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Article

Construction of 2D-2D TiO₂ nanosheet/layered WS₂ heterojunctions with enhanced visible-light-responsive photocatalytic activity

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ARTICLE INFO

Article history:

Received 21 July 2018

Accepted 21 September 2018

Published 5 January 2019

Keywords:

WS₂TiO₂

Nanosheet

Heterojunction

Photocatalysis

Visible-light responsive

ABSTRACT

Constructing nanocomposites that combine the advantages of composite materials, nanomaterials, and interfaces has been regarded as an important strategy to improve the photocatalytic activity of TiO₂. In this study, 2D-2D TiO₂ nanosheet/layered WS₂ (TNS/WS₂) heterojunctions were prepared via a hydrothermal method. The structure and morphology of the photocatalysts were systematically characterized. Layered WS₂ (~4 layers) was wrapped on the surface of TiO₂ nanosheets with a plate-to-plate stacked structure and connected with each other by W=O bonds. The as-prepared TNS/WS₂ heterojunctions showed higher photocatalytic activity for the degradation of RhB under visible-light irradiation, than pristine TiO₂ nanosheets and layered WS₂. The improvement of photocatalytic activity was primarily attributed to enhanced charge separation efficiency, which originated from the perfect 2D-2D nanointerfaces and intimate interfacial contacts between TiO₂ nanosheets and layered WS₂. Based on experimental results, a double-transfer photocatalytic mechanism for the TNS/WS₂ heterojunctions was proposed and discussed. This work provides new insights for synthesizing highly efficient and environmentally stable photocatalysts by engineering the surface heterojunctions.

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1. Introduction

Photocatalysis has been regarded as a promising strategy for environmental remediation because it is a clean process and has high degradation ability as well as low energy consumption [1,2]. As one of the most important photocatalysts, TiO₂ has attracted considerable attention since the first report by Fujishima et al. [3]. To date, various TiO₂ nanostructures with different crystalline phases have been developed and used to photodegrade organic pollutants [4–6]. However, the wide

band gap of TiO₂ (3.2 eV) makes it difficult for activation by visible light, which leads to inefficient utilization of sunlight [7], and moreover, the low quantum efficiency in photocatalytic reactions is not satisfactory for practical applications [8]. Therefore, it is highly desirable to overcome these inherent shortcomings of TiO₂ to enhance its photocatalytic activity.

Coupling TiO₂ with co-catalysts to construct hybrid photocatalysts is an effective approach to achieve this goal. Compared to single-component photocatalysts, hybrid photocatalysts combine individual advantages and show better photo-

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This work was supported by the National High Technology Research and Development Program of China (863 Program, 2012AA063504), the National Natural Science Foundation of China (U1407116, 21511130020, 21276193), and the Tianjin Municipal Natural Science Foundation (13JCZDJC35600).

DOI: 10.1016/S1872-2067(18)63170-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 1, January 2019

catalytic performance [9,10]. Furthermore, the presence of heterojunctions between host and guest materials changes the band bending at the interfaces and provides a driving force to separate photogenerated electrons and holes [11,12]. Therefore, combining these aspects, i.e., morphology, phase structure, and heterojunctions, may offer an ideal way to fabricate stable and efficient photocatalysts.

Transition metal dichalcogenides (TMDs) have been a focus of research for a long time owing to their extraordinary optical and electrical properties [13,14]. A typical TMD, WS₂, has been extensively studied for multiple applications in solar cells, electrocatalysis, photocatalysis, and bioimaging labels [15,16]. WS₂ has a typical graphene-like layered structure and a tunable bandgap [17,18]. The bandgap of WS₂ is about 1.35 eV, which is close to the bandgap value for the optimum utilization of solar radiant energy [19]. More importantly, the conduction-band minimum of WS₂ is higher than that of TiO₂, indicating that it is a possible co-catalyst candidate to photosensitize TiO₂ in visible light. Guo et al. [20] reported that high photocatalytic activity and low recombination of photogenerated carriers were achieved by the deposition of nanosized WS₂ on the surface of mesoporous TiO₂. Liu et al. [21] synthesized nanoscale WS₂/TiO₂ composites and predicted that they may have potential applications in visible-light photocatalysis. More recently, Qi et al. [22] prepared WS₂/TiO₂ heterostructures and confirmed their good photoresponse activity and structural robustness. However, these studies only focused on the nanosize effect and ignored the crystal surface effect of the TiO₂ substrate. Moreover, the TiO₂ substrates used in these WS₂/TiO₂ composites were three-dimensional nanospheres or nanoparticles, which led to loose and non-uniform contact between WS₂ and TiO₂ and reduced the separation efficiency of photogenerated carriers. Hence, it is highly desirable to develop new WS₂/TiO₂ composites with higher photocatalytic activity and stability.

