In this study, branch-like SnO$_2@$ZnO heterojunction photocatalyst was successfully fabricated via a simple two-step hydrothermal process. The optical and electronic properties were characterized in detail and the results indicated that SnO$_2@$ZnO nanocomposites (TZNCs) exhibited superior photocatalytic performance under visible light irradiation as compared to pure SnO$_2$ and ZnO. The excellent photocatalytic performance of TZNCs can be ascribed to the heterojunction structure between ZnO and SnO$_2$ which depresses the recombination of photogenerated electron-hole pairs. In addition, the branch-like morphology can provide large specific surface. Moreover, the density functional theory (DFT) computation on the Fermi level results confirmed that heterojunction structure between ZnO and SnO$_2$ is more favorable of the transfer of photogenerated eletrons from ZnO to SnO$_2$, effectively improving separation of photogenerated electron-hole pairs. Noteworthy, this work would pave the route for the two semiconductor materials with a big work function difference which would lead to the high contact potential difference, surely contributing to improving the performance of photocatalysts.

© 2019 Published by Elsevier Inc.
1. Introduction

In recent years, environmental pollution, especially waste water containing organic matter, heavy metal ions, other pollutants and their derivatives, has become a major challenge with the development of modern human society under the global problem of water resource shortage [1,2]. As an efficient and green way, photocatalysis has been regarded as one of the promising technologies for degrading the organic pollutants and water pollution control [3–5]. TiO₂, a traditional photocatalyst, has been extensively researched because of its low cost, non-toxicity and excellent optical and electronic properties. However, it only responds to UV irradiation that only constitutes about 4% of solar energy, which seriously limited its practice application [6–9]. Therefore, it’s urgent to design new and efficient photocatalysts to utilize visible light in current study of photocatalysis.

Among various photocatalysts under investigation, zinc oxide (ZnO), is a well-known wide direct band (Eg = 3.37 eV, 300 K) gap semiconductor and has attracted wide attention due to its low cost, high chemical/physical/thermal stability, broad adsorption spectrum and relatively simple conditions for crystal growth [10–12]. Nevertheless, as a photocatalyst, ZnO exhibits a poor photogenerated-electron-hole pairs separation efficiency, which reduces the photocatalytic degradation efficiency [13,14]. Thus, great efforts have been devoted to overcome these shortcomings and maximize its photocatalytic performance. For instance, fabricating photocatalyst with heterojunction structure can efficiently improve photocatalytic activity. Zhang et al. have successfully constructed Bi₂MoO₆/ZnO hierarchical heterostructures with enhanced visible-light photocatalytic activity [15]. Wang et al. have fabricated ZnO@ZnS heterojunction photocatalyst via a templated method [16]. Gao et al. Have successfully synthesized large-area ZnO/Cu₂O heterojunction on Cu foil through a simple two-step solution method [17]. Our previous results suggest that performances of heterojunction photocatalysts are superior to those of single material [18].

In our work, SnO₂@ZnO heterojunction nanocomposites with novel branch-like morphology, in which SnO₂ nanowires (NWs) as the shell vertically grown on ZnO nanorods (NRs) core, was designed and synthesized inspiring from their different formation energies. The photocatalytic results revealed that TZNCs showed much higher photocatalytic performance for degradation Rhodamine B (RhB) than that of ZnO and SnO₂, which can be ascribed to two aspects. On the one hand, the hierarchical core-shell nanostructures tremendously increased the specific surface areas and provided more active sites for redox reactions. On the other hand, the heterojunction formed at the interface due to work function difference of SnO₂ and ZnO, greatly improving the efficiency of charge separation, thus enhancing the photocatalytic performance. In addition, the separation and transfer mechanism of photogenerated electron-hole pairs was elucidated through first principle density functional theory (DFT). Noteworthy, this work may provide a new insight into constructing heterojunction photocatalysts of two semiconductor materials with different work function.

2. Experiment

2.1. Materials

All chemicals and reagents were analytical grade and were used without further purification. The TZNCs were fabricated using a two-step hydrothermal process. The fabrication of TZNCs was identical to the previous work [12,19].

