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Oxygen Vacancy-Enhanced Visible Light-driven Photocatalytic Activity of TiO₂ Sphere-W₁₈O₄₉ Nanowire Bundle Heterojunction

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Abstract

In this study, the $W_{18}O_{49}$ nanowire bundles were grown on the surface of nanoporous TiO_2 sphere by a two-step solvothermal method to fabricate a novel TiO_2 - $W_{18}O_{49}$ nanowire bundle (TW) heterojunction structure. The TiO_2 core and ethylene glycol play important roles in the synthesis. The prepared TW photocatalysts possess larger specific surface area, higher porosity, and stronger visible light absorption than that of TiO_2 . All the TW composites exhibit higher photocatalytic activity in the degradation of rhodamine B (RhB) under visible light and UV light irradiation than that of pure TiO_2 sphere and neat $W_{18}O_{49}$ urchin. The TW125 with the W/Ti ratio of 0.38 presents the highest photocatalytic activity under visible light irradiation, while TW100 with the W/Ti ratio of 0.20 shows the highest photocatalytic activity under UV light irradiation. The W^{5+} defects and oxygen vacancies significantly affected the visible light-driven photocatalytic activity of TW composites. The significantly improved photocatalytic activity is attributed to the synergetic effect of larger surface area, extended visible light absorption and the promoted electron-hole separation. Our study will be helpful to design and optimize the heterojunction photocatalysts, and the novel TW heterojunctions will have great application potential in the field of environmental purification and clean energy.

1. Introduction

Over the past years, visible light photocatalysis has been widely considered as a desirable way to generate clean energy and deal with the environmental purification issues.^[1] Generally, the visible light-driven photocatalytic process involves the visible light absorption, the separation and diffusion of photogenerated charge carrier, and the reactions between photo-induced charge carriers and the adsorbed molecules.^[2, 3] However, their photocatalytic activity under visible light irradiation is still too low to be used in the practical application. The fabrication of efficient heterojunction structures by combining different nanomaterials together is an effective way to extend the light absorption, prevent the charge recombination and further increase the photocatalytic activity.^[4]

Till now, several kinds of heterojunctions such as CdS/TiO₂, WO₃/TiO₂, Fe₂O₃/TiO₂ and Bi₂WO₆/TiO₂ are reported to have the improved visible light-driven photocatalytic activity.^[5] Among them, WO₃/TiO₂ heterojunctions are special and interesting because both TiO₂ and WO₃ are stable and non-toxic. Titanium dioxide (TiO₂) is the most widely used photocatalysts in removal of hazardous compounds.^[7, 8] However, its application in photocatalysis is severely limited by its poor response to visible light and the fast recombination of photogenerated electron-hole pairs.^[9] Although it has a band gap of 2.4~2.8 eV with the effective excitation under visible light irradiation, WO₃ is not a suitable photocatalyst to oxidize the organic pollutants because its single electron reduction potential around +0.5 V is more positive than the reduction potential of O₂.^[10-12] The combination of TiO₂ and WO₃ can effectively integrate both their merits and enhance the photocatalytic activity under visible light irradiation. Up to date, there are some works in the improved photocatalytic activity with the TiO₂ and WO₃ composite.^[13-20] Possessing monoclinic structures with abundant oxygen vacancies and W⁵⁺ defects, W₁₈O₄₉ nanomaterials show stronger visible light absorption with a wide absorption tail in the near

infrared region than WO_3 nanomaterials, which can only utilize the light shorter than 450 nm.

^[21,22] However, growing $\text{W}_{18}\text{O}_{49}$ nanowire on the surface of TiO_2 sphere for the improved photocatalytic activity has never reported yet.

Controlling the size and morphology of nanomaterials makes it possible to tailor and optimize these materials to achieve higher photocatalytic activity.^[23] $\text{W}_{18}\text{O}_{49}$ nanowire has a short charge diffusion length and large surface generating more reactive sites, which offers it good photocatalytic properties in the CO_2 reduction.^[21] Due to the oxygen vacancies and the W^{5+} defects, the blue $\text{W}_{18}\text{O}_{49}$ nanowires have strong light absorption in the visible and near infrared region.^[24, 25] However, the presence of W^{4+} and W^{5+} defects is the main pathway for the photo-excited electron-hole recombination,^[26, 27] which significantly decreases its photocatalytic activity. It is highly expected that the growth of $\text{W}_{18}\text{O}_{49}$ nanowires on the surface of TiO_2 will effectively improve the electron and hole separation, prevent the charge recombination, and enhance the visible light-driven photocatalytic activity.

