Photocatalytic reduction of Cr(VI) by WO₃@PVP with elevated conduction band level and improved charge carrier separation property

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1. Introduction

With the rapid development of industry, heavy metal contamination of water has become a worldwide environmental concern. Hexavalent chromium (Cr(VI)), a heavy metal ion originated mostly from industrial processes such as electroplating, metal finishing, leather tanning, dying, and textiles, is very hazardous to humans and other living beings due to its carcinogenicity and mutagenicity [1, 2]. Therefore, technologies for Cr(VI) removal have attracted much attention. In general, converting Cr(VI) into its nontoxic counterpart Cr(III) is considered a feasible approach to solve this issue [3–6]. Nowadays, compared with the chemical reduction methods, the photocatalytic reduction process is proved to be a potential technology as it uses only solar light as an energy source and produces no secondary pollutants [7–10]. Comparing with other photocatalysts (TiO₂, ZnO, sulfides, etc.), WO₃, with a band gap of ~2.7 eV, is a promising photocatalyst material for visible light responsive photocatalytic reactions with high chemical stability and non-toxicity. Its stability in crystal structure, high resistance to photo-corrosion and stable recyclability make it prominent and suitable for practical applications [11–14]. However, although it shows excellent oxidation capacity due to its deep energy level of valence band edge, the energy level of its conduction band edge is not negative enough for energetic reduction reactions (lower than ~0.1 V vs. NHE, pH = 7) [15–18]. Even though the conduction band energy level of WO₃ is higher than some of the redox potentials of heavy metals, the relatively small difference between them as well as the fast recombination rate of photo-generated electrons and holes always result in slow
reaction rates. To address this problem, on one hand, some methods were used to elevate the conduction band of WO3, such as modifying its surface by graphene [15], diminishing the size of WO3 to nanometer [19,20], or altering the surface electronic and atomic structures by facet engineering [21], on the other hand, noble metal deposition [22], carbon or transition-metal dichalcogenide incorporation [23–25] were commonly used to lower the reaction barriers and enhance the charge carrier separation.

However, although the above methods are able to improve the reaction rate and the utilization efficiency of electrons and holes on the surface of WO3, the poor separation and transportation of the photo-generated charge carriers inside the semiconductor restrict the further improvement of the total photocatalytic efficiency. Actually, controlling the growth of the nano-material into an ordered structure is one of the most effective approaches for the above issue [26]. The ordered and oriented structure could ensure fluent charge carrier transportation and separation behaviors inside WO3 since fewer crystal defects or boundaries formed as the recombination centers of the electrons and holes [27]. Moreover, the oriented growth with different exposed crystal facets could lead to different energy band structures with varied redox capabilities [21].

Organic ligand molecules generally play crucial roles in the growing processes of nanoparticles. Polyvinylpyrrolidone (PVP) is a widely used polymeric surfactant to control the morphologies of nanomaterials and has attracted much attention for the reason that it is soluble, biocompatible and environmental friendly [28]. It was able to control the primarily exposed facets of the fabricated photocatalysts and could also adjust their band gaps through charge transfer between the functional groups of pyrrolidone ring and metal oxide nanostructures during the synthetic process [29–32]. These virtues make it possible to realize designed features and expected photocatalytic performance of nano-materials. Moreover, it has been reported that PVP as a modifier of photocatalysts could induce defects on the surface of photocatalysts [33], enhance the adsorption of pollutants [34,35], or adjust the energy band structure [36], all leading to improved photocatalytic activity.

In this work, by taking advantage of PVP both in the hydrothermal process and as a modifier of WO3, a PVP capped WO3 photocatalyst (WO3@PVP) was fabricated with a simple one-step hydrothermal method. The morphology, composition, photocurrent density and UV–vis absorption spectrum of the prepared composite were investigated and discussed. Finally, the WO3@PVP material was used for the photocatalytic reduction of Cr(VI).

2. Experimental

2.1. Materials and reagents

All the chemicals were purchased and used directly without further purification. Na2WO4·2H2O (95%) was purchased from Damao Reagent Factory, PVP (K30, 99%) was purchased from Wuhan Lullaby Pharmaceutical Chemical Co., Ltd., hydrochloric acid (HCl) was purchased from Tianjin Kemiou Chemical Reagent Co., anhydrous ethanol (99.7 wt%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd., and deionized water (18.3 MΩ) was obtained by an ultra-pure water system (Direct-Pure UP).