2.1.1. Preparation of ZnO NRs

The 2.8 mol/L sodium hydroxide (NaOH) (96%) solution was added to the 0.2 mol/L zinc acetate (Zn(CH₃COO)₂·2H₂O) (99%) solution stirred for 30 min, which formed transparent and stable precursor solution. Next, the 70 ml precursor solution was poured into a 100 ml Teflon-lined stainless steel autoclave and heated at 100 °C for 12 h. After that, the obtained product was allowed to cool down to the room temperature naturally and washed with deionized water and ethanol for several times, then dried in air at 70 °C for 12 h. The prepared ZnO NRs were used as the starting zinc sources in the next experiments.

2.1.2. Preparation of branch-like TZNCs

0.1 mol/L stannic chloride (SnCl₄·5H₂O) (99%) solution was added dropwise into 1.1 mol/L NaOH (96%) solution drop by drop. Then, 0.0167 mol ZnO NRs (the mole rate of Sn and Zn equal to 6) was added into the solution accompanied with magnetic stirring for an hour and then ultrasonic treatment for 10 min. Next, 70 ml mixture solution was transferred into Teflon-lined stainless steel autoclave and heated at 200 °C for 20 h. Eventually, the obtained product was allowed to cool down to the room temperature naturally and washed with deionized water and ethanol for several times, then dried in air at 70 °C for 12 h for further characterization. On the basis of the above experiment, we carried out experiments on the addition order of ZnO. The detailed experiment conditions are shown in Table S1.

2.2. Material characterization

The crystalline phase of the samples were determined at room temperature by powder X-ray diffraction (XRD, SHIMADZU 6100, Japan) with Cu Kα X-ray radiation operated at 40 kV and 30 mA. The scanning rate of 6 deg/min and step size of 0.02° were used. Photoluminescence (PL, Horiba Jobin-Yvon, USA) spectra were obtained by a Fluoromax-4 spectrophotometer with an excitation wavelength of 325 nm. X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, Japan) characterizations were performed on a photoelectron spectrometer with a monochromatized Al Kα X-ray source. The samples were characterized by a XPLORA PLUS Raman spectrometer (HORIBA Scientific, France) with excitation source of an Ar laser (λ = 532 nm). The UV−vis diffuse reflectance spectra (UV−vis DRS) was recorded to measure the optical properties of the samples by Lambda 950 UV−VIS−NIR spectrophotometer (Perkin−Elmer, USA). The morphology and microstructure of the product were observed by scanning electron microscope (SEM, Zeiss SIGMA/VP, Germany) and analyses were performed at 3 kV with a working distance of ~9 mm. Transmission electron microscope (TEM, JEM-3010, Japan) was performed at operating voltage of 200 kV.

2.3. Photocatalytic activity measurements

The photocatalytic performance of the as-prepared products were measured by a 300 W Xe lamp under visible light irradiation. Initially, 50 mg TZNCs was dispersed to the RhB solution (50 ml, 10 mg/L) and stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium. Then, mixed solutions were then irradiated using a 300 W Xe lamp under continuous stirring. During the irradiation, 3 ml of suspension solution was taken out every 10 min and then analysis RhB concentration using a UV−VIS spectrophotometer (QEpro, Ocean Optics).
3. Results and discussion

3.1. Phase structure, surface elemental composition and morphology characterization

The phase composition and crystal structure of the synthesized samples were characterized by X-ray diffraction, and the XRD pattern of TZNCs is shown in Fig. 1a. As shown, the XRD pattern of TZNCs demonstrates that all the diffraction peaks match well with diffraction planes of SnO2 (JCPDS card No. 41-1445) and ZnO (JCPDS card No. 36-1451), respectively, suggesting a high purity and crystallinity of TZNCs.

Fig. 1b shows the Raman spectra of ZnO, SnO2 and TZNCs. TZNCs show three main peaks at 438, 632 and 776 cm⁻¹. The peak at 438 cm⁻¹ was assigned to the vibration modes E₂ for wurtzite ZnO[20,21], and the other peaks at 632 cm⁻¹ and 776 cm⁻¹ were ascribed to A₁g and B₂g for cassiterite SnO₂[22], respectively. Therefore, the Raman spectra also confirmed the co-existence of ZnO and SnO₂ in the TZNCs.

To further obtain the surface chemical composition and the chemical states of each element of TZNCs heterojunction photocatalyst, the TZNCs were investigated by XPS (Fig. 2). The analysis of chemical states of each element of TZNCs heterojunction photocatalyst, which is highly in correspondence with the XRD and Raman results.

