YAlO}_3$ as up-conversion luminescence agent was coated into the BiPO_4 particles. While irradiated by continuous simulated solar-light, the $\text{Er}^{3+}:\text{YAlO}_3$ can be excited and then emit the ultraviolet-light, which can effectively activate the BiPO_4 . Based on the energy level data of $\text{Er}^{3+}:\text{YAlO}_3$, the up-conversion process can be accomplished through the chains of ground state absorption (GSA) and excited state absorption (ESA) [63]. By absorbing two or more low-energy

photons, the $\text{Er}^{3+}:\text{YAlO}_3$ could generate one high-energy photon while under excitation of continuous simulated solar-light. The bands around 326–342 nm and 354–359 nm were observed under the excitation of 652 nm (or 658 nm) [64]. Additionally, the bands around 318 nm and 320 nm could be observed under the excitation of 486 nm and 542 nm (or 548 nm) [65], respectively. Therefore, the $\text{Er}^{3+}:\text{YAlO}_3$, who will demonstrate the response in solar-light region to emit high-energy ultraviolet-light, can emit the ultraviolet-light which efficiently stimulates BiPO_4 to carry out simulated solar-light photocatalytic conversion of nitrite.

Secondly, the modified Z-scheme photocatalytic system was constructed by employing Au/rGO as the electron mediator. Since the simulated solar-light is acted as irradiation source, BiPO_4 can be activated under the irradiation of ultraviolet light emitted by $\text{Er}^{3+}:\text{YAlO}_3$, the photo-generated electrons from valence-band (VB) of BiPO_4 leaped to the conduction-band (CB), creating photogenerated holes in the valence-band (VB). At the same time, CdS was activated under the simulated solar-light, leading electrons to transfer from the valence band (VB) to conduction band (CB) generating electron-hole pairs. The photo-generated electrons from the conduction band (CB) of BiPO_4 could directly bond with the photo-generated holes from the valence band of CdS through the Au/rGO. Then the photo-generated electrons and holes could annihilate at Au. Therefore, the bonding of electron-hole pairs in Au could efficiently restrain the recombination rate of electron-hole pairs in BiPO_4 and CdS. And the left photo-generated holes in the valence-band (VB) of BiPO_4 could be injected into PdS deposited on the surface of BiPO_4 as valence-band co-catalyst. Due to the high oxidization capacity, the photo-generated holes were quickly convert NO_2^- to NO_3^- . In the meantime, the photo-generated electrons, which were injected into the Au/rGO as valence-band co-catalyst of CdS, reduced the NO_2^- to NH_4^+ or N_2 due to the highly reduction capacity. Overall, according to the Z-scheme electrons and

holes transfer process, the reduction and oxidation capacities of electrons and holes could be strengthened, thus enhancing the photocatalytic ability.

The possible mechanism on the simulated solar-light photocatalytic conversion of nitrite over $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ was as follows:

Fig. 15.

4. Conclusions

In this study, the modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalyst for simulated solar-light photocatalytic conversion of nitrite was successfully prepared by hydrothermal, ultrasonic dispersion, deposition-precipitation and ultrasonic-assisted methods. Due to the uses of the up-conversion luminescence agent ($\text{Er}^{3+}:\text{YAlO}_3$), the co-catalysts (PdS and Au/rGO) and the electron

mediator (Au/rGO), the photocatalyst exhibited an excellent photocatalytic activity, resulting in 91.25% under simulated solar light irradiation. Therefore, the modified Z-scheme $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ photocatalyst is suitable to be applied in dealing with nitrite and other contaminants by utilizing solar energy. Otherwise, the prepared photocatalyst can be effectively recycled for five repetitive cycles without an apparent deactivation on the photocatalytic activity. It is wished that these research results could provide a promising strategy to prepare the novel and efficient photocatalysts for utilization of solar energy and purification of drinking water in the future.