In this work, TiO_2 sphere- $\text{W}_{18}\text{O}_{49}$ nanowire bundle (TW) heterojunction composites with high photocatalytic activity were scaled up through growing $\text{W}_{18}\text{O}_{49}$ nanowire bundles on the surface of TiO_2 sphere. The nucleation and growth of $\text{W}_{18}\text{O}_{49}$ nanowires were well controlled in the synthetic process. The prepared TW composites have large surface area, good visible light absorption and effective electron-hole separation to prevent the charge recombination. The novel TW composites were used in the photocatalytic degradation of rhodamine B (RhB) under visible light and UV light irradiation. The photocatalytic mechanism and the effect of oxygen vacancies on the TW composites were also investigated. Our study will be interesting and helpful to design high efficient heterojunction photocatalysts. The novel TW heterojunction systems will be widely applied in the Li-ion battery, hydrogen generation and dye-sensitized solar cells.

2. Experimental part:

2.1 Materials

Tetrabutyl titanate (TBT), acetic acid (HAc), tungsten(VI) chloride (WCl_6 , 99%), ethylene glycol (EG, 99%), rhodamine B (RhB, 97%), and ethylene diamine tetraacetic acid (EDTA, 99%), isopropanol (iPP, 99%) and benzoquinone (BQ, 99%) were purchased from Sigma Aldrich Company. Deionized (DI) water was produced from Millipore Milli-Q water purification system. All the solvents were purchased from Merck Company.

2.2 Synthesis of TiO_2 sphere

The TiO_2 sphere was synthesized by the method described in the previous report.^[28, 29] In a typical synthesis, 1.5 mL of TBT was added dropwise to 75 mL of HAc with continuous stirring for 10 min. Thereafter, the obtained white suspension was transferred to a 125 mL Teflon-lined stainless-steel autoclave, which was then heated to 200 °C for 24 h. The product was collected by centrifugation after the autoclave cooled to room temperature and followed by ethanol washing. Finally, the material was vacuum-dried at -50 °C for 24 h for further usage.

2.3 Synthesis of TW heterojunction composites

30 mg of TiO_2 sphere and 100~150 mg of WCl_6 were added into the mixed solvents of 13.3 ml ethanol and 3.3 ml EG under sonication for 10 minutes (named as TW100, TW125, and TW150 according to the quantity of WCl_6). Then the mixture was transferred into a 45 mL autoclave with the purging of N_2 . At last the autoclave was put into the electronic oven at 180 °C for 24 h. The product was centrifuged at 8000 rpm, and washed with ethanol twice. The collected solid was vacuum dried for 2 h for the future applications.

2.4 Characterizations

The morphology and energy-dispersive X-ray spectroscopy (EDX) of TiO₂ sphere and TW composite were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F and SU-8000, Hitachi). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEOL 3010-H microscope operating at 300 kV. The UV-vis absorption spectra were recorded by using a Cary 5000 UV-Vis-NIR spectrophotometer. X-ray powder diffraction (XRD) patterns were taken on a D8-Advance Bruker-AXS diffractometer using Cu K α irradiation operated at 40 kV and 30 mA. Pore volume and size distributions were derived from the desorption branches of the isotherms by the Barrett-Joyner-Halenda (BJH) model, and the Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area from the adsorption data. X-ray photoelectron spectroscopy (XPS) measurements were conducted by using a Kratos Axis Ultra Spectrometer with a monochromic Al K α source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA.