The morphologies and microstructures of the synthesized samples were characterized by scanning electron microscopy (SEM), and the results are shown in Fig. 3. As shown, TZNCs are presented as a branch-like structure. It’s also visible that a number of SnO₂ NWs was successfully grown on the six non-polar planes of the ZnO NRs. And they are scattering orderly, forming a typical needle-like clusters morphology. Fig. 3c and d clearly present the side of the hexagram TZNCs structure. The SnO₂ NWs are needle-like and the tips are clustered together, and the center ZnO NRs of the branch-like TZNCs structure has been partly dissolved for hollow branch structure, a part of ZnO NRs has not been dissolved, the top of ZnO NRs is still hexagonal structure. In Fig. 3, the length of the TZNCs structure is approximately from 15 to 20 μm, and the diameter of the center hole of ZnO NRs is about 250 nm.

Fig. 4a shows the TEM image of the synthesized TZNCs, in which uniform SnO₂ NWs grow on the six non-polar planes of ZnO NRs vertically, forming a test-tube branch-like morphology. The selected area electron diffraction (SAED) is shown in Fig. 4b, and we can acquire that zone axis direction is [1–10] which shows that the SnO₂ NWs are single crystalline. Besides, the HRTEM image of the individual SnO₂ NWs was also characterized in Fig. 4c. The lattice fringes of TZNCs display interplanar spacings of 0.33 nm, which match well with the (1 1 0) planes of SnO₂ NWs.

In order to investigate the connection between the adding order of ZnO and the morphological evolution, the sample 2 was synthesized as shown in Table 1. The XRD pattern of TZNCs affected by the addition order of ZnO are shown in Fig. S1a. As shown, it can be found in sample 2 that all the diffraction peaks correspond to the crystal characteristic peaks of SnO₂, ZnSn(OH)₆, and Zn₂SnO₄, which indicates that the prepared products contain SnO₂, ZnSn(OH)₆, and Zn₂SnO₄. Nevertheless, the diffraction peaks of XRD in sample 1 are both ZnO and SnO₂ diffraction peaks. The SEM images of the sample 2 are demonstrated in Fig. S1b–d. As shown, the sheet structure and rod like structure gather together and are in a right mess, and the length of rod structure can reach micron level.

For the sample 1, ZnO NRs was added after the SnCl₄ titration to NaOH. The concentration of OH⁻ was quite low, which leads that most of ZnO NRs has not been dissolved before the hydrothermal process. When the precursor solution was under the hydrothermal reaction, the ZnO NRs were dissolved in alkali solution to generate Zn(OH)₄²⁻ (Eq. (1)). Then, the Zn(OH)₄²⁻, Sn⁴⁺ and OH⁻ combined to form octahedral ZnSn(OH)₆ crystal (Eq. (2)). Under the hydrothermal conditions, an interesting phenomenon was that the octahedral ZnSn(OH)₆ can be decomposed with the hydrothermal time increased and generated the growth unit Zn(OH)₂⁶⁻ (Eq. (3)). When the supersaturation of the solution reached the critical value required for nucleation of ZnO NRs, ZnO NRs precipitated at the edges and corners of the ZnSn(OH)₆ (Eq. (4)). When most of the ZnSn(OH)₆ crystals dissolved and the concentration of the Sn (OH)₂⁶⁻ solution increased to the critical value required for nucleation of SnO₂, moreover, a large number of unsaturated dangling bonds on the surface of ZnO NRs provided a large number of nucleation sites for SnO₂. Therefore, SnO₂ precipitated on the surface of ZnO and grew into nanowire structure on the six non-polar surfaces of ZnO NRs (Eq. (5)).
Fig. 2. (a) XPS survey spectrum of TZNCs photocatalyst, (b) Sn 3d region, (c) Zn 2p region and (d) O 1s region (full) with the corresponding fits for lattice oxygen in crystalline ZnO (red) and SnO$_2$ (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. The SEM patterns of TZNCs.
The growth mechanism of TZNCs based on the addition order of ZnO NRs is investigated (sample 2). For the sample 2, ZnO NRs were added to the NaOH alkali solution after continuous mixing, most of the ZnO NRs had been dissolved to generate Zn(OH)$_4^{2-}$ because of the higher concentration of OH$^-$. At the same time, a large number of growth unit of SnO$_2$, Sn(OH)$_6^{2-}$ existed in the reaction solution. Under the hydrothermal conditions, ZnSn(OH)$_6$ crystal nucleus increased tremendously within a short time, therefore, the number of ZnSn(OH)$_6$ in sample 2 was far more than the number in sample 1, and the concentration of OH$^-$ in sample 2 was lower than that of the sample 1, causing that the dissolution rate of ZnSn(OH)$_6$ nanostructure in sample 2 was lower than that of the sample 1. On the one hand, ZnSn(OH)$_6$ nanostructure was dissolved in the reaction system of sample 2 slowly. On the other hand, a part of ZnSn(OH)$_6$ and Zn(OH)$_2^{2-}$ combined to generate Zn$_2$SnO$_4$ (Eq. (6)). Therefore, it’s more difficult for the supersaturation of the reaction system in sample 2 to reach the critical value required for nucleation of ZnO. When ZnSn(OH)$_6$ crystals dissolved further and the solution reached the critical value of supersaturation of SnO$_2$, nucleation, SnO$_2$ NWs began to nucleate and grow. Eventually, ZnO didn’t appear in sample 2, but there were undissolved ZnSn(OH)$_6$ nanoparticles and small amount of Zn$_2$SnO$_4$ crystal.

