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Preparation of recyclable MoO_3 nanosheets for visible-light driven photocatalytic reduction of Cr(VI)

Wenxian Wei,[a] Zhenxin Zhang,[a] Guoxiang You,[b] Yun Shan*[c] and Zuozheng Xu[a]

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The exploitation of stable and earth-abundant photocatalysts with high catalytic activity remains a significant challenge for removing heavy metals from wastewater. Different from complex nanostructuring, this work focuses on a simple and feasible way to design catalysts. Herein, MoO_3 nanosheets were fabricated and grown vertically on the surface of a quartz tablet using a one-step chemical vapor deposition method. The morphology, construction and optical properties of the MoO_3 were characterized by XRD, XPS, SEM, HRTEM and UV-Vis methods, and the