2.5 Photocatalytic Experiments

The degradation of RhB dyes under visible light irradiation ($\lambda > 420$ nm) was tested by a BL-GHX-X photochemical reactor system irradiated by a 500 W Xe lamp. The UV light below 420 nm was filtered by the 1 mmol mL⁻¹ NaNO₂ solution, and the distance between the light source and the solution surface was 15 cm. Typically, aqueous solution of the *RhB* dyes (1.5 mL of 0.5 mg mL⁻¹ solution) was added into the 48.5 mL aqueous dispersions of 50 mg photocatalysts (TiO₂ sphere, W₁₈O₄₉ urchin and TW composites) in quartz capsule of 120 mL. The photocatalytic reaction was started by turning on the lamp. After given time intervals, the 5 mL photo-reacted dispersions were took out and centrifuged for 5 minutes. The centrifuged clear dye solution was analyzed by recording variations of the absorption band maximum in the UV-vis

spectra of RhB. The degradation of RhB under UV light irradiation was conducted by the same reactor system and procedure except the lamp was changed by a 500 W Hg lamp ($\lambda_{\text{max}}=365$ nm).

The investigation of the photocatalytic active species was done with TW125 at the same procedure as the normal visible-light driven photocatalytic degradation of RhB except the addition of benzoquinone (BQ, 1.2 mM), isopropanol (IPP, 1.2 mM) and ethylene diamine tetraacetic acid (EDTA, 1.2 mM) to the photocatalytic system for the capture of the superoxide radicals ($\cdot \text{O}_2^-$), hydroxyl radicals ($\cdot \text{OH}$), and holes (h^+).^[30] The total organic carbon (TOC) remaining in the photoreaction mixture without sacrificial agents after visible light irradiation was measured using a Shimadzu ASI-V TOC analyzer.

3. Results and discussions

The synthesis of TW heterojunction composites was performed by two-step solvothermal approaches. Through varying the quantity and concentration of tungsten chloride, different mass of $\text{W}_{18}\text{O}_{49}$ nanowire bundles can be nucleated and grown on the surface of prepared TiO_2 core. It is highly expected that the apparent morphology of the prepared TW heterojunction composite can be porous core-shell microsphere with inhibited charge recombination and enhanced photocatalytic activity under visible light irradiation.

3.1 synthesis and characterization of TW heterojunction composites

The size and morphology of TiO_2 sphere and the TW100 heterojunction composites are observed from the FESEM and TEM images. As shown in Figure 1a, the original TiO_2 core are sphere-like with the size of around 200-400 nm. After growing a certain quantity of $\text{W}_{18}\text{O}_{49}$ on the surface of TiO_2 sphere, the microsphere-like TW100 heterojunction composite has the size from 500 nm to 2 μm (Figure1b), which is much larger than that of TiO_2 sphere. The increased

average size of TW100 composite may be resulted from the growth of $\text{W}_{18}\text{O}_{49}$ on the surface of TiO_2 sphere. Under TEM observation, it is interesting to find that a lot of anisotropic $\text{W}_{18}\text{O}_{49}$ nanowires are attached on the surface of TiO_2 sphere (Figure 1c). The enlarged TEM images (Figure 1d and e) show that the diameter of the $\text{W}_{18}\text{O}_{49}$ nanowires is about 15-20 nm and composed of individual thinner nanowires. The HRTEM image in Figure 1f gives the clear lattice fringes with the interval spacing of 0.378 nm, which is well indexed as (010) lattice spacing of $\text{W}_{18}\text{O}_{49}$ crystalline.^[31, 32] The individual $\text{W}_{18}\text{O}_{49}$ nanowire has the similar diameter of 3.3 nm, which is a little bigger than that of 1.2 nm in the earlier work.^[33] The $\text{W}_{18}\text{O}_{49}$ nanowire bundles are formed by the attractive forces between the individual nanowires, which can be separated into individual nanowires by the ligands.^[34] The SEM and TEM images confirm the successful growth of $\text{W}_{18}\text{O}_{49}$ nanowire bundles on the surface of TiO_2 sphere, which is very important for the effective electron transfer.

