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Crystalline phase engineering in WO$_3$/g-C$_3$N$_4$ composites for improved photocatalytic performance under visible light

Junmei Liang$^1$, Yuhui Li$^1$, Jing Zhang$^2$, Chun Li, Xia Yang, Xuebing Chen, Fangfang Wang and Changdong Chen

College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, Liaoning, People’s Republic of China

$^1$ These authors contributed equally to this work.

E-mail: jingzhang_dicp@live.cn

Abstract

The photocatalytic performance of a semiconductor material is significantly related to its crystalline phase, thus, crystalline phase engineering is of importance for designing the semiconductor composites fabricated between two semiconductor materials. In this work, WO$_3$/g-C$_3$N$_4$ composites was taken as an example, we designed and prepared the WO$_3$/g-C$_3$N$_4$ composites with different crystalline phases of WO$_3$. The important role of the crystalline phase of WO$_3$, which is hexagonal phase (h-WO$_3$), monoclinic phase (m-WO$_3$), and mixed phases of h-WO$_3$ and m-WO$_3$ on the morphology, photoabsorption property, charge separation efficiency, and photocatalytic activity of the WO$_3$/g-C$_3$N$_4$ composites were systematically investigated. By evaluating the photocatalytic degradation of RhB, it is found that the highest photocatalytic activity was achieved by WO$_3$/g-C$_3$N$_4$ with 25 wt% h-WO$_3$ and 75% g-C$_3$N$_4$ (H1G3). The enhanced photocatalytic performance of H1G3 was mainly attributed to the improvement in the separation efficiency of photogenerated electron-hole pairs, which was confirmed by surface photovoltage results. Our work sheds a light on the design of composite photocatalysts based on semiconductor oxides.

1. Introduction

Photocatalysis has been receiving much attention as one of the promising alternatives to solve the imminent issues of industrial wastes and pollutants. For their satisfying performance and robust stability, semiconductor photocatalysts, such as TiO$_2$ and WO$_3$ were considered as promising candidates for photocatalytic pollutants degradation or hydrogen production [1–3]. However, the application for the photocatalytic technology based on the semiconductor photocatalysts is restricted its low photocatalytic efficiency, which is strongly influenced by the separation efficiency between the photoinduced electrons and holes [1]. Based on the intensive studies on the semiconductor materials, it is found that there are many semiconductor materials in nature that have more than one crystalline phases [5, 6]. Moreover, the photocatalytic performance of a semiconductor material is significantly related to its crystalline phase because different crystalline phases usually display the different physical and chemical properties [7]. For example, TiO$_2$ has anatase and rutile crystalline phase, in which anatase usually shows the higher photocatalytic activity [6].

Tungsten oxide (WO$_3$), which is a famous visible-light photocatalyst possesses polymorphs as commonly investigated hexagonal (h-WO$_3$) and monoclinic phase (m-WO$_3$), which drew considerable attention on the crystalline phase dependent photocatalytic performance [5, 8]. Wang et al [9] designed two-dimensional WO$_3$ nanoplates with hexagonal phase, and the resulted nanoplates h-WO$_3$ showed the high photogenerated charges separation efficiency and the high photocatalytic activity in water oxidation. However, in some cases, WO$_3$ nanoplates and nanorods with m-WO$_3$ phase synthesized by the hydrothermal process showed high photocatalytic activity [10]. Recently, we designed and prepared the heterophase junction between h-WO$_3$ and...
m-WO₃, which is the interface region between h-WO₃ and m-WO₃ by finely controlled thermal treatment of tungsten precursor, and the formation of the heterophase junction was found to greatly enhance charge separation and then boost the photocatalytic performance [11].