In this work, we chose 2D TiO₂ nanosheets as the substrate to fabricate 2D-2D TiO₂ nanosheets/layered WS₂ (2D-2D TNS/WS₂) heterojunctions via a facile hydrothermal method. The structure and morphology of the TNS/WS₂ heterojunctions were systematically characterized. As expected, the layered WS₂ were tightly coated on the surface of TiO₂ nanosheet with a plate-on-plate stacked structure and connected to each other by W=O chemical bonds. The introduction of layered WS₂ improved the light absorption properties of the TNS/WS₂ heterojunctions and the heterogeneous interface enhanced the separation efficiency of the photo-induced carriers. As a result, the TNS/WS₂ heterojunctions showed higher photocatalytic activity than pure TiO₂ nanosheets and layered WS₂. The photodegradation mechanism and degradation process were also discussed.

2. Experimental

2.1. Preparation of TNS/WS₂ heterojunctions

Anatase TiO₂ nanosheets with exposed (001) and (101) facets were prepared by a facile hydrothermal process as previ-

ously reported [23]. The synthesis process of TNS/WS₂ heterojunctions is described below. Typically, 2.5 mmol sodium tungstate (Na₂WO₄·2H₂O) was dissolved in 80 mL deionized water under magnetic stirring and the pH value of the solution was adjusted to 3 by dropping 2 mol/L hydrochloric acid. Then 7.5 mmol L-cysteine was added into the mixture, which was stirred until it became transparent again. Subsequently, a certain amount of TiO₂ nanosheets was added to the above solution under vigorous stirring. The solution was transferred to a Teflon-lined stainless steel autoclave and reacted at 200 °C for 24 h. The black products were collected, washed, and dried in a vacuum oven at 60 °C for 12 h. The TNT/WND heterojunctions with different W:Ti molar ratios (0.20, 0.10, 0.07, and 0.05) were prepared by adjusting the amount of TiO₂ nanosheets and were named TNS/WS₂-0.20, TNS/WS₂-0.10, TNS/WS₂-0.07, and TNS/WS₂-0.05. For comparison, pure WS₂ was synthesized under the same conditions without adding TiO₂ nanosheets. A TiO₂ hollow microsphere/layered layered WS₂ (THS/WS₂) composite was synthesized under the same conditions by adding TiO₂ hollow microspheres instead of TiO₂ nanosheets.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 Focus X-ray diffractometer (Germany) with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) was conducted using a PerkinElmer PHI 1600 ESCA X-ray photoelectron spectrometer with monochromatic Mg K_α radiation and binding energies normalized to the C 1s peak at 284.6 eV. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were performed on a Hitachi S-4800 instrument. Transmission electron microscopy (TEM) was performed with a JEM-2100F (JEOL, Japan) instrument. Raman spectra were gathered from a confocal microscope-based Raman spectrometer (Renishaw InVia) in ambient air environment with an excitation laser line of 532 nm. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joiner-Halenda (BJH) pore-size distribution measurements were obtained using a NOVA-2000 volumetric gas sorption instrument (Quantachrome, USA). UV-Vis diffuse reflectance spectra (DRS) of the samples were obtained using a Shimadzu UV-2550 spectrophotometer using BaSO₄ as a reference. Photoluminescence (PL) spectra were obtained with a Fluorolog3 spectrofluorometer (Horiba Jobin Yvon) with an excitation wavelength of 325 nm. High-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) was performed on Bruker Daltonics micrOTOF-QII.

2.3. Photoreaction procedures

In the photocatalytic test, the light source was a 300-W Xe lamp with a 420 nm cut-off filter (to remove all incoming wavelengths shorter than 420 nm) placed 15 cm above the liquid surface. 20 mg of photocatalyst was dispersed in 100 mL of a rhodamine B (RhB) solution (20 mg/L). Prior to light irradiation, the suspensions were vigorously stirred for 60 min in the dark to establish an adsorption-desorption equilibrium.