2.2. Synthesis of PVP capped WO3 (WO3@PVP) photocatalyst

WO3@PVP was synthesized by a one-step hydrothermal method. Firstly, 0.1 g PVP (K30) was dissolved into 15 mL deionized water under continuous stirring at 80 °C (Solution A). Meanwhile, 0.5 g Na2WO4·2H2O was dissolved into another 15 mL deionized water (Solution B). Under stirring, Solution B was added dropwise into Solution A to form a mixed solution. Then, the pH of the mixed solution was adjusted to 1.0 by hydrochloric acid, and then the mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave, maintained at 180 °C for 12 h. After the reaction, the autoclave was naturally cooled down to room temperature, and the precipitate was centrifuged and washed with deionized water and ethanol for several times to remove excessive PVP and HCl. Finally, the obtained sample was dried at 60 °C. For comparison, pure WO3 was synthesized under the same experimental condition except for the addition of PVP.

2.3. Characterization

The crystal structures were investigated using an X-ray diffractometer (XRD, EMPIREAN, PANalytical), and the element states of the samples were analyzed by an X-ray photoelectron spectrometer (XPS, VG ESCALAB250) with Al-Kα irradiation (1486.6 eV). The morphologies of WO3 nanoparticles and WO3@PVP composite were observed using an S-4800 field emission scanning electron microscope (SEM, Hitachi Co., Japan), and the crystal structure of WO3@PVP was studied by transmission electron microscopy (TEM) on a Tecnai G2 F30 S-Twin (FEI Company, USA). Ultraviolet–visible diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2450 spectrophotometer. The photocurrent densities were measured in Na2SO4 electrolyte (0.1 M) on an electrochemical station (CHI660E, Shanghai Chenhua Instrument Co., China). The photoluminescence (PL) spectra were recorded on a SHIMADZU RF-6000 spectrometer with an excitation wavelength of 270 nm.

2.4. Photocatalytic experiments

The photocatalytic reduction of Cr(VI) on WO3@PVP was evaluated under the irradiation of xenon lamp (PLS-SXE300C, Beijing Bofeilai Co. Ltd., Beijing, China) with a visible light cut-off filter (>400 nm). The light intensity was 60 mW/cm2 measured by a digital radiometer (FZ-A, Photoelectric Instrument Factory Beijing Normal University). Before the photocatalytic process, 20 mg WO3@PVP was added into 20 mL Cr(VI) solution (10 mg/L) and the mixture was stirred in the dark for 30 min to ensure adsorption equilibrium. During the photocatalytic process, 1 mL suspension was taken from the reaction solution at specific reaction time (10 min, 30 min, 60 min, 90 min, 120 min and 240 min) to determine the remaining concentration of Cr(VI). After the mixture was centrifuged at 3000 rpm for 5 min and the sediments were eliminated, the Cr(VI) concentration was determined using the normal diphenylcarbazide (DPC) method, by measuring the absorbance at 540 nm on a UV–vis spectrophotometer (UV–1901PC). Afterwards, the degradation rate constants of Cr(VI) on different photocatalysts were calculated and compared. Finally, the stability test of WO3@PVP for Cr(VI) reduction was conducted.

3. Results and discussion

The crystal structures of the samples were investigated by an X-ray diffractometer. The XRD patterns were shown in Fig. 1. The diffraction peaks of WO3@PVP could be well indexed as monoclinic WO3 (PDF#20–1323) due to the typical diffraction peaks such as (002), (020), and (200) crystal planes at 2θ = 23.1°, 23.6°, and 24.4°, respectively. However, the XRD pattern of pure WO3 presented the hexagonal phase of WO3 (PDF#33–1387) was obtained when PVP was not added, with a few WO3 molecules binding with water (peaks at 17.8° and 20.4° indexed to WO3·0.33H2O). These results demonstrated PVP facilitated the growth of monoclinic WO3 and could stabilize the monoclinic phase [37], which can be addressed to a rapid growth of H2WO4 on the PVP induced by the attraction
between WO and the protonated NH\textsuperscript{+} group of PVP in acidic medium \[38\]. And it was noteworthy that the characteristic peak of PVP \[39\] was not observed in XRD patterns of WO\textsubscript{3}@PVP, which might be due to the low content of PVP.