Apart from a single semiconductor material, it is known that the formation of the composites structure between two semiconductor materials is a common strategy for improving the photogenerated charge carriers separation efficiency and the photocatalytic performance. Recently, g-C₃N₄ has drawn attention in research fields of photocatalytic degradation, water splitting and CO₂ reduction [12–14]. As one type of carbon based material, g-C₃N₄ possesses the advantages of multiply available synthetic methods for designing fine nanostructures and accommodating with other materials to form composite materials for efficient photocatalysis [15–17]. For example, Liang et al [16] prepared WO₃/g-C₃N₄ composites tuned by facile acid-mediated self-assembly, which obtained enhanced photocatalytic degradation under visible light. Shanavas et al [18] prepared all solid state 2D/3D/2D rGO/Fe₂O₃/g-C₃N₄ nanocomposite efficiently boosts the photocatalytic degradation tetracycline and ciprofloxacin under visible light. As noted above, since the photocatalytic performance of a semiconductor is directly related to its crystalline phase, the crystalline phase engineering is great importance for designing the semiconductor composites with high photocatalytic performance.

In this work, a WO₃/g-C₃N₄ composite was taken as an example, we systematically investigated the important role of the crystalline phase of WO₃, which is hexagonal phase (h-WO₃), monoclinic phase (m-WO₃), and mixed phases of hexagonal and monoclinic phase (HMA and HMB), and monoclinic phase (m-WO₃) were prepared by calcining APT at 350 °C for 20 min, 400 °C for 10 min, 450 °C for 4 h, and 450 °C for 10 h, respectively. The WO₃/g-C₃N₄ composites were prepared through co–calcining of WO₃ and g-C₃N₄. Typically, the prepared HMB and g-C₃N₄ were firstly mixed thoroughly with the weight ratio of HMB as 25, 50 and 75 wt%.

2. Experimental section

2.1. Materials

Ammonium tungstate hydrate (APT), urea (CO(NH₂)₂), rhodamine B (RhB), diammomium oxalate ((NH₄)₂C₂O₄), ascorbic acid (AA), potassium dichromate (K₂Cr₂O₇), and isopropanol (IPA) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis of WO₃/g-C₃N₄

The g-C₃N₄ was prepared by directly heating 20 g urea to 500 °C for 4 h at the heating rate of 10 °C·min⁻¹. The WO₃ samples were synthesized by heating APT at different temperatures, among which hexagonal phase (h-WO₃), mixed phases of hexagonal and monoclinic phase (HMA and HMB), and monoclinic phase (m-WO₃) were prepared by calcining APT at 350 °C for 20 min, 400 °C for 10 min, 450 °C for 4 h, and 450 °C for 10 h, respectively.

The WO₃/g-C₃N₄ composites were prepared through co–calcining of WO₃ and g-C₃N₄. Typically, the prepared HMB and g-C₃N₄ were firstly mixed thoroughly with the weight ratio of HMB as 25, 50 and 75 wt%, respectively. The obtained powder mixtures were then calcined in the muffle furnace at 400 °C for 10 min with a heating rate of 5 °C·min⁻¹ to obtain the WO₃/g-C₃N₄ composites, which is denoted as HMB1G3, HMB1G1, and HMB3G1, respectively according to the ratio of HMB and g-C₃N₄. The HMA1G3, H1G3 and M1G3 were prepared in the similar methods, wherein WO₃ with the weight ratio of 25% was HMA, h-WO₃ and m-WO₃, respectively.

2.3. Characterization

The crystal phases of the obtained samples were characterized by x-ray diffraction (XRD) on a Rigaku MiniFlex diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) at a scan rate of 5°·min⁻¹. The morphology was characterized by scanning electron microscopy (SEM, Quanta 200 F). Raman spectra excited at 532 nm were acquired on a home-assembled UV Raman spectrograph (DL-3 UV Raman spectroscopy with operando system). The specific surface area was determined by Brunauer–Emmett–Teller method (BET) using an Autosorb-IQ2–MP. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded using a JASCOV-550 UV–
vis spectrophotometer in the range of 200 to 800 nm. The surface photovoltage measurements (SPV) were conducted by an assembled instrument including a photovoltaic cell where the photocatalyst powders are stuck in the middle of two ITO electrodes ($d = 1.2 \text{ mm}$, resistivity: $8 \sim 12 \Omega \cdot \text{cm}^{-2}$, Sigma-Aldrich, USA). A lock-in amplifier (SR830 DSP, Stanford research systems, USA) was applied to amplify the photovoltage signal of samples, and a 500 W xenon lamp (CHF-XM-500W, Beijing Perfect Light Co., China) was used as the optical source coupling with a grating monochromator (Omni-λ3007, Zolix, China) providing monochromatic light. No external bias was applied.