During the photocatalytic reaction, at given intervals, 5 mL samples were collected to test the concentration of RhB. The RhB concentration was calculated by UV-vis spectroscopy (Perkin Elmer, lambda 35).

2.4. Electrochemical measurement

Electrochemical tests were carried out on a three-electrode electrochemical workstation (CHI 660E, Chenhua, China) equipped with an FTO electrode deposited with the samples as a photoanode, a Pt wire as counter electrode, and Hg/Hg₂Cl₂/saturated KCl (SCE) as the reference electrode. In a typical experiment, 0.05 mol/L Na₂SO₄ (40 mL, pH = 6.8) purged with N₂ was used as the electrolyte. For the fabrication of the photoanode, 10 mg of the solid sample was homogeneously mixed with 2 mL of absolute ethanol by using a vortex oscillator. The obtained sample was deposited onto the as-washed FTO glass with a controlled area of 1 cm² by dip-coating to form a film electrode and then dried in air. Impedance-potential scanning (I-P) was carried out in the potential scanning range of −1.5–1.0 V with an increase potential of 0.05 V and a frequency of 1000 Hz.

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD patterns of layered WS₂, TiO₂ nanosheets, and TNS/WS₂ heterojunctions. For pure layered WS₂, there are three diffraction peaks at 17.7°, 32.5°, and 56.9°, which are ascribed to the (002), (101), and (110) lattice planes of hexagonal-phase WS₂ (JCPDS 084-1398) [24]. The diffraction peaks of TiO₂ nanosheets and corresponding heterojunctions matched the standard diffraction patterns of anatase TiO₂ (JCPDS: 73-1764) [25]. No diffraction patterns associated with WS₂ are observed in the TNS/WS₂ heterojunctions, indicating that WS₂ coated on the surface of TiO₂ nanosheets may contain too few layers and are too thin to be detected by XRD [26]. In addition, the (101) peak experiences a chemical shift from

25.5° to 25.2° after WS₂ is incorporated into TiO₂, revealing the intimate contact and strong interaction between TiO₂ nanosheets and layered WS₂ [27]. Furthermore, the photos of photocatalysts show that increasing the WS₂ content changes the color of the TiO₂ nanosheets from white to black, implying an increased absorption of light.

To further explore the properties of the hybrid nanostructure, phonon spectra of the layered WS₂, TiO₂ nanosheets, and TNS/WS₂-0.10 were measured by Raman scattering (Fig. 2). TiO₂ nanosheets were characterized by well-defined peaks at 148 (*E_g*(1)), 201 (*E_g*(2)), 398 (*B_{1g}*(1)), 519 (*A_{1g}* + *B_{1g}*(2)), and 643 cm^{−1} (*E_g*(3)), which corresponded to the anatase structure [28]. For pure WS₂, the two dominant Raman scattering peaks can be observed at 377 and 404 cm^{−1}, and are attributed to *E_{2g}*¹ and *A_{1g}*, respectively [29]. When the layered WS₂ was deposited on the surface of TiO₂ nanosheets, characteristic peaks of WS₂ and TiO₂ can be detected in TNS/WS₂-0.10. Thus, layered WS₂ was successfully introduced into the TiO₂ nanosheets. Interestingly, there is an extra peak at 972 cm^{−1}, which may be attributed to the W=O bond of tungsten trioxide [30]. This extra peak suggests that the layered WS₂ and TiO₂ nanosheets are tightly combined, which leads to high reliability.

The SEM images and corresponding EDX images of layered WS₂, TiO₂ nanosheets, and TNS/WS₂-0.10 are presented in Fig. 3. As shown in Fig. 3(a), the pure WS₂ nanosheets are stacked together to form WS₂ microspheres, with petal-like features observed on the surface. For TiO₂ nanosheets (Fig. 3(c)), the SEM image shows well-dispersed sheets. After the introduction of WS₂, the surface of TNS/WS₂-0.10 (Fig. 3(e)) becomes rough, owing to the layered WS₂ coating on the surface of the TiO₂ nanosheets. The corresponding EDX spectrum shows that Ti, O, W, and S simultaneously exist in TNS/WS₂-0.10; the atomic ratio of W:Ti is about 1:20, which indicates that the actual content of WS₂ in TNS/WS₂-0.10 is about 13.4 wt%.