When increasing the quantity of WCl_6 precursors, no apparent increase in the sizes of TW heterojunction sphere is observed compared to that of TW100 (Figure 2). However, the TEM images show thicker $\text{W}_{18}\text{O}_{49}$ nanowire bundles on the surface of TiO_2 sphere, suggesting that more WCl_6 precursors generate more nuclei and then grow more $\text{W}_{18}\text{O}_{49}$ nanowire bundles on the surface of TiO_2 (Figure 2c and f). This indicates that the mass of $\text{W}_{18}\text{O}_{49}$ nanowire bundles can be simply adjusted by changing the WCl_6 quantity, which is significantly essential for the optimization of the TW heterojunction composite.

The exact ratios of W/Ti in the prepared TW heterojunction composites are identified by the EDX spectroscopy. As shown in Figure 3, the TW composites are composed of Ti, W, and O elements with uniform distribution. The calculated atom ratios of W/Ti for TW100, TW125 and TW150 are 0.20, 0.38, and 0.98, respectively.

To thoroughly understand the growth mechanism, a series of comparative experiments were employed to investigate the effects of EG and TiO₂ core in the controllable synthesis of TW composite. As shown in Figure 4a, without the addition of EG, only the mixture of TiO₂ sphere and W₁₈O₄₉ nanowires were obtained. When 10 ml of EG was added in the synthetic system, no W₁₈O₄₉ nanomaterials were produced except the original TiO₂ sphere (Figure 4b). The previous work reported that the EG can react with WCl₆ to form the [EG-W]⁶⁺ composite, which can slow down the reaction speed of WCl₆.^[35] In the absence of EG, the reaction speed of WCl₆ and ethanol is too fast to prevent the homogeneous nucleation of W₁₈O₄₉ nanocrystals. While in the case of excessive addition of EG, the nucleation and growth speed of W₁₈O₄₉ are too slow to generate the W₁₈O₄₉ nanocrystals. Figure 4c and d shows the SEM images of the tungsten oxide products synthesized without the TiO₂ sphere core. Only W₁₈O₄₉ aggregation is produced without the TiO₂ core in EG, which is attributed to the slow nucleation of W₁₈O₄₉. W₁₈O₄₉ urchin spheres with the size of 2 μm were formed without both the TiO₂ core and EG. The controllable synthetic experiments indicate the addition of EG and TiO₂ core are crucial to prepare the TW heterojunction composites. The growth progress can be summarized as follows (Figure 5): 1) WCl₆ reacts with the H₂O in the surface of TiO₂ to generate the W₁₈O₄₉ nuclei; 2) the nuclei of W₁₈O₄₉ grow into W₁₈O₄₉ nanowire bundles on the surface of TiO₂ sphere.

Figure 6a shows the XRD patterns of TiO₂ sphere, TW 100, TW 125, and TW 150. The strong diffraction peaks at $2\theta = 25.4^\circ, 38^\circ, 48.1^\circ, 54.05^\circ, 55.10^\circ$ and 62.85° are observed, which are connected to the (101), (004), (200), (105), (211) and (204) facets of anatase TiO₂ (JCPDS no. 21-1272). The diffraction peaks at 23.35° and 27.72° corresponds to the (010) and (203) crystal faces of the monoclinic W₁₈O₄₉ structure (JCPDS card no. 36-101). The intense (010) peak at 23.35° indicates the anisotropic growth of W₁₈O₄₉ nanocrystals.^[36] With the increase of WCl₆

quantity, the XRD patterns show stronger peaks from monoclinic $W_{18}O_{49}$ crystalline, which is in good accordance with our TEM, SEM and EDX analysis. The UV-vis absorption spectra of TiO_2 and TW heterojunction composites are shown in Figure 6b. The pure TiO_2 sphere has an absorption onset of 374 nm without any visible light absorption. However, after the growth of $W_{18}O_{49}$ nanowire bundles on the surface of TiO_2 , the absorption onset of TW composites are at 410 nm, which is red-shift a lot in comparison with that of pure TiO_2 . Furthermore, all the TW composites show strong absorption in the visible and near infrared area, which is caused by the oxygen vacancy and W^{5+} defects.^[37, 38] With the increase of $W_{18}O_{49}$ quantity, the TW composites present stronger visible light absorption.