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References

- [1] W.L. Gao, J.X. Chen, X.X. Guan, R.C. Jin, F.X. Zhang, N.J. Guan, Catalytic reduction of nitrite ions in drinking water over Pd–Cu/TiO₂ bimetallic catalyst, *Catal. Today* 93 (2004) 333–339.
- [2] Y.Y. Zhang, Y. Jia, G.G. Xu, Y.N. He, W. Kang, Photocatalytic reduction of nitrite over TiO₂-Graphene oxide composites, *Environ. Eng. Sci.* 32 (2015) 631–636.
- [3] H.J. Hamlin, B.C. Moore, T.M. Edwards, I.L.V. Larkin, A. Boggs, W.J. High, K.L. Main, L.J.G. Jr,

- Nitrate-induced elevations in circulating sex steroid concentrations in female Siberian sturgeon (*Acipenser baeri*) in commercial aquaculture, *Aquaculture* 281 (2008) 118–125.
- [4] I. Galavizvilla, Agricultural contamination of subterranean water with nitrates and nitrites: an environmental and public health problem, *J. Agr. Sci. Cambridge* 12 (2010) 6630–6646.
- [5] C.L. Constantinou, C.N. Costa, A.M. Efstathiou, Catalytic removal of nitrates from waters, *Catal. Today* 151 (2010) 190–194.
- [6] N. Barrabés, J. Sá, Catalytic nitrate removal from water, past, present and future perspectives, *Appl. Catal. B: Environ.* 104 (2011) 1–5.
- [7] F.A. Sayão, L. Nuñez, M.V.B. Zanoni, Efficient photoelectrochemical reduction of nitrite to ammonium and nitrogen containing gaseous species using Ti/TiO₂ nanotube electrodes, *J. Braz. Chem. Soc.* 25 (2014) 1153–1160.
- [8] S. Samatya, N. Kabay, Ümran, Yüksel, M. Arda, M. Yüksel, Removal of nitrate from aqueous solution by nitrate selective ion exchange resins, *React. Funct. Polym.* 66 (2006) 1206–1214.
- [9] Y.L. Zhao, D. Zhao, D.L. Li, Electrochemical and Other Methods for Detection and Determination of Dissolved Nitrite: A Review, *Int. J. Electrochem. Sci.* 10 (2015) 1144–1168.
- [10] M. Mishra, D.M. Chun, α -Fe₂O₃ as a photocatalytic material: A review, *Appl. Catal. A: Gen.* 498 (2015) 126–141.
- [11] Y. Peng, M. Yan, Q.G. Chen, C.M. Fan, H.Y. Zhou, A.W. Xu, Novel one-dimensional Bi₂O₃-Bi₂WO₆ p-n hierarchical heterojunction with enhanced photocatalytic activity, *J. Mater. Chem. A* 2 (2014) 8517–8524.
- [12] Y. Wang, L.X. Liu, L. Xu, X.X. Cao, X.H. Li, Y.J. Huang, C.M. Meng, Z.G. Wang, W.J. Zhu, Ag₂O/TiO₂/V₂O₅ one-dimensional nanoheterostructures for superior solar light photocatalytic activity, *Nanoscale* 6 (2014) 6790–6797.
- [13] C. Chen, W. Ma, J. Zhao, Semiconductor-mediated photodegradation of pollutants under visible-light irradiation, *Chem. Soc. Rev.* 39 (2010) 4206–4219.
- [14] Y.D. Wang, B.W. Li, G.S. Li, Y. Y. Huang, D. W. Fang, J. Wang, Y.T. Song, Photocatalytic conversion of nitrite in aqueous solution over nanocomposite photocatalyst Er³⁺:Y₃Al₅O₁₂/BiPO₄ using different photosources, *J. Ind. Eng. Chem.* 47 (2017) 74–85.
- [15] M.Tu, H.A. Abbood, Z. Zhu, H. Li, Z. Gao, Investigation of the photocatalytic effect of zinc oxide nanoparticles in the presence of nitrite, *J. Hazard. Mater.* 244 (2013) 311–321.