The microstructures of layered WS₂, TiO₂ nanosheets, and TNS/WS₂-0.10 were further investigated by TEM. As shown in Fig. 4(a), WS₂ is a well-layered structure and the number of layers ranges from one to six. The TEM image of the TiO₂ nanosheets indicates that the product consists of well-defined

Fig. 1. XRD patterns of pure WS₂ (a), TNS/WS₂-0.20 (b), TNS/WS₂-0.10 (c), TNS/WS₂-0.07 (d), TNS/WS₂-0.05 (e), and pure TiO₂ (f). Insets are the photos of corresponding photocatalysts.

Fig. 2. Raman spectra of pure WS₂ (a), TNS/WS₂-0.10 (b), and pure TiO₂ (c).

Fig. 3. SEM images and EDS spectra of WS₂ (a, b), TiO₂ (c, d) and TNS/WS₂-0.10 (e, f).

sheet-shaped structures and that the (101) slab exhibits a clear crystal lattice. To gain a clear understanding of the interface between WS₂ and the TiO₂ nanosheets, the morphology of the TNS/WS₂-0.10 nanostructure was vividly studied by TEM. As shown in Fig. 4(c), the TEM images of TNS/WS₂-0.10 present layered and sheet-shaped morphologies, which are attributed to layered WS₂ and TiO₂ nanosheets, respectively. The top-view (Fig. 4(d)) image reveals that WS₂ forms a homogeneous coat on the surface of the TiO₂ nanosheets and that the crystal lattice can hardly be distinguished, except for the uncovered part. The side views shown in Fig. 4(e) and (f) clearly show that the lay-

Fig. 4. HRTEM images of WS₂ (a) and TiO₂ (b), inset is TEM image. TEM image (c), HRTEM images (d–f), and EDX elemental mapping (g) of TNS/WS₂-0.10.

ered WS₂ is coated closely on the (004) and (101) facets of TiO₂ nanosheets and that the number of coating layers is about four. Furthermore, the EDX elemental mapping of TNS/WS₂-0.10 (Fig. 4(g)) show that O dovetails well with Ti and S dovetails well with W. The intensity of W (or S) is lower than that of Ti (or O), consistent with the content of WS₂, which was in the minority. The uniform color and luster of the S and W mappings imply that the layered WS₂ are homogeneously wrapped around the TiO₂ nanosheets.

The surface chemical states and components of the as-prepared heterojunctions were recorded by XPS. The full range XPS spectrum shown in Fig. 5(a) reveals that the domi-

Fig. 5. XPS spectra of TNS/WS₂-0.10. (a) full scan; (b) Ti 2p_{3/2}; (c) W 4f; (d) S 2p. Inset in (a) is local enlarged picture.

Fig. 6. N_2 adsorption-desorption isotherms and textural parameters (inset) of TiO_2 , WS_2 , and TNS/WS₂-0.10.

nant elements are Ti, O, W, and S in TNS/WS₂-0.10. A typical high-resolution XPS spectrum of Ti 2p is shown in Fig. 5(b). Two peaks at 458.8 and 464.6 eV are ascribed to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. The separation energy is close to 5.8 eV between Ti 2p_{1/2} and Ti 2p_{3/2}, indicating a normal state of Ti⁴⁺ in TiO_2 [31]. Fig. 5(c) shows the XPS spectrum of W 4f, which can be fitted to three peaks. The peaks at 35.6, 37.6, and 40.6 eV are assigned to W 4f_{7/2}, W 4f_{5/2}, and W 5p_{3/2}, respectively. This result is in accordance with previous reports [32]. As for the high-resolution spectrum of S 2p (Fig. 5(d)), the fitted peaks at 161.3 and 163.4 eV are attributed to S 2p_{3/2} and S 2p_{1/2}, respectively [33]. The XPS analysis further confirms that the layered WS_2 was successfully introduced into the TiO_2 nanosheets.