The specific surface areas are important for the high effective photocatalysts. Large surface area can offer more active sites for the photocatalytic reaction. We tested the surface area and pore size by nitrogen adsorption and desorption. The N_2 adsorption-desorption isotherm by all the TW composites in Figure S2 exhibits a type I isotherm with H4 hysteresis loop typical of microporous materials, indicating the mesoporous structures.^[39] The calculated BET values for TiO_2 sphere, TW100, TW125, and TW150 are 1.6, 34.3, 59.3, 66.8 $m^2 g^{-1}$, respectively. The pure TiO_2 sphere without sintering process doesn't have a nanoporous structure with low BET values. Because of the large surface area of ultrathin $W_{18}O_{49}$ nanowires, the TW composite have much larger specific surface area than that of pure TiO_2 sphere. The pore size distribution curves in Figure S2 clearly show the peaks concentrating at 37 nm and 43 nm for the TiO_2 sphere and TW composites, indicating the larger silt-like pores formed after the growth of $W_{18}O_{49}$ nanowire bundles on the surface of TiO_2 .^[39] The BET analyses confirm the significantly increased surface area and pore size with the growth of $W_{18}O_{49}$ nanowire bundles on the surface of TiO_2 .

3.2 Photocatalysis properties and mechanism

The photocatalytic activity of TiO₂ sphere and TW composites with different W/Ti ratios were evaluated by the photodegradation of 0.75 mgmL⁻¹ RhB by the 1 mgmL⁻¹ photocatalysts under visible light irradiation ($\lambda > 420$ nm) and UV light irradiation ($\lambda_{\text{max}} = 365$ nm). Before starting the photocatalytic reaction, the mixture of RhB and photocatalysts were stirring for 1 h to reach the adsorption equilibrium (FigureS3). Figure 7a presents the UV-vis absorption spectra of RhB after adsorbed by photocatalysts. The original RhB aqueous solution shows the strong absorption peak centered at 554 nm with the intensity of 3.03. After equilibrium adsorption by TiO₂, TW100, TW125 and TW150, the adsorption intensity drops down to 2.25, 1.93, 1.31, and 1.03, respectively. This indicates that more RhB dyes were absorbed by the TW composites with the increased W/Ti ratios. The adsorption capability of photocatalysts contributes a lot to the removal of RhB and the photocatalytic activity.

The photocatalytic degradation kinetic curves of RhB by TiO₂ sphere, W₁₈O₄₉ urchin and TW composites under visible light irradiation ($\lambda > 420$ nm) are shown in Figure 7b. The results show that 23% and 31% of RhB can be degraded by pure TiO₂ sphere and neat W₁₈O₄₉ urchin after 90 minutes of irradiation. It is interesting that W₁₈O₄₉ urchin with strong visible light absorption shows weak photocatalytic activity, which is only slightly higher than that of pure TiO₂. The low photocatalytic activity of pure W₁₈O₄₉ is ascribed to its lower conduction band (CB) edge and fast electron- hole recombination.^[40, 41] After the growth of W₁₈O₄₉ nanowire bundles on the surface of TiO₂, the 39%, 51% and 45% of RhB were degraded by TW100, TW125 and TW150 after 90 minutes of irradiation, respectively. It is clear that TW125 with the W/Ti ratio of 0.38 presents higher photocatalytic activity than TW100 and TW150. The polynomial fit results show that the photocatalytic reactions follow the pseudo second-order kinetics (Figure 7c). The related degradation rate constants of k for the TiO₂, W₁₈O₄₉ urchin,

TW100, TW125 and TW150 are 0.00566, 0.00751, 0.01063, 0.0153, 0.01337 min^{-1} , respectively. The TW125 heterojunction composite shows the highest k value, which is about 3 times of pure TiO_2 and 2 times of neat $\text{W}_{18}\text{O}_{49}$ urchin. This indicates that the fabrication of TW heterojunction can significantly increase the photocatalytic activity under visible light irradiation. The photocatalytic stability under visible light irradiation was examined by the photocatalytic cycling experiments. As shown in Figure 7d, after the 4 recycling degradation of RhB, the TW125 composite shows very similar photocatalytic activity to that of the first cycle, demonstrating the good photocatalytic stability under visible light irradiation.