- [16] A. Hérissan, J.M. Meichtry, H. Remita, C. Colbeau-Justin, M.I. Litter, Reduction of nitrate by heterogeneous photocatalysis over pure and radiolytically modified TiO₂ samples in the presence of formic acid, *Catal. Today* 281 (2017) 101–108.
- [17] L.F. Liu, Y. Zhang, F.L. Yang, G. Chen, J.C. Yu, Simultaneous photocatalytic removal of ammonium and nitrite in water using Ce³⁺-Ag⁺ modified TiO₂, *Sep. Purif. Technol.* 67 (2009) 244–248.
- [18] X. Liu, N. Chen, Y.X. Li, D.Y. Deng, X.X. Xing, Y.D. Wang, Study of dynamic recrystallization in a Ni-based superalloy by experiments and cellular automaton model, *Sci. Rep.* 6 (2016) 39531.
- [19] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, All-solid-state Z-scheme in CdS-Au-TiO₂ three-component nanojunction system, *Nat. Mater.* 5 (2006) 782–786.
- [20] J. Li, H. Yuan, Z. Zhu, Selective silver seeding on laser modified polyimide for electroless copper plating, *Appl. Surf. Sci.* 385 (2016) 34–41.
- [21] A. Iwase, Y. H. Ng, Y. Ishiguro, A. Kudo, R. Amal, Reduced graphene oxide as a solid-state electron mediator in Z-scheme photocatalytic water splitting under visible light, *J. Am. Chem. Soc.* 133 (2011) 11054–11057.
- [22] K. Maeda, Solar-driven Z-scheme water splitting using modified BaZrO₃-BaTaO₂N solid solutions as photocatalysts, *ACS Catal.* 3 (2013) 1486–1503.
- [23] H. Lin, J. Cao, B. Luo, B. Xu, S. Chen, Synthesis of novel Z-scheme AgI/Ag/AgBr composite with enhanced visible light photocatalytic activity, *Catal. Commun.* 21 (2012) 91–95.
- [24] Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, Solar water splitting using powdered photocatalysts driven by Z-schematic interparticle electron transfer without an electron mediator, *J. Phys. Chem. C* 113 (2009) 17536–17542.
- [25] Y. Zhu, C. Zhi, G. Tong, Q. Huang, N. Feng, L. Qin, Construction of hybrid Z-scheme Pt/CdS-TNTAs with enhanced visible-light photocatalytic performance, *Appl. Catal. B: Environ.* 163 (2015) 16–22.
- [26] C.S. Pan, Y.F. Zhu, New type of BiPO₄ oxy-acid salt photocatalyst with high photocatalytic activity on degradation of dye, *Environ. Sci. Technol.* 44 (2010) 5570–5574.
- [27] F. Duo, Y. Wang, X. Mao, X. Zhang, Y. Wang, C. Fan, A BiPO₄/BiOCl heterojunction photocatalyst with enhanced electron-hole separation and excellent photocatalytic performance, *Appl. Surf. Sci.* 340 (2015) 35–42.
- [28] Y. Chen, C.X. Lu, L. Tang, S.N. Wei, Y.H. Song, J. Wang, Efficient photocatalytic hydrogen evolution