The morphology of the as-prepared composite can be observed from the SEM and TEM images in Fig. 2. As seen in Fig. 2a, in the presence of PVP, the WO\textsubscript{3} particles grew into cubic shape with a size of \(\sim 100\)–\(250\) nm at \(180\) \(^\circ\)C, while the SEM image of pure WO\textsubscript{3} in Fig. 2c and d showed nanoparticles with diameters of tens of nanometers were obtained after the same hydrothermal process but without PVP. The particles of pure WO\textsubscript{3} were in irregular and non-uniform shapes, and serious agglomeration occurred for these WO\textsubscript{3} nanoparticles. The irregular shapes could be caused by the inhomogeneity of the precursor in reaction solution during the growing process of WO\textsubscript{3}, and the agglomeration phenomenon can be attributed to the high bond energy among the WO\textsubscript{3} nanoparticles \[40\]. This result suggested that PVP served as a crystal template as well as the dispersant during the growing process of WO\textsubscript{3}. Moreover, Fig. 2a displayed the WO\textsubscript{3} cubes were wrapped by a transparent wrinkle layer, which was speculated as the PVP. The image of high-resolution transmission electron microscopy (HRTEM) (Fig. 2b) revealed that the lattice spacing value of WO\textsubscript{3}@PVP was 0.388 nm, which was in keeping with the (002) facet of the monoclinic phase of WO\textsubscript{3} (0.384 nm, PDF\#20–1323). And it confirmed the crystal lattice inside the WO\textsubscript{3}@PVP was of good consecution with few lattice defects, which would supply a favorable charge carrier transfer pathway and lead to improved photo-generated electron-hole separation performance.

The surface atomic compositions and the chemical states of the prepared samples were investigated using X-ray photoelectron spectroscopy (XPS). Fig. 3a displayed the survey scan spectra of WO\textsubscript{3}@PVP and WO\textsubscript{3} nanoparticles, and the spectra exhibited that WO\textsubscript{3} nanoparticles were composed of W and O elements, whereas WO\textsubscript{3}@PVP were composed elements of W, O and N. The high resolution spectrum of N in Fig. 3b showed the binding energy of elemental N was 399.0 eV, corresponding to pyrrolic nitrogen from PVP \[41\], which implied PVP remained in WO\textsubscript{3}@PVP after a series of treatments of this material. From the W4f regions in Fig. 3c and d, it was clearly observed that WO\textsubscript{3}@PVP and WO\textsubscript{3} samples presented similar doublets with the binding energies centered at 35.6 and 37.7 eV for WO\textsubscript{3} nanoparticles, and 34.3 and 36.4 eV for WO\textsubscript{3}@PVP, respectively. This was assigned to the W4f\textsubscript{7/2} and W4f\textsubscript{5/2} of the W\textsuperscript{6+} oxidation state. A 1.3 eV red shift of the binding energy for WO\textsubscript{3}@PVP can be explained by the introduction of the electron-rich PVP, which could increase the electron density of WO\textsubscript{3} by electron transfer.

Fig. 1. XRD patterns of WO\textsubscript{3}@PVP and WO\textsubscript{3} nanoparticles.

Fig. 2. Electron images of the as-prepared photocatalysts: (a) SEM of WO\textsubscript{3}@PVP, (b) TEM of WO\textsubscript{3}@PVP, and (c–d) SEM of the WO\textsubscript{3} nanoparticles.
leading to the lower binding energy of W\textsuperscript{6+}. Moreover, a component located at approximately 32.7 eV and 34.8 eV was observed in the W4f region for WO\textsubscript{3}@PVP, which was absent in the W4f spectrum for WO\textsubscript{3} nanoparticles. These two weak peaks were in accordance with the reduced species of W\textsuperscript{5+} \cite{42}, implying that PVP contributed to the formation of W\textsuperscript{5+}. The reason might be that PVP was able to reduce W\textsuperscript{6+} into W\textsuperscript{5+} at the reaction temperature of 180 °C \cite{37}.

The light absorption performance of WO\textsubscript{3}@PVP was investigated by the UV–vis diffuse reflectance spectra (DRS), with the result exhibited in Fig. 4a. As can be seen from the spectra, pure WO\textsubscript{3}
nanoparticles showed strong absorption in the spectral region with $\lambda \leq 460$ nm. And the absorption edge of WO$_3$@PVP composite exhibited a red shift of $\sim 10$ nm compared with that of WO$_3$. As a result, the energy band gaps of WO$_3$ and WO$_3$@PVP were calculated to be 2.65 eV and 2.62 eV from the Tauc plots of WO$_3$ and WO$_3$@PVP, respectively (Fig. 4b and c). The decreased band gap of the composite maybe caused by the interaction between WO$_3$ and PVP at the interface. And this result suggested that the WO$_3$@PVP material could be excited by more photons from visible light.