2.4. Photocatalytic activity test
Under the visible light of a 500 W iodine tungsten lamp, the photocatalytic activities of various WO$_3$/g-C$_3$N$_4$ composites were evaluated by the degradation of RhB in aqueous solution. In each experiment, 60 mg sample was added into a 40 mg·l$^{-1}$ RhB aqueous solution of 60 ml, and the suspension was magnetically stirred in the dark for 30 min to reach an adsorption-desorption equilibrium before the visible light irradiation. A 3 ml of the suspension were collected at the irradiation time intervals of 30 min, and then immediately centrifuged (9000 r·min$^{-1}$, 30 min) to remove the photocatalyst. The concentration of RhB was analyzed by the UV–vis absorption at a wavelength of 553 nm.

2.5. Active species trapping experiments
In order to study the main active species in the photocatalytic degradation process of RhB, the following steps were used for active species trapping experiments. In the photocatalytic degradation of RhB, 1 mM K$_2$Cr$_2$O$_7$, 1 mM (NH$_4$)$_2$C$_2$O$_4$, 1 mM AA, and 1 mM IPA were respectively applied as the scavengers for photo-induced electron ($e^-$), holes ($h^+$), superoxide radical ($\cdot$O$_2^-$) and hydroxyl radical ($\cdot$OH), while other conditions remain unchanged.

3. Results and discussion

3.1. Structural analysis of h-WO$_3$, m-WO$_3$ and mixed phases of h-WO$_3$ and m-WO$_3$ (HMA and HMB)
The WO$_3$ with different crystalline phases was designed and prepared in this study. Figure 1(a) shows the XRD patterns of the as-prepared WO$_3$ samples. The peaks located at 13.9$^\circ$ and 28.1$^\circ$ in green line were ascribed to h-WO$_3$ (JCPDS No. 85-2459), confirming the formation of hexagonal phase when APT was calcined at 350$^\circ$C for 20 min. The peaks observed at 23.1$^\circ$, 23.6$^\circ$, 24.4$^\circ$ and 34.2$^\circ$ in blue line were in well accordance with the standard characteristic peaks of m-WO$_3$ (JCPDS No. 71-2141), indicating the formation of pure m-WO$_3$ when APT was calcined 450$^\circ$C for 10 h. The formation of m-WO$_3$ was due to the complete transformation from hexagonal to monoclinic WO$_3$ [11]. Obviously, the mixed phases of hexagonal and monoclinic WO$_3$ was obtained by calcination of 450$^\circ$C for 4 h (HMA) or 400$^\circ$C for 10 min (HMB) because of the incomplete transformation from h-WO$_3$ to m-WO$_3$, which is similar as our previous results [19].

According to the XRD diffraction pattern, the phase content of m-WO$_3$ and h-WO$_3$ phases (Wm, Wh) in the above HMA and HMB samples can be estimated by using the following formula [20]:

![Figure 1. XRD patterns (a) and Raman spectra (b) of WO$_3$ samples.](image)
where the \( I_m \) and \( I_h \) are the intensities of the strongest lines of the XRD patterns of m-WO\(_3\) and h-WO\(_3\), respectively. The RIR values for m-WO\(_3\) and h-WO\(_3\) is 5.57 (PDF #71-2141) and 7.92 (PDF #85-2459), respectively. Therefore, the calculated contents of h-WO\(_3\) and m-WO\(_3\) in HMA are 88% and 12%, respectively, and the calculated contents of h-WO\(_3\) and m-WO\(_3\) in HMB are 15% and 85%, respectively.