- from methanol/water splitting over $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles under infrared-visible light irradiation, *Sol. Energ. Mat. Sol. C.* 149 (2016) 128–136.
- [29] H.B. Zhang, C.H. Ma, Y. Li, Y. Chen, C.X. Lu, J. Wang, Sol–gel-hydrothermal synthesis of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Pt-TiO}_2$ membrane and visible-light driving photocatalytic hydrogen evolution from pollutants, *Appl. Catal. A: Gen.* 503 (2015) 209–217.
- [30] T. Grzyb, A. Gruszczyńska, S. Lis, Up-conversion luminescence of Yb^{3+} and Er^{3+} doped YPO_4 , LaPO_4 and GdPO_4 nanocrystals, *J. Lumin.* 175 (2016) 21–27.
- [31] Y. Zhang, R. Selvaraj, M. Sillanpää, Y. Kim, C.W. Tai, Coprecipitates synthesis of CaIn_2O_4 and its photocatalytic degradation of methylene blue by visible light irradiation, *J. Ind. Eng. Chem.* 24 (2014) 161–165.
- [32] C.H. Ma, L. Zhang, Y. Li, J.Q. Gao, J. Wang, Study on photocatalytic activity of $\text{Er}^{3+}:\text{YAlO}_3/\text{TiO}_2$ composite films supported on electrically conductive glass (FTO) in visible-light photocatalytic degradation of organic dye, *Sep. Purif. Technol.* 148 (2015) 76–84.
- [33] T. Lv, L. Pan, X. Liu, Z. Sun, Enhanced visible-light photocatalytic degradation of methyl orange by $\text{BiPO}_4\text{-CdS}$ composites synthesized using a microwave-assisted method, *RSC Adv.* 2 (2012) 12706–12709.
- [34] D. Chen, Z. Kuang, Q. Zhu, Y. Du, H. Zhu, Synthesis and characterization of CdS/BiPO_4 heterojunction photocatalyst, *Mater. Res. Bull.* 66 (2015) 262–267.
- [35] D.F. Zhang, L. Zhang, Construction of a three-dimensional nest-like lithium ferrite/reduced graphene oxide composite with enhanced visible-light photocatalytic activity, *New J. Chem.* 40 (2016) 7171–7180.
- [36] D.B. Nimbalkar, Improved photocatalytic activity of RGO/MoS_2 nanosheets decorated on TiO_2 nanoparticles, *Rsc Adv.* 6 (2016) 31661–31667.
- [37] J.Q. Li, H. Yuan, Z. Zhu, Fabrication of $\text{Cu}_2\text{O}/\text{Au}/\text{BiPO}_4$ Z-scheme photocatalyst to improve the photocatalytic activity under solar light, *J. Mol. Catal. A: Chem.* 410 (2015) 133–139.
- [38] F. Hung, Y.C. Yu, N.T. Suen, G.Q. Tzeng, C.W. Tung, Y.Y. Hsu, C.S. Hsu, C.K. Chang, T.S. Chan, H.S. Sheu, J.F. Lee, H. M. Chen, The synergistic effect of a well-defined Au@Pt core–shell nanostructure toward photocatalytic hydrogen generation: interface engineering to improve the Schottky barrier and hydrogen-evolved kinetics, *Chem. Commun.* 52 (2016) 1567–1570.
- [39] A.L. Luna, E. Novoseltceva, E. Louarn, P. Beaunier, E. Kowalska, B. Ohtanic, M.A. Valenzuelad, H.