\[
\begin{align*}
\text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} &= \text{Zn(OH)}_2^{2-} \\
\text{Sn}^{4+} + \text{Zn(OH)}_2^{2-} + 2\text{OH}^- &= \text{ZnSn(OH)}_6^{2-} \\
\text{ZnSn(OH)}_6^{2-} + 4\text{OH}^- &= \text{Sn(OH)}_2^{2-} + \text{Zn(OH)}_2^{2-} \\
\text{Zn(OH)}_2^{2-} &= \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \\
\text{Sn(OH)}_2^{2-} &= \text{SnO}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \\
\text{ZnSn(OH)}_6^{2-} + \text{Zn(OH)}_2^{2-} &= \text{Zn}_2\text{SnO}_4 + 4\text{H}_2\text{O} + 2\text{OH}^- \\
\end{align*}
\]

3.2. Optical properties

The optical properties of as-prepared samples were investigated by UV–visible diffuse reflectance (DRS). As shown in Fig. 5, the absorption edges of ZnO and SnO$_2$ were determined to be 394 and 355 nm, corresponding to band gap energies of 3.2 and 3.7 eV, respectively, which is in good agreement with the reported value of ZnO (3.37 eV) and SnO$_2$ (3.6 eV)[12]. The appearance of two kinds of characteristic absorption band confirms that the TZNCs photocatalyst is a composite material which is composed of SnO$_2$ and ZnO.

![Fig. 4. (a) TEM image of TZNCs, (b) SAED patterns and (c) HRTEM image of SnO$_2$ NWs.](image)

![Fig. 5. The UV–vis diffuse reflectance spectra of primary pure ZnO NRs, SnO$_2$ NWs and TZNCs.](image)

![Fig. 6. PL spectra excited by the wavelength of 325 nm of the as-prepared samples.](image)

It is well known that the photocatalytic activity directly depends on the competition between the charge separation and recombination processes [29]. PL emission is resulted from the radiative recombination of excited electrons and holes, therefore it can be used to evaluate the performance of photocatalyst. As shown in Fig. 6, the position of luminescence peak of TZNCs is basically in correspond with that of pure ZnO. The yellow-orange emission band centered near 590 nm in ZnO is strong, which is closely
associated with the surface zinc vacancy defects ($V_{Zn} \rightarrow V_{Zn}$, at ~2.1 eV) [30,31], while the luminescence peak is relatively weak after compounding with SnO$_2$. The reason is that the increase of defects in the nanocomposites due to the introduction of SnO$_2$, resulting in the enhancement of non-radiative recombination of carriers. The weakening of the peak intensity indicates that the recombination of carriers is inhibited at some extent, which can effectively separate the photogenerated electrons and holes, thus improving the catalytic performance. Combined with the results of XRD, UV–vis DRS, Raman, XPS, SEM, TEM and PL, we can further confirm the existence of the SnO$_2$ and ZnO, and the heterojunction would greatly improve photocatalytic activity of TZNCs.