Raman spectroscopy (figure 1(b)) was also conducted to investigate the crystalline phases of as-prepared WO\(_3\) samples. According to the results from Gu Z’s work [21], the Raman bands located in the range of 900–980, 600–850 and 200–400 cm\(^{-1}\) can be assigned to W=O stretching, O=W–O stretching, and O=W–O bending modes, respectively. As shown in figure 1(b), the Raman bands at 68, 106, 190, 278, 332, 716 and 814 cm\(^{-1}\) observed in the green line of h-WO\(_3\) sample were attributed to pure h-WO\(_3\), while Raman bands of pure monoclinic WO\(_3\) (68, 138, 190, 278, 332, 716 and 814 cm\(^{-1}\)) were observed in the blue line of m-WO\(_3\) sample [22,23], respectively. Both the characteristic bands of h-WO\(_3\) and m-WO\(_3\) were observed in the HMA and HMB (pink line and red line in figure 1(b)), indicating that the coexistence of h-WO\(_3\) and m-WO\(_3\). Combined with the results from XRD and Raman spectra (figure 1), the crystalline phase of WO\(_3\) was precisely controlled by tuning the calcination temperature and calcination time, which was necessary for the preparation of WO\(_3\)/g-C\(_3\)N\(_4\) composites with different WO\(_3\) crystalline phases.

3.2. Effect of weight ratio of WO\(_3\) on the photocatalytic performance of WO\(_3\)/g-C\(_3\)N\(_4\) composites

To investigate the effect of WO\(_3\) weight ratio on the photocatalytic performance of WO\(_3\)/g-C\(_3\)N\(_4\) composites, HMB was taken as an example to prepare WO\(_3\)/g-C\(_3\)N\(_4\) composites with different weight ratios of WO\(_3\) (HMB1G3, HMB1G1 and HMB3G1). As shown in figure 2, major diffraction peaks at 13.9° and 27.2° can be observed in the XRD pattern of pure g-C\(_3\)N\(_4\), corresponding to the (100) and (002) plane of the characteristic interplanar stacking structures of graphitic materials [24,25]. The XRD pattern of HMB1G3, HMB1G1, and HMB3G1 sample is quite similar as that of HMB, in addition to a weak peak at 27.2° attributed to g-C\(_3\)N\(_4\). These results clearly indicate that the successful fabrication of the WO\(_3\)/g-C\(_3\)N\(_4\) composites, and the crystalline phase of HMB was not changed after combination with g-C\(_3\)N\(_4\).

Furthermore, to make it clear the effect of weight ratio of HMB on the photocatalytic activity in WO\(_3\)/g-C\(_3\)N\(_4\) composites under visible light, RhB was chosen as the model pollutant to evaluate the photocatalytic performance on HMB1G3, HMB1G3 and HMB1G3 (figure 3). The apparent reaction rate constant (\( k \), min\(^{-1}\)) was linearly fitted to pseudo-first-order kinetics of RhB photocatalytic degradation (figures 3(a) and (b)) to quantitatively compare the photocatalytic performance [26]:

\[
\ln \left( \frac{C}{C_0} \right) = kt
\]

where \( C_0 \) and \( C \) are the initial concentration and concentrations at an irradiation time \( t \) (min) of RhB, respectively.

![Figure 2](image-url)
As shown in figure 3(c), the k constant was 0.0016 min⁻¹ for HMB, but the k constant was greatly increased to 0.0073, 0.0045 and 0.0036 min⁻¹ for HMB1G3, HMB1G1 and HMB3G1, respectively. These results suggest the formation of the WO₃/g-C₃N₄ composites greatly enhanced the photocatalytic activity, as compared to pristine HMB-WO₃. Especially, the HMB1G3 composite, which possessed the highest k value among the WO₃/g-C₃N₄ composites exhibited ~4 times higher k value than HMB. The enhancement in the photocatalytic activity can be attributed to the formation of heterojunction between WO₃ and g-C₃N₄ in the WO₃/g-C₃N₄ composites. The formation of heterojunction between WO₃ and g-C₃N₄ is beneficial for the separation of photogenerated electron and hole [27], which is verified by the surface photovoltage spectroscopy (figure S1 is available online at stacks.iop.org/MRX/7/065503/mmedia). These results indicated that the weight ratio of WO₃ was one of the important factors affecting the photocatalytic performance in WO₃/g-C₃N₄ composites, which is similar as previous results [28].