Because RhB can strongly absorb the visible light, we also investigated the photocatalytic activity of all the WT photocatalysts (50 mg/mL) by monitoring the photocatalytic degradation of 10 ppm phenol under visible light irradiation. As shown in Figure 8a, the adsorbed amounts of phenol are less than that of RhB by all the photocatalysts, which may be caused by the weaker coordination capability of phenol than RhB. All the TW composites show good performances in the photocatalytic degradation of phenol with 31%, 64% and 54% of phenol degraded by TW100, TW125 and TW150 after 90 minutes of visible light irradiation. The related degradation rate constants (k) are 0.00037, 0.00957, 0.02502 and 0.01214 min^{-1} for TiO_2 , TW 100, TW125, and TW150 photocatalysts (Figure 8b). It is glad to see that the photocatalytic degradation of phenol by TW composites shows the similar activity series as TW 125>TW150>TW100 to that from the photodegradation of RhB. Figure 8c shows the removal of TOC in solutions of phenol by TW composites under visible light irradiation. After 1.5 h of irradiation, 21%, 47% and 38% of TOC were removed by TW100, TW125 and TW150 composites, which is lower than that from the UV-vis spectra monitoring (Figure 8d). This suggests that the mineralization of phenol is not enough after 1.5 h of visible light irradiation and the degraded phenol moleculars are not

totally oxidized into harmless gaseous CO₂. Moreover, the TOC analyses show the similar kinetic plots to the UV-visible results, indicating the mineralization keep synchronization with the degradation of the phenol solution.

In order to further explore the photocatalytic mechanism more clearly, we tested the photocatalytic degradation of RhB under UV light ($\lambda_{\text{max}}=365$ nm) irradiation by all the TiO₂ sphere and TW heterojunction composites. Because the absorption onset of TiO₂ is at around 374 nm, we chose the UV light with the maximum wavelength of 365 nm as the excitation light source. As shown in Figure 9a, after irradiation under UV light for 1 h, 37%, 61%, 55% and 49% of RhB were degraded by TiO₂, TW 100, TW125 and TW150 photocatalysts, respectively. The related degradation rate constants (k) are 0.00912, 0.02776, 0.02381 and 0.01925 min⁻¹ for TiO₂, TW 100, TW125, and TW150 photocatalysts (Figure 9b). It is clearly shown that the TW heterojunction composites also have much higher photocatalytic activity than that of TiO₂ under UV light irradiation. We notice that the TW100 with lower W/Ti ratios of 0.20 has the highest photocatalytic activity with the k value of 0.02776 min⁻¹, which is 3 times of that of TiO₂ sphere. It is different with the result under visible light irradiation, which shows the TW125 with medium W/Ti ratio of 0.38 has the highest photocatalytic activity.

In order to investigate the active species and further confirm the photocatalytic mechanism, we added 1.2 mM of BQ, iPP and EDTA into the photocatalytic system to capture the superoxide radicals ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$), and holes (h^+).^[30] As shown in Figure 10a, under the visible light irradiation, the photocatalytic activity of TW125 doesn't show evident decrease with the addition of BQ. This indicates that the $\cdot\text{O}_2^-$ is not main active specie for the TW photocatalysts under visible light irradiation. The conduction band level of W₁₈O₄₉ is lower than

the reduction potential of O_2 to generate the $\cdot O_2^-$,^[11] and our result is in good consistence with this analyses. With the addition of hole scavenger (EDTA) and $\cdot OH$ radical scavenger (iPP), the photocatalytic activity of TW125 decreased significantly under visible-light irradiation. This suggests that the exposed hole plays a decisive role in the photocatalytic activity of TW 125, and the hydroxide radicals are the main active species in the photocatalytic degradation of RhB.