3.3. Photocatalytic properties

In order to investigate the photocatalytic activity of the as-prepared TZNCs, the RhB was selected as the target organic pollutants in aqueous solution under visible light irradiation to evaluate the photocatalytic properties of the as-prepared samples. The evolutions of the visible light spectra at the wavelength of absorbance maximum during the degradation are illustrated in Fig. 7a. Note that the concentration of RhB did not change during photolysis under visible light irradiation in the absence of photocatalyst. Obviously, the main absorption peak locates at 554 nm, which corresponds to the RhB molecules. RhB concentration decreases rapidly with the extension of the exposure time, and almost completely disappears after 80 min of visible light irradiation, which indicates that RhB dye can be almost completely degraded in a photocatalytic system with TZNCs. Moreover, the maximum absorbance peak shifted slightly to shorter wavelengths during visible light irradiation, which can be attributed to the formation of some methylated products of RhB during photodegradation over the cleavage of the aromatic ring of RhB [32]. Fig. 7b shows the relationship between the concentration of RhB solution ($C/C_0$) and visible light irradiation time for the above mentioned three samples. Note that the concentration of RhB did not change during photolysis under visible light irradiation in the absence of photocatalyst. Clearly, the RhB solution is very stable and no degradation can be observed at all in absence of photocatalysts. However, the photocatalysts can lead to an obvious degradation of RhB, and it can be concluded that the decomposition rates among all samples are high within the first 20 min. It can also be seen that TZNCs show the highest photocatalytic activity for the degradation of RhB compared with other samples, whose degradation efficiency at 80 min is about 97%, while that of ZnO and SnO$_2$ are about 90% and 55%, respectively. This enhancement can be explained by the different energy levels of their corresponding conduction and valence bands to form the TZNCs heterojunction, leading to more efficient photogenerated electrons and holes separation and higher photocatalytic activity, which is further confirmed by photoelectrochemical measurements.
Photocatalytic activity is closely related to the transfer and separation rate of photogenerated electron-hole pairs, therefore, the carrier separation behavior is often investigated through the transient photocurrent measurement. To explore the photocurrents of the three samples, the electrochemical measurements were performed with electrochemical workstation using a three-electrode system at room temperature under simulated sunlight glowed from a 300 W Xe lamp, and the electrolyte was 0.1 M Na2SO4 aqueous solution. Under the above conditions, PEC cells of ZnO, SnO2 and TZNCs were acquired and their curves collected with four light on/off cycles within 10 s are shown in Fig. 7c. Apparently, the photocurrents of the three samples increase rapidly once the light is switched on and almost revert to zero once the light is switched off, of which the photocurrent of TZNCs rises and falls faster than that of ZnO and SnO2. Such faster rise and fall of the photocurrent indicates that the generation and transfer of photogenerated carriers in the TZNCs proceed more quickly than in ZnO and SnO2. Moreover, the photocurrent of the TZNCs is obviously improved comparing with that of single ZnO and SnO2, which is in good agreement with the results of degradation efficiency. To be specific, the photocurrent of ZnO and SnO2 are about 12.5 μA/cm² and 8.0 μA/cm², respectively, while photocurrent of TZNCs reaches about 18 μA/cm². Furthermore, the photocurrent of the TZNCs shows no decrease after four switch lamp cycles in 80 s. In brief, this enhancement in the photocurrent response is mainly due to the heterojunction structure which promotes efficient separation and transfer of photogenerated electron-hole pairs, thus promotes efficient photogenerated charge separation rate and transfer rate, enhancing the photocatalytic activity and stability [33,34]. In order to find out which reactive species are the core factors in the degradation of pollutants, the trapping agent experiment by ammonium oxalate, isopropyl alcohol and benzoquinone has been discussed in detail in the Supplementary Information.

3.4. Photocatalytic mechanism

The photocatalytic mechanism in aqueous media is based on the reaction of the photogenerated electrons (e⁻) with dissolved oxygen molecules to form superoxide radicals (O²⁻), and of holes (h⁺) with surface hydroxyl groups and adsorbed water molecules, or hydroxyl ions (OH⁻) to form hydroxyl radicals (·OH). h⁺, O²⁻ and ·OH all own strong oxidizing properties, so oxidation or total mineralization of many organic compounds can be degraded to become CO₂ and H₂O [35]. However, some photogenerated electrons and holes may be rapidly and directly recombine on the surface of the nanocatalyst, which reduces the efficiency of the photocatalytic processes. In this paper, based on the photocatalytic property tests of TZNCs, the heterojunction structure formed at the contact surface of the SnO2-ZnO can significantly improve photocatalytic activity.