- Remita, C.C. Justin, Synergetic effect of Ni and Au nanoparticles synthesized on titania particles for efficient photocatalytic hydrogen production, *Appl. Catal. B: Environ.* 191 (2016) 18–28.
- [40] Y. Li, Y.W. Guo, S.G. Li, L. Ying, J. Wang, Efficient visible-light photocatalytic hydrogen evolution over platinum supported titanium dioxide nanocomposites coating up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Pt-TiO}_2$), *Int. J. Hydrogen Energy* 40 (2015) 2132–2140.
- [41] C.S. Pan, D. Li, X.G. Ma, Y. Chen, Y.F. Zhu, Effects of distortion of PO_4 tetrahedron on the photocatalytic performances of BiPO_4 , *Catal. Sci. Technol.* 1 (2011) 121–131.
- [42] Y.H. Pai, C.T. Tsai, S.Y. Fang, Enhanced photocatalytic hydrogen generation with Pt nanoparticles on multi-phase polycrystalline microporous MnO_2 photocatalyst, *J. Power Sources* 223 (2013) 107–113.
- [43] J.L. Meng, Z.M. Yu, Y. Li, Y.D. Li, PdS-modified CdS/NiS composite as an efficient photocatalyst for H_2 evolution in visible light, *Catal. Today* 225 (2014) 136–141.
- [44] N.T. Khoa, S.W. Kim, D.V. Thuan, H.N. Tien, S.H. Hur, E.J. Kim, S.H. Hahn, Fast and effective electron transport in Au-graphene-ZnO hybrid for enhanced photocurrent and photocatalysis, *RSC Adv.* 5 (2015) 63964–63969.
- [45] C.X. Lu, Y. Chen, H.B. Zhang, L. Tang, S.N. Wei, Y.H. Song, J. Wang, Photocatalytic degradation of organic dyes by $\text{Er}^{3+}:\text{YAlO}_3/\text{Co}$ - and Fe-doped ZnO coated composites under solar irradiation, *Res. Chem. Intermediat.* 42 (2016) 4651–4668.
- [46] Y. Shimizu, K. Ueda, Determination of 4f energy levels for trivalent lanthanide ions in YAlO_3 by X-ray photoelectron spectroscopy, *Thin Solid Films* 614 (2016) 69–72.
- [47] Q. Gu, J.L. Long, H.Q. Zhuang, C.Q. Zhang, Y.Q. Zhou, X.X. Wang, Ternary $\text{Pt/SnO}(x)/\text{TiO}_2$ photocatalysts for hydrogen production: consequence of Pt sites for synergy of dual co-catalysts, *Phys. Chem. Chem. Phys.* 16 (2014) 12521–12534.
- [48] J. Batista, A. Pinar, D. Mandrino, M. Jenko, V. Martin, XPS and TPR examinations of γ -alumina-supported Pd-Cu catalysts, *Appl. Catal. A: Gen.* 206 (2001) 1131–124.
- [49] Y.Y. Huang, H.B. Zhang, C.S. Wei, G.S. Li, Q. Wu, J. Wang, Y.T. Song, Assisted sonocatalytic degradation of pethidine hydrochloride (dolantin) with some inorganic oxidants caused by CdS-coated ZrO_2 composite, *Sep. Purif. Technol.* 172 (2017) 202–210.
- [50] S. Obregón, Y. Zhang, G. Colón, Cascade charge separation mechanism by ternary heterostructured $\text{BiPO}_4/\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalyst, *Appl. Catal. B: Environ.* 184 (2016) 96–103.

- [51] L. She, G. Tan, H. Ren, C. Xu, C. Zhao, A. Xia, BiPO₄@glucose-based C core-shell nanorod heterojunction photocatalyst with enhanced photocatalytic activity, *J. Alloy Compd.* 662 (2015) 220–231.
- [52] Y.H. Zhang, B. Shen, H.W. Huang, Y. He, B. Fei, F.Z. Lv, BiPO₄/reduced graphene oxide composites photocatalyst with high photocatalytic activity, *Appl. Surf. Sci.* 319 (2014) 272–277.
- [53] L.C. Kravitz, J.D. Kingsley, E.L. Elkin, Raman and infrared studies of coupled PO₄³⁻ vibrations, *J. Chem. Phys.* 49 (1968) 4600–4610.
- [54] Q.L. Zhang, Y.W. Zhang, Z.H. Gao, H.L. Ma, S.J. Wang, J. Peng, J.Q. Li, M.L. Zhai, A facile synthesis of platinum nanoparticle decorated graphene by one-step γ -ray induced reduction for high rate supercapacitors, *J. Mater. Chem. C* 1 (2012) 321–328.
- [55] S. Mancipe, F. Tzompantzi, R. Gómez, Synthesis of CdS/MgAl layered double hydroxides for hydrogen production from methanol-water decomposition, *Appl. Clay Sci.* 136 (2017) 67–74.
- [56] A.S. Sabah, A. Siddiqi, S. Ali, Fabrication and characterization of CdS nanoparticles annealed by using different radiations, *World Acad. Sci. Eng. Technol.* 70 (2010) 82–89.
- [57] A. Arabzadeh, A. Salimi, One dimensional CdS nanowire@TiO₂ nanoparticles core-shell as high performance photocatalyst for fast degradation of dye pollutants under visible and sunlight irradiation, *J. Colloid Interf. Sci.* 479 (2016) 43–54.
- [58] G. Lakshminarayana, T.D. Dao, K. Chen, M. Sharma, T. Takeda, M.G. Brik, I.V. Kityk, S. Singh, T. Nagao, Effect of different surfactants on structural and optical properties of Ce³⁺ and Tb³⁺ co-doped BiPO₄ nanostructures, *Opt. Mater.* 39 (2015) 110–117.
- [59] R. Rossetti, S. Nakahara, L.E. Brus, Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution, *Chem. Phys.* 79 (1983) 1086–1088.
- [60] T.N. Reddy, J. Manna, R.K. Rana, Biomimetic method to assemble nanostructured Ag@ZnO on cotton fabrics: application as self-cleaning flexible materials with visible-Light photocatalysis and antibacterial activities, *ACS Appl. Mater. Interfaces* 7 (2015) 19684–19690.
- [61] X. Zou, Y. Dong, X. Zhang, Y. Cui, X. Ou, X. Qi, Synthesize and characterize of Ag₃VO₄/TiO₂ nanorods photocatalysts and its photocatalytic activity under visible light irradiation, *Appl. Surf. Sci.* 391 (2016) 525–534.
- [62] P.W. Huo, M.J. Zhou, Y.F. Tang, X.L. Liu, C.C. Ma, L.B. Y, Y.S. Yan, Incorporation of N-ZnO/CdS/Graphene oxide composite photocatalyst for enhanced photocatalytic activity under visible