The positions of conduction band (CB), valance band (VB) and their bandgap play key roles in the charge separation and transportation. As shown in Figure 10b, the CB and VB values of $W_{18}O_{49}$ nanowire bundles lies at +0.61 and +3.27 eV, while those values for anatase TiO_2 are at -0.38 and +2.82 eV.^[27] It is evident that the hole can transfer from $W_{18}O_{49}$ to the VB of TiO_2 under visible light irradiation, which leads to better charge separation and higher photocatalytic activity. The higher $W_{18}O_{49}$ quantity offers more separated electrons and holes under visible light irradiation. However, too much $W_{18}O_{49}$ on the surface of TiO_2 will cover the surface of TiO_2 and prevent the hole to oxidize the dye during the photocatalytic process. On the other hand, under UV light irradiation, the irradiated electron can transfer from the CB of TiO_2 to the CB of $W_{18}O_{49}$, which improves the photocatalytic activity by inhibition of charge recombination as well. However, more $W_{18}O_{49}$ on the surface will shield TiO_2 from the UV light irradiation and block the holes to contact with the RhB dye, resulting in a decreased photocatalytic activity. This indicates that the balance of light absorption and the exposed hole of TiO_2 are crucial to achieve high photocatalytic activity of TW photocatalysts.

The oxygen vacancies and the W^{5+} defects have important influence on the visible light absorption of $W_{18}O_{49}$.^[42, 43] In the earlier work, Ye et al. found that the photocatalytic reduction of CO_2 under visible light irradiation was significantly affected by the oxygen vacancies of

W₁₈O₄₉ nanowires.^[21] Here we also investigate the effect of the oxygen vacancies in the photocatalytic degradation of RhB under visible light irradiation. For comparison, we oxidized TW125 at 180 °C for 1 and 3 h, and then tested the visible light-driven photocatalytic degradation of RhB. Figure 11a shows the UV-vis absorption spectra of TW125 after different oxidation times at 180 °C in the air. After oxidation, the main band-gap absorption onset is red-shifted slightly from 410 to 440 nm, and the absorption intensity in the visible and near infrared region caused by the oxygen vacancies decreases remarkably. After oxidation for 3h, the TW125 has nearly no evident absorption in the visible light and near infrared area with colour turning to yellow-white. Figure 11b shows the high resolution XPS spectra of W4f from TW125 and TW125 after oxidation for 3 h. The peaks at a binding energy of 35.5 and 37.6 eV are corresponded to the reported values of the W⁶⁺ oxidation state while the peaks at 34.2 and 36.3 eV are consistent with the values of the W⁵⁺ oxidation state.^[44] The weak peak of W5p, which is typical for W⁶⁺, can be observed for the oxidized TW125 samples. The calculated W⁵⁺:W⁶⁺ ratios for TW125 and TW125 after oxidation for 3h are 1:8 and 1:20, respectively. This suggests that the W⁵⁺ defects can be oxidized and plays a key role in the visible and near infrared absorption of W₁₈O₄₉. The photocatalytic degradation of RhB and kinetic plots by the TW125 and oxidized TW125 under visible light irradiation are shown in Figure 11c and d. The degradation rate constants (*k*) for TW125, TW125 after oxidation for 1h and 3h are 0.0153, 0.01035, and 0.00649 min⁻¹. This indicates that the photocatalytic activity of TW composites under visible light irradiation declines with the reduced oxygen vacancies and W⁵⁺ defects.

The significant improved photocatalytic activity of TW composites can therefore be assigned to the synergistic effects of the increased surface area, the enhanced visible light absorption caused by the oxygen vacancy and W⁵⁺ defects, and the promoted charge separation.

4. Conclusions

In summary, we rationally designed and prepared a series of TW heterojunction photocatalysts by growing $W_{18}O_{49}$ nanowire bundles on the surface of TiO_2 sphere. TiO_2 core and EG play important roles in the controllable synthesis of $W_{18}O_{49}$ nanowires on the surface of TiO_2 sphere. The TW heterojunction composites present larger specific surface area and stronger visible light absorption than that of pure TiO_2 core. The TW heterojunction photocatalysts show significantly stronger adsorption capability of RhB and higher photocatalytic activity than that of pure TiO_2 and neat $W_{18}O_{49}$ urchin under both visible light and UV light irradiation. The TW125 heterojunction composite with the W/Ti ratio of 0.38 exhibits the highest photocatalytic activity under visible light irradiation, while the TW100 composite with the W/Ti ratio of 0.20 presents the highest photocatalytic activity under UV light irradiation. The oxygen vacancies and W^{5+} defects have great influence on the visible light-driven photocatalytic activity of TW composites. The significantly enhanced visible light-driven photocatalytic activity is attributed to the synergistic effects of the increased surface area, the enhanced visible light absorption, and the improved charge separation.