To further illustrate that the TZNCs heterojunction plays a decisive role in the enhanced photocatalytic activity, we calculated electrostatic potentials of SnO2, ZnO and TZNCs heterojunction based on density functional theory (DFT) using Cambridge Serial Total Energy Package (CASTEP) package [36], as displayed in Fig. 8a–c. The Ultrasoft pseudo potential (UPP) [37] and general-
ized gradient approximation (GGA) \cite{38} are adopted to deal with the interaction between ions and electrons, and Perdew-Burke-Ernzerhof (PBE) is adopted to cope with the exchange-correlation functional. The cutoff energy is set to be 480 eV for SnO$_2$, ZnO and TZNCs heterojunction, and the convergence criteria with energy and force are $10^{-5}$ eV and 0.02 eV/Å, respectively. The Brillouin-zone approach is sampled with $6\times6\times1$ and $6\times6\times4$ k-point grid for work function and electronic properties, respectively. Moreover, in order to avoid the interaction between slab layers for work function, the vacuum region is set as 15 Å. The calculated work functions of SnO$_2$, ZnO and TZNCs heterojunction are 4.86, 5.17 and 4.96 eV, respectively. The calculated results are consistent with the experimental described results, and the electron-hole transition process is shown in Fig. 9.

At the same time, the space charge region is formed at the interface between SnO$_2$ and ZnO. As shown in Fig. 9a, one side is the positive space charge region and the other is the negative space charge region, thus forming the built-in electric field at the interface of the SnO$_2$–ZnO \cite{12}. Due to the existence of the built-in electric field, the potential of electrons in the space charge region changes, which results in the bending of the energy band in the space charge region, promoting that the electrons transfer from ZnO to SnO$_2$ and holes from SnO$_2$ to ZnO. The charge transfer equations are as follows:

$$\text{SnO}_2@\text{ZnO} \xrightarrow{\text{hv}} \text{SnO}_2@\text{ZnO}(h^+ + e^-)$$  \hspace{1cm} (7)

$$\text{ZnO}(e^-) + \text{SnO}_2 \rightarrow \text{ZnO} + \text{SnO}_2(e^-)$$  \hspace{1cm} (8)

$$\text{SnO}_2(h^+) + \text{ZnO} \rightarrow \text{SnO}_2 + \text{ZnO}(h^+)$$  \hspace{1cm} (9)

When the TZNCs are irradiated by visible light, the same number of photogenerated electrons and holes, in the conduction band (CB) and valence band (VB), is produced, respectively. Because of the built-in potential, electrons can easily transfer from the CB of ZnO to the CB of SnO$_2$. Similarly, holes transfer from the VB of SnO$_2$ to the VB of ZnO (in Fig. 9b). Thus, the recombination of electrons and holes is suppressed so that the lifetime of carriers is increased, improving the oxidation-reduction reaction efficiency, and the photocatalytic activity is enhanced.

4. Conclusion

In summary, branch-like TZNCs heterojunction photocatalyst were successfully fabricated via a simple two-step hydrothermal process. The crystal structure, surface morphology, optical and photocatalytic properties of the products were comprehensively characterized by XRD, XPS, SEM, TEM, HRTEM, Raman, UV–vis and PL. As shown in the experimental results, TZNCs perform more excellent photocatalytic activity for the degradation of RhB compared with the single ZnO and SnO$_2$. The photocatalytic efficiency of TZNCs was almost 97% when the illumination time reached to 80 min, while that of ZnO and SnO$_2$ are about 90% and 55%, respectively. The heterojunction structure of TZNCs was proposed to explain the observed high photocatalytic efficiency. It is believed that the introduction of heterojunction can facilitate charge transfer and suppress recombination of photogenerated electron-hole pairs, further enhancing the photocatalytic activity.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (Grants 61701402), the General Program for International Science and Technology Cooperation Projects of Shaanxi Province (Grants, 2019KW-029) and the Key Program for International Science and Technology Cooperation Projects of Shaanxi Province (Grants 2018KWZ-08).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2019.06.053.

References