- light, J. Alloy Compd. 670 (2016) 198–209.
- [63] L. Diamandescu, M. Feder, D. Tarabasanu, F. Vasiliu, Hydrothermal synthesis and structural characterisation of $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ mixed oxide nanoparticles, Appl. Catal. A 325 (2007) 270–275.
- [64] H. Yang, Z. Dai, Z. Sun, Upconversion luminescence and kinetics in $\text{Er}^{3+}:\text{YAlO}_3$ under 652.2 nm excitation, J. Lumin. 124 (2007) 207–212.
- [65] H.L. Xu, Z.K. Jiang, Dynamics of visible-to-ultraviolet upconversion in $\text{YAlO}_3: 1\% \text{Er}^{3+}$, Chem. Phys. 287 (2003) 155–159.

Content of Figures:

Fig. 1. XRD patterns of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) CdS, (f) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (g) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 2. SEM patterns of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) CdS, (f) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (g) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 3. TEM patterns of (a) rGO, (b) Au/rGO, (c) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and (e) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 4. EDX patterns of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 5. XPS spectra of (o) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio), (a) Cd (3d), (b) Pd (3d), (c) P (2p) and (d) Au (4f).

Fig. 6. UV-vis DRS of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) CdS and $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (e) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS

content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 7. The band-gap energy patterns of (a) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (b) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) CdS and (d) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 8. FT-IR spectra of (a) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (b) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 9. Raman spectra of (a) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (b) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 10. PL spectra of (a) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio) and (b) CdS and $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 11. The effects of different photosources (■: simulated solar-light and ■: ultraviolet-light) on photocatalytic activities of (a) CdS, (b) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and (f) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 12. The effects of simulated solar-light irradiation time (a) on photocatalytic conversion rate of nitrite and corresponding reaction kinetics (b) in the presences of (■) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio), (◆) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and (▲) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 13. The effects of electron scavenger (Ag^+) (a) and hole scavenger (EDTA) (b) on simulated solar-light photocatalytic conversion rate of nitrite. 1: $\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content), 2: $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and 3: $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 14. Effects of used times on simulated solar-light photocatalytic conversion rate of nitrite over $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 15. Possible mechanism on simulated solar-light photocatalytic conversion of nitrite in the presence of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Figures:

Fig. 1. XRD patterns of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) CdS, (f) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (g) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 2. SEM patterns of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) CdS, (f) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (g) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 3. TEM patterns of (a) rGO, (b) Au/rGO, (c) (Au/rGO)/CdS (0.25 wt% Au content and 0.12 wt% rGO content), (d) Er³⁺:YAlO₃@(PdS/BiPO₄)/(Au/rGO) (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er³⁺:YAlO₃ and BiPO₄ mass ratio) and (e) Er³⁺:YAlO₃@(PdS/BiPO₄)/(Au/rGO)/CdS (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er³⁺:YAlO₃@(PdS/BiPO₄) and (Au/rGO)/CdS mass ratio).