The nitrogen adsorption-desorption isotherms and BJH pore-size distribution plots of the TiO_2 nanosheets,

TNS/WS₂-0.10, and WS_2 are shown in Fig. 6. The appearance of distinct hysteresis loops at high relative pressure suggests that these materials consist of mesopores. From the textural parameters present in the inset, we can see that the surface areas of TNS/WS₂-0.10 sharply increase, which is beneficial for the dye adsorbed on the surface. The high surface areas TNS/WS₂-0.10 validate their highly porous structure, which could provide a more flexible response to active sites.

3.2. UV-vis diffuse reflectance spectra and PL spectra analysis

The light-absorption property of the as-prepared heterojunctions was determined by UV-vis diffuse reflectance spectra and is displayed in Fig. 7(a). For comparison, the spectra of pure TiO_2 nanosheets and layered WS_2 are also plotted. As we can see, pure TiO_2 nanosheets exhibit a sharp fundamental absorption band edge at about 380 nm, suggesting that they are excited by UV light. In contrast, the layered WS_2 display strong absorption from the ultraviolet to visible-light regions as well as in the near-infrared light region. Notably, when WS_2 is introduced into TiO_2 , the photoabsorption regions of the TNS/WS₂ heterojunctions are significantly broadened and the absorption intensity is enhanced.

The band gaps, conduction band (CB), and valence band (VB) of TiO_2 and WS_2 were estimated by Tauc's plots and Mott-Schottky (M-S) measurements. The band gaps of the photocatalysts can be calculated using the following formula [34]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

Where α is the absorption coefficient, A is a constant, h is Planck's constant, E_g is the band energy, and ν is the frequency of the incident light. The value of n is decided by the property of the semiconductor. Anatase TiO_2 is an indirect-band-gap semiconductor and its value of n is 1/2 [35]; layer-like WS_2 is a direct-band-gap semiconductor and its value of n is 2 [36,37].

Fig. 7. (a) UV-vis spectra of TiO_2 , WS_2 and TNS/WS₂ heterojunctions; (b, d) Tauc's plots of TiO_2 and WS_2 ; (c, e) Corresponding Mott-Schottky curves; (f) PL spectra of TiO_2 , WS_2 , and TNS/WS₂-0.10.

Fig. 8. Photocatalytic degradation of Rh B (a), first-order kinetic model fitting curves (b) and degradation rate constant of RhB (c) with as-prepared samples. (d) Time-dependent absorption spectra of RhB solution over TNS/WS₂-0.10 (d). Inset shows the photos of RhB at different irradiation times.

The corresponding calculated results for TiO₂ nanosheets and layered WS₂ are displayed in Fig. 7(b) and (d), where the slopes of the tangents are band gap energies. The band gaps of TiO₂ and WS₂ are 3.23 and 1.43 eV, respectively. Fig. 7(c) and (e) shows the CB for TiO₂ and WS₂. The CBs of TiO₂ and WS₂ are determined to be -0.40 and -0.73 eV vs. NHE, respectively. Therefore, according to the empirical formula $E_{VB} = E_{CB} + E_g$, the VBs of TiO₂ and WS₂ are calculated to be 2.83 and 0.7 eV vs. NHE, respectively. Therefore, type-II band alignment is produced at the interface of the TNS/WS₂ heterojunctions, which is beneficial for the separation of electron-hole pairs.

The PL spectra of TiO₂, WS₂, and TNS/WS₂-0.10 are shown in Fig. 7(f). Clearly, the PL intensity of TNS/WS₂-0.10 is lower than that of either TiO₂ or WS₂. These results directly confirm that TNS/WS₂-0.10 possesses more efficient carrier separation, which is a result of the heterojunctions between the TiO₂ nanosheets and layered WS₂ suppressing the excited electron-hole pair recombination.

3.3. Photocatalytic studies

To evaluate the photocatalytic activity, photocatalytic degradation of RhB was carried out under visible-light irradiation. As illustrated in Fig. 8(a), the self-degradation of RhB is negli-

ble without photocatalysts. The TiO₂ nanosheets show low adsorption capacity and unsatisfactory activity. In contrast, despite the unsatisfactory photocatalytic activity of WS₂, its adsorption capacity is higher than that of TiO₂ nanosheets. The excellent adsorption capacity of WS₂ was due to the TNS/WS₂ heterojunctions. In addition, the photocatalytic performance of TNS/WS₂ heterojunctions was obviously enhanced, especially TNS/WS₂-0.10, which showed the highest photocatalytic activity as almost 100% RhB was decomposed after 90 min irradiation under visible light. It is noteworthy that the TNS/WS₂ composites still showed higher photocatalytic activity than pure TiO₂ nanosheets under UV irradiation (Fig. S1).