The reduction and oxidation capacities of electrons and holes in WO$_3$@PVP were estimated by determining the energy band levels. The valence band X-ray photoelectron spectroscopy (XPS) was conducted, and the results in Fig. 5a showed the binding energies of the onset edges ($E_{\text{vb}}$, the energy between valence band top and Fermi level) for WO$_3$@PVP and WO$_3$ were 1.43 eV and 2.60 eV, respectively. Considering that the Fermi level of WO$_3$ was 0.57 eV [16] and the energy band gaps of WO$_3$ and WO$_3$@PVP were 2.65 eV and 2.62 eV, respectively, the energy band alignments of the two materials were schematically illustrated in Fig. 5b. It illustrated that the addition of PVP caused a shift of the WO$_3$ conduction band edge to the negative potential by 1.14 eV. Therefore, it was supposed that the as-prepared WO$_3$@PVP could be used for most reduction reactions of heavy metal ions.

The photocurrent densities were examined to study the charge carrier separation capacities of WO$_3$@PVP and WO$_3$ nanoparticles (Fig. 6). The photocurrent density of pure WO$_3$ nanoparticles was tested to be 0.05 mA/cm$^2$ at 0 V vs SCE under visible light irradiation, and it decayed to an even smaller value. For WO$_3$@PVP, it displayed an improved photocurrent density compared with that of WO$_3$, with the value stabled at $\sim 0.7$ mA/cm$^2$, which is 14 times higher than that of WO$_3$. The results clarified that the introduction of PVP improved the charge carrier separation performance of WO$_3$, which can be ascribed to the consecutive crystal lattice with few defects as well as the enhanced light utilization of the composite. Moreover, the PL results were in agreement with the photocurrent test, with higher photoluminescence intensity observed for WO$_3$ (Fig. S1), indicating its higher photogenerated electron-hole recombination rate, and the lower photoluminescence intensity of WO$_3$@PVP proved its suppressed electron-hole recombination process. The increased separated charge carriers were expected to react with more pollutant molecules in the same reaction time and improve the photocatalytic performance.

Finally, the photocatalytic reduction reaction of Cr(VI) on WO$_3$@PVP was evaluated. The adsorption tests of Cr(VI) on the photocatalysts were conducted in dark condition, with results shown in Fig. S2. As seen from the adsorption curves, the
adsorption-desorption equilibrium could be reached at about 30 min for both materials. And the adsorption contents of Cr(VI) on WO3@PVP and WO3 in the dark were 15.5% and 8.74%, respectively, which indicated that the adsorption capacity of WO3@PVP was improved than that of WO3 owing to the adding of PVP. This can be ascribed to the increased surface defects such as W5+, which could serve as adsorption sites improving the adsorption performance. Therefore, 30 min of the adsorption process was performed to ensure the adsorption-desorption equilibrium between the photocatalysts and Cr(VI) before the photocatalytic process (before "light on"), as shown in Fig. 7. From the concentration versus time plots after "light on", it can be observed that the concentration of Cr(VI) exhibited almost no change in the absence of photocatalyst, indicating it was stable under visible light irradiation. The pseudo-first order kinetic constants of Cr(VI) reduction were calculated during the reaction time 10–180 min, with results shown in Fig. S3. For WO3, the degradation rate constant of Cr(VI) on it was 0.174 h⁻¹. And a superiority was observed for WO3@PVP, with the reduction rate constant of Cr(VI) on it (0.532 h⁻¹) was 3.1 times as high as that on WO3. According to the results of energy band levels, the photocurrent density test and the adsorption data of Cr(VI), the excellent photocatalytic reduction performance of WO3@PVP was attributed to its negative conduction band energy level, high electron-hole separation property, and the improved adsorption performance. Therefore, the WO3@PVP composite photocatalyst was proved as an available photocatalyst for the treatment of heavy metal ions in wastewater.

The stability of the prepared WO3@PVP photocatalyst was investigated by recycling WO3@PVP for the photocatalytic reduction of Cr(VI) under visible light irradiation (Fig. 8). The reduction reaction of Cr(VI) was repeated for five successive cycles (each for 240 min). No significant decrease of the photocatalytic activity was observed during the consecutive cycles, which exposed the good stability of the prepared WO3@PVP photocatalyst.

4. Conclusion

WO3@PVP with PVP capped WO3 was prepared by the hydrothermal method. The experimental results illustrated the composite possessed good crystallinity, elevated conduction band energy level and increased surface defects (W5+), which attributed to the high electron-hole separation property, improved reduction ability and improved adsorption performance than those of pure WO3, caused by the interfacial effect of PVP and WO3. Benefiting from the improved properties of WO3@PVP, a superior photocatalytic performance for Cr(VI) reduction was obtained. These findings provide a new method for improvement of photocatalytic reduction ability of WO3 and further promote the application of photocatalysis in the removal of heavy metal ion in wastewater.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jese.2020.100034.

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