Fig. 4. EDX patterns of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 5. XPS spectra of (o) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio), (a) Cd (3d), (b) Pd (3d), (c) P (2p) and (d) Au (4f).

Fig. 6. UV-vis DRS of (a) $\text{Er}^{3+}:\text{YAlO}_3$ (heat-treated at 1100 °C for 2.0 h), (b) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) CdS and $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (e) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 7. The band-gap energy patterns of (a) $Er^{3+}:YAlO_3@BiPO_4$ (1:1 $Er^{3+}:YAlO_3$ and $BiPO_4$ mass ratio), (b) $Er^{3+}:YAlO_3@(PdS/BiPO_4)/(Au/rGO)$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $Er^{3+}:YAlO_3$ and $BiPO_4$ mass ratio), (c) CdS and (d) (Au/rGO)/CdS (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 8. FT-IR spectra of (a) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (b) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content) and (c) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 9. Raman spectra of (a) Er³⁺:YAlO₃@(PdS/BiPO₄)/(Au/rGO) (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er³⁺:YAlO₃ and BiPO₄ mass ratio), (b) (Au/rGO)/CdS (0.25 wt% Au content and 0.12 wt% rGO content) and (c) Er³⁺:YAlO₃@(PdS/BiPO₄)/(Au/rGO)/CdS (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er³⁺:YAlO₃@(PdS/BiPO₄) and (Au/rGO)/CdS mass ratio).

Fig. 10. PL spectra of (a) $\text{Er}^{3+}:\text{YAlO}_3@\text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio) and (b) CdS and $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 11. The effects of different photosources (■: simulated solar-light and ■: ultraviolet-light) on photocatalytic activities of (a) CdS, (b) (Au/rGO)/CdS (0.25 wt% Au content and 0.12 wt% rGO content), (c) $\text{Er}^{3+}:\text{YAlO}_3@ \text{BiPO}_4$ (1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (d) $\text{Er}^{3+}:\text{YAlO}_3@ (\text{PdS}/\text{BiPO}_4)$ (0.13 wt% PdS content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio), (e) $\text{Er}^{3+}:\text{YAlO}_3@ (\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and (f) $\text{Er}^{3+}:\text{YAlO}_3@ (\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@ (\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 12. The effects of simulated solar-light irradiation time (a) on photocatalytic conversion rate of nitrite and corresponding reaction kinetics (b) in the presences of (■) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio), (◆) $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3$ and BiPO_4 mass ratio) and (▲) $(\text{Au}/\text{rGO})/\text{CdS}$ (0.25 wt% Au content and 0.12 wt% rGO content).

Fig. 13. The effects of electron scavenger (Ag^+) (a) and hole scavenger (EDTA) (b) on simulated solar-light photocatalytic conversion rate of nitrite. 1: Au/rGO)/CdS (0.25 wt% Au content and 0.12 wt% rGO content), 2: Er^{3+} : YAlO_3 @(PdS/BiPO_4)/(Au/rGO) (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er^{3+} : YAlO_3 and BiPO_4 mass ratio) and 3: Er^{3+} : YAlO_3 @(PdS/BiPO_4)/(Au/rGO)/CdS (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 Er^{3+} : YAlO_3 @(PdS/BiPO_4) and (Au/rGO)/CdS mass ratio).

Fig. 14. Effects of used times on simulated solar-light photocatalytic conversion rate of nitrite over $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).

Fig. 15. Possible mechanism on simulated solar-light photocatalytic conversion of nitrite in the presence of $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)/(\text{Au}/\text{rGO})/\text{CdS}$ (0.13 wt% PdS content, 0.25 wt% Au content, 0.12 wt% rGO content and 1:1 $\text{Er}^{3+}:\text{YAlO}_3@(\text{PdS}/\text{BiPO}_4)$ and $(\text{Au}/\text{rGO})/\text{CdS}$ mass ratio).