The RhB photodegradation kinetics was fitted by applying a first-order model. The $-\ln(C/C_0)$ plot is shown in Fig. 8(b) and the fitted degradation rates (k) of RhB are illustrated in Fig. 8(c). It is obvious that the TNS/WS₂-0.10 has the highest degradation rate constant, which is about 9.8 and 4.6 times higher than that of TiO₂ nanosheet and layered WS₂, respectively. The notably facilitated photocatalytic performance of TNS/WS₂ heterojunctions may be derived from the synergistic effect of the improvement of light-harvesting properties and the effective separation of photogenerated electrons and holes.

In order to confirm this conclusion, TiO₂ hollow microsphere/layered WS₂ (THS/WS₂) composites were pre-

Fig. 9. HPLC-MS/MS of degradation products toward RhB under different irradiation times over TNS/WS₂-0.10.

pared by the same method for comparison. The TEM images (Fig. S2) indicate that the THS/WS₂ composites are core/shell-structured. Exposed (004) and (101) facets of the TiO₂ hollow microsphere are also found in THS/WS₂-0.10. The surface area of THS/WS₂-0.10 (Fig. S3(a)) is 72.43 m²·g⁻¹, which is close to that of TNS/WS₂-0.10 (76.10 m²·g⁻¹). Furthermore, the light-harvesting properties of THS/WS₂-0.10 (Fig. S3(b)) are greatly improved compared to the pristine TiO₂ hollow microsphere. These experimental data showed that the exposed facets, surface areas, or light-harvesting properties did not primarily contribute to improving the photocatalytic activity. The charge separation efficiency (Fig. S4) of TNS/WS₂-0.10 is higher than that of THS/WS₂-0.10. Meanwhile, the photocatalytic activity of THS/WS₂-0.10 (Fig. S5(a)) is higher than that of the pristine TiO₂ hollow microsphere, but is still lower than that of TNS/WS₂-0.10. The reaction rate of TNS/WS₂-0.10 (Fig. S5(b)) is about five times that of THS/WS₂-0.10. Hence, the 2D-2D heterojunction nanostructure is key to improving the photocatalytic activity of TNS/WS₂ heterojunctions.

Fig. 8(d) shows the time-dependent absorption spectra of the RhB solution under visible-light irradiation in the presence of TNS/WS₂-0.10. The continuous decrease in the absorption intensity at 553 nm indicates the gradually decreasing concentration of RhB with prolonged irradiation time. Interestingly, the major absorption peak of RhB exhibits a small blue-shift from 553 to 530 nm, corresponding to the stepwise formation of a series of *N*-de-ethylated intermediates [38]. With increasing irradiation time, the peak located at 530 nm continues to shift and decrease, which indicates that the RhB molecules are

further decomposed into smaller molecular fragments and the structure of RhB is also destroyed in the end.

The degradation products of RhB over TNS/WS₂-0.10 were further analyzed by HPLC-MS/MS and showed in Fig. 9. The peak at a retention time of 7.5 min is attributed to RhB, and the area of peak decreases with increasing irradiation time. Finally, the peak for RhB almost disappears, demonstrating that RhB is completely decomposed. The results confirm the conclusion of Fig. 8(d). As is well known, the photocatalytic degradation of RhB involves a series of complex chemical reactions, mainly including diethyl, ring-opening, and redox reactions [39,40]. With increasing reaction time, some new peaks appear in the HPLC chromatograms. The new peaks appear at elution times of 4.4, 2.6, 1.9, and 1.6 min, and were further analyzed by MS/MS. The mass-to-charge ratios (*m/z*) were 415.2, 387.2, 359.1, and 331.1, respectively (Fig. S6). The difference between two successive *m/z* values is 28, indicating that the diethyl reaction occurs during photocatalytic degradation. After 90 min of irradiation, the intensity of the peak at 1.1 min is obviously enhanced. The *m/z* for this peak is 89.5, and the chemical composition may be ethylene diacid. The results show that RhB molecules are further decomposed into smaller molecular fragments by the ring-opening reaction [41]. This conclusion could serve as a reference for the degradation of other organic contaminants over the TNS/WS₂ heterojunction photocatalyst.