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Figure Captions:

Figure 1. SEM images of a) TiO_2 sphere and b) TW 100. c) TEM image of TW100 heterojunction, d) enlargement of image c, e) enlargement of image d, f) HRTEM image of $\text{W}_{18}\text{O}_{49}$ nanowire bundles.

Figure 2. SEM images (a, b) and TEM image (c) of TW 125. SEM images (d, e) and TEM image (f) of TW 150.

Figure 3. EDX and elemental mapping of TiO_2 sphere- $\text{W}_{18}\text{O}_{49}$ nanowire heterojunction.

Figure 4. a) TiO_2 sphere- $\text{W}_{18}\text{O}_{49}$ composite synthesized without ethylene glycol (30 mg TiO_2 , 100 mg WCl_6). b) TiO_2 sphere- WO_3 composite synthesized with 10 mL of ethylene glycol (30 mg TiO_2 , 100 mg WCl_6). c) $\text{W}_{18}\text{O}_{49}$ synthesized without TiO_2 core (100 mg WCl_6 , 13.3 mL ethanol, 3.3 mL ethylene glycol). d) $\text{W}_{18}\text{O}_{49}$ synthesized without ethylene glycol (100 mg WCl_6 , 17 mL ethanol).

Figure 5. Schematic illustration of the growth mechanism of TW heterojunction

Figure 6. XRD patterns (a) and UV-vis absorption (b) of TiO_2 sphere, TW100, TW125 and TW 150.

Figure 7. a) UV-vis absorption spectra of RhB after 1 h adsorption by TiO_2 sphere and TW composites. b) The photocatalytic degradation of RhB by TiO_2 sphere, WO_3 urchin and TW composites. c) Kinetic plots by TiO_2 sphere, WO_3 urchin and TW composites. d) Recyclability of the photocatalytic decomposition of RhB by TW125 composite.

Figure 8. a) The photocatalytic degradation of phenol by TiO_2 sphere and TW composites under visible light irradiation. b) Kinetic plots by TiO_2 sphere and TW composites. c) TOC degradation efficiency of phenol under visible light irradiation. d) Photocatalytic removal of phenol by TW composites under visible light irradiation.

Figure 9. The photocatalytic degradation of RhB (a) and kinetic plots (b) by TiO_2 sphere and TW composites under UV light irradiation ($\lambda_{\text{max}}=365 \text{ nm}$).

Figure 10. a) The photocatalytic degradation of RhB by TW125 composites with the addition of 1.2 mM BQ, 1.2 mM iPP and 1.2 mM EDTA under visible light irradiation. b) Schematic illustration of energy band diagrams and the photogenerated charge-carrier transfer in TiO_2 - $\text{W}_{18}\text{O}_{49}$ composite.

Figure 11. UV-vis absorption spectra (a), XPS spectra (b) of TW125 after oxidation at 180°C in air. The photocatalytic degradation of RhB (c) and kinetic plots (d) by TW125 after oxidation in air at 180°C under visible light irradiation ($\lambda > 420 \text{ nm}$).

Figure 1. SEM images of (a) TiO₂ sphere and (b) TW 100. c) TEM image of TW100 heterojunction, d) enlargement of image c, e) enlargement of image d, f) HRTEM image of W₁₈O₄₉ nanowire bundles.

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Supplementary Information

Oxygen Vacancy-Enhanced Visible Light-driven Photocatalytic Activity of TiO₂ Sphere- W₁₈O₄₉ Nanowire Bundle Heterojunction

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Figure S1 EDX of TiO_2 sphere- WO_3 composite synthesized with 10 mL of ethylene glycol (30 mg TiO_2 , 100 mg WCl_6)

Figure S2 N₂ adsorption-desorption isotherms (top) and pore sizes (bottom) of TiO₂ sphere, TW100, TW125 and TW 150.

Figure S3 Adsorption dynamic graphs of RhB by TiO₂ and TW composite.