3.3. Photocatalytic performance of WO₃/g-C₃N₄ composite with different Crystal phases of WO₃

After confirming the optimal weight ratio of WO₃ in the WO₃/g-C₃N₄ composites, we prepared the WO₃/g-C₃N₄ composites, including composites based on pure hexagonal WO₃ (H1G3), monoclinic WO₃ (M1G3) and mixed phases of hexagonal and monoclinic WO₃ (HMA1G3 and HMB1G3) using WO₃ weight ratio as 25 wt%, respectively. As displayed in figure 4(a), XRD patterns of H1G3, M1G3, HMA1G3, and HMB1G3 are quite similar as that of h-WO₃, m-WO₃, HMA, and HMB, respectively. These results again indicate that the crystalline phase of WO₃ was not changed after combination with g-C₃N₄. Additionally, a typical peak at 27.3° of g-C₃N₄ was also observed in the patterns of all four composites, indicating the coexistence of WO₃ and g-C₃N₄.

The SEM was used to study the morphology of the WO₃/g-C₃N₄ composites with different crystalline phases of WO₃. As shown in figures 4(b)–(d), g-C₃N₄ in H1G3, HMB1G3, and M1G3 samples showed aggregated and layered stacking morphology, in accordance with the typical g-C₃N₄ morphology prepared through the thermal polymerization method [29, 30]. In H1G3, HMB1G3, and M1G3 samples, WO₃ exhibiting mainly grain-like particles was loaded and dispersed onto the surface of g-C₃N₄. Moreover, an intimate contact between g-C₃N₄ and WO₃ are observed in figures 4(b)–(d), suggesting the formation of heterojunction between them. Clearly, the particles of h-WO₃ possessed considerable dispersion, and no obvious aggregation was observed, as shown in figure 4(b). However, the particles of HMB or m-WO₃ aggregated on the surface of g-C₃N₄ are observed in figures 4(c) and (d). It is known that the well particles dispersion is beneficial for the enhancement in the photocatalytic performance [31].

The effect of the WO₃ phase on the photocatalytic performance of WO₃/g-C₃N₄ composites was evaluated by degradation of RhB under visible light (figure S2). As shown in figure 5, the degradation rate constants (k) of g-C₃N₄, H1G3, HMA1G3, HMB1G3 and M1G3 were determined to be 0.0093, 0.031, 0.012, 0.0073 and 0.0097 min⁻¹, respectively (figure 5). Obviously, the formation of the WO₃/g-C₃N₄ composites boosts the photocatalytic activity. Moreover, it is found that H1G3 exhibits the highest photocatalytic activity among these WO₃/g-C₃N₄ composites and shows ~3 times enhancement as compared with g-C₃N₄. Interestingly, specific degradation rate constants (the apparent k constant is divided by the surface area) show the similar trend as apparent k constant for the WO₃/g-C₃N₄ composites, suggesting the surface area is not a main factor for the greatly enhancement in the photocatalytic activity.

To investigate why H1G3 exhibits the highest photocatalytic activity, the photophysical properties of the WO₃/g-C₃N₄ composites were studied in this work. Figure 6(a) shows the UV–vis diffuse reflectance
spectroscopy of g-C₃N₄ and WO₃/g-C₃N₄ composite samples. Obviously, all the samples display the very similar photoabsorption properties, and the absorption edges ($\lambda_{ab}$) for g-C₃N₄, H1G3, HMA1G3, HMB1G3 and M1G3 about 444, 447, 442, 443 and 447 nm, respectively. These results show that, as compared with g-C₃N₄, the absorption edges ($\lambda_{ab}$) of the WO₃/g-C₃N₄ composites has not changed too much. Additionally, the band gap energy of g-C₃N₄ was estimated to be 2.69 eV by Kubelka-Munk method and the results are shown in figure 6(a).