3.4. Reusability studies

The renewable stability is an important index for practicali-

Fig. 10. Recyclability (a) and XRD patterns (b) of TNS/WS₂-0.10 after three cycles.

ty of the photocatalysts. Here, we investigated the photocatalytic cycle stability of TNS/WS₂-0.10. As shown in Fig. 10(a), the photocatalytic activity of TNS/WS₂-0.10 is effectively maintained, except for a 7% decrease from 96% to 89% after three cycles. To further understand the stability of the samples, the XRD pattern of the sample reused for three cycles was measured. The XRD pattern of TNS/WS₂-0.10 in Fig. 10(b) shows no obvious change. This confirms that TNS/WS₂-0.10 has relatively good stability.

3.5. Photocatalytic mechanism studies

In order to further determine the main active species involved in the degradation process and possible photodegradation mechanism, trapping experiments of TNS/WS₂-0.10 were conducted. For this, K₂Cr₂O₇, ammonium oxalate (AO), tert-butyl alcohol (TBA), and benzoquinone (BQ) were employed as scavengers for the reactive species of e^- , h^+ , $\cdot OH$, and $O_2^{\cdot -}$, respectively. A comparative experiment with no quencher was also performed under the same conditions. As presented in Fig. 11, in the presence of different quenchers, the corresponding photocatalytic efficiency is partly restrained. The degradation of RhB is slightly inhibited by the addition of K₂Cr₂O₇ or

Fig. 11. Effects of a series of scavengers on RhB degradation over TNS/WS₂-0.10. Conditions: irradiation time = 90 min, K₂Cr₂O₇ and AO dosage = 0.2 g, TBA dosage = 4 mL, BQ dosage = 2 mg.

TBA, implying that $\cdot OH$ or e^- is not the main active species responsible for the decomposition of RhB. However, when AO or BQ was added into the reactive solution, the photocatalytic activity of TNS/WS₂-0.10 was remarkably lowered. The degradation efficiency of RhB decreased to 33% in the presence of BQ. Surprisingly, RhB was not entirely degraded after adding AO adding to the reactive solution. Given the above results, holes (h^+) and superoxide anion radicals ($O_2^{\cdot -}$) were the main active species in the reaction process, and h^+ played a dominant role for RhB degradation under visible-light irradiation.

On the basis of the experimental results discussed above and the band positions of TiO₂ and WS₂, the plausible photocatalytic mechanism of TNS/WS₂ heterojunctions was proposed and is illustrated in Fig. 12. From analyses in the above section, we could conclude that the $n-n$ heterojunction is formed and is type-II. When the TNS/WS₂ heterojunctions are exposed to visible light, WS₂ can be excited and yield electron-hole pairs. Because the CB level of WS₂ is more negative than that of TiO₂, the photoexcited electrons in the CB of WS₂ can be injected easily into the CB of TiO₂ and reacted with O₂ in the aqueous solution to form $O_2^{\cdot -}$ and thus degrade RhB. Meanwhile, because the potential of $\cdot OH/H_2O$ (2.32 eV vs NHE) is more positive than that of WS₂ (0.70 eV vs NHE), photogenerated holes accumulate in the VB of WS₂ and directly react with RhB. The large number of holes accelerate the decomposition of RhB into a non-toxic substance. This is why the hole

Fig. 12. Schematic illustration of RhB degradation mechanism over TNS/WS₂ heterojunctions.

plays a dominant role in RhB degradation, rather than $O_2^{\cdot-}$. Finally, the photoinduced electrons and holes are effectively separated through the traditional heterojunction structure, so as to solve the high recombination rate of the photogenerated electron-hole of TiO_2 and greatly enhance its photocatalytic activity under visible light.

4. Conclusions

In summary, 2D-2D TiO_2 nanosheets/layered WS_2 (TNS/ WS_2) heterojunctions were successfully fabricated via a simple hydrothermal reaction. Physical characterization revealed that the layered WS_2 was well-coated on the surface of the TiO_2 nanosheet, which resulted in the formation of a perfect heterojunction structure. There were four coating layers, and WS_2 was connected with TiO_2 by a W=O bond. The as-prepared heterojunction composite exhibited excellent photocatalytic activity and reusability for the degradation of RhB under visible-light irradiation. The degradation products were traced by HPLC-MS/MS and the reaction process was explored. In addition, the typical type-II mechanism was confirmed, demonstrating that holes and superoxide anion radicals ($O_2^{\cdot-}$) played specific roles in the photodegradation process. This work could provide insights toward understanding TiO_2/WS_2 -based composites.

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Graphical Abstract

Chin. J. Catal., 2019, 40: 60–69 doi: 10.1016/S1872-2067(18)63170-5

Construction of 2D-2D TiO_2 nanosheet/layered WS_2 heterojunctions with enhanced visible-light-responsive photocatalytic activity

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The 2D-2D TNS/ WS_2 heterojunction was successfully constructed by in-situ growing the layered WS_2 on the surface of TiO_2 nanosheet. The 2D-2D nanointerfaces boosted the separation of photogenerated carriers, thereby resulting in a higher photocatalytic activity.

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构建2D-2D TiO₂纳米片/层状WS₂异质结用以增强可见光响应光催化活性

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摘要: 自Fujishima等首次报道以来, TiO₂作为一种重要的光催化剂引起了人们的广泛关注. 迄今为止, 研究人员已经开发出了各种形貌的具有不同晶型结构的TiO₂, 并用于光催化降解有机污染物. 然而, TiO₂的宽禁带(3.2 eV)使其难以被可见光激活, 导致对太阳光的利用效率低下. 而且, 在光催化反应中, 低的量子效率无法满足实际应用. 因此, 开发具有可见光响应的高催化活性的TiO₂基催化剂具有重要意义. 集成复合材料、纳米材料和界面的优势构建纳米复合材料已成为提高TiO₂光催化活性的重要策略. WS₂具有典型的类石墨烯层状结构和窄的带隙(1.35 eV), 且其导带高于TiO₂的导带, 适合作为助催化剂修饰TiO₂, 使其具备可见光响应光催化活性.

本文采用一步水热法, 以二维(2D)TiO₂纳米片作基质材料, 直接在其表面原位生长WS₂层, 制得了2D-2D TiO₂纳米片/层状WS₂(TNS/WS₂)异质结. XRD及Raman结果表明, 层状WS₂与TiO₂纳米片紧密结合在一起, 且两者之间形成了W=O键. TEM结果显示, 层状WS₂以面-面堆叠方式均匀地包覆在TiO₂纳米片表面, 包覆层数约为4层. 光催化性能测试结果表明, 可见光照射下, TNS/WS₂异质结对RhB的光催化降解能力高于原始TiO₂纳米片和层状WS₂, 光催化活性得到明显增强.

紫外可见光谱试验结果显示, 层状WS₂的引入极大地增强了异质结的光吸收性能. PL光谱测试表明, TNS/WS₂异质结具有更高效的载流子分离效率. 为了进一步证实是光吸收性能的提升还是载流子分离效率的增强对光催化性能提起其主要作用, 本文还研究了3D-2D TiO₂空心微球/层状WS₂(THS/WS₂)复合材料. 结果表明, TNS/WS₂异质结比THS/WS₂复合材料具有更高效的光生电子和空穴的分离能力. 从而证明了TiO₂纳米片与层状WS₂之间完美的2D-2D纳米界面和紧密的界面结合, 显著增加了载流子分离效率, 因此光催化活性得到明显提高.

为了研究TNS/WS₂异质结光催化剂的光催化机理, 采用重铬酸钾、草酸铵、叔丁醇和对苯醌作自由基猝灭剂进行了自由基捕捉剂实验. 结果表明, 空穴在RhB降解过程中起主要作用, 超氧自由基起次要作用. 基于自由基猝灭实验结果和带隙结构分析, 提出了TNS/WS₂异质结对RhB的光催化机理为双转移光催化机理. 可见, 界面异质结工程化可能是制备高效和环境稳定的光催化剂的新思路.

关键词: WS₂; TiO₂; 纳米片; 异质结; 光催化; 可见光响应

收稿日期: 2018-07-21. 接受日期: 2018-09-21. 出版日期: 2019-01-05.

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基金来源: 国家高技术研究发展计划(863计划, 2012AA063504); 国家自然科学基金(U1407116, 21511130020, 21276193); 天津市自然科学基金(13JCZDJC35600).

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