SPV spectroscopy is a powerful tool for investigating the charge separation efficiency in the semiconductor materials [32]. SPV technology is an excellent way to study the photoinduced charge behavior at the interface of semiconductors, which obtain relevant information by analyzing the change of the surface voltage of the material [33]. It is known that SPV signal intensity is sensitive to the charge separation efficiency [34]. As shown in figure 6(b), the SPV response of H1G3 was apparently strongest among all WO₃/g-C₃N₄ composites samples, indicating that the junction formed by h-WO₃ and g-C₃N₄ possessed better charge separation, which results in improving the enhancement in the photocatalytic performance. Combining the results from UV–vis diffuse reflectance (figure 6(a)) and SPV spectra (figure 6(b)), it is found that charge separation efficiency rather than
light absorption or surface area is the main factor affecting photocatalytic activity for WO3/g-C3N4 composites. An increase in photocatalytic activity on H1G3 is mainly attributed to the improvement in the charge separation efficiency, which might due to the suitable energy band structure between h-WO3 and g-C3N4. Furthermore, the well dispersion h-WO3 particles on the g-C3N4 surface enable the abundant amounts of the heterojunction for charge separation. Thus, the WO3/g-C3N4 composites with h-WO3 show the higher visible light photocatalytic performance.

3.4. Understanding of photocatalytic mechanism

To further investigate the photocatalytic mechanism in H1G3, the active species involved in the photocatalytic process were determined by adding trapping agents in photocatalytic process. The K2Cr2O7, (NH4)2C2O4, AA and IPA were applied as the trapping agent for photo-induced electron (e−), holes (h+), superoxide radical (·O2−) and hydroxyl radical (·OH), respectively. As shown in figure 7(a), (NH4)2C2O4 and AA dramatically depressed the photocatalytic activity of H1G3, while K2Cr2O7 and IPA showed no obvious effect on the RhB degradation rate. These results indicate that h+ and ·O2− derived from e− were the active species of photocatalytic activity of H1G3. The VB and CB potentials of g-C3N4 were 1.57 eV and −1.12 eV versus NHE (normalized hydrogen electrode) [35], and those of h-WO3 were 3.18 eV and 0.41 eV versus NHE, respectively [36].

Accordingly, the charge transfer in the H1G3 occurs via a Z-scheme mechanism (figure 7(b)) because the adjacency of CB of h-WO3 and VB of g-C3N4. The photogenerated e− and h+ in CB of h-WO3 and VB of g-C3N4 may recombine. Therefore, the h+ in VB of h-WO3 can directly oxidize RhB and e− in CB of g-C3N4 can reduce the dissolved oxygen O2 to ·O2−, which degrade RhB into degradation products. The possible mechanism of RhB photodegradation on H1G3 is presented in equations (4)–(9).

$$\text{h} - \text{WO}_3 + \text{hv} \rightarrow e^-_{\text{CB}(\text{h} - \text{WO}_3)} + h^+_{\text{VB}(\text{h} - \text{WO}_3)}$$  

(4)
4. Conclusions

In summary, WO₃/g-C₃N₄ composites with different crystalline phases of WO₃ were designed and prepared through one-step co-calcining of prepared WO₃ and g-C₃N₄ powders with controlled weight ratios. The influence of the crystalline phase of WO₃ on the morphology, the photoabsorption property, and the photogenerated charge carriers separation efficiency of the WO₃/g-C₃N₄ composites was investigated by SEM, UV–vis diffuse reflectance spectroscopy, and SPV spectroscopy, respectively. Furthermore, photocatalytic activity of WO₃/g-C₃N₄ composites was evaluated by visible light photocatalytic degradation of Rhodamine B (RhB). It is found that WO₃/g-C₃N₄ composites with h-WO₃ show the better dispersion of WO₃, higher charge separation and thus higher photocatalytic activity. Moreover, photocatalytic mechanism of h-WO₃/g-C₃N₄ was investigated. Our work made a systematical investigation into performance determining factors of composites based on g-C₃N₄ and semiconductor polymorphs, and shed a light on their design and fabrication.

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ORCID iDs

Jing Zhang https://orcid.org/0000-0002-9342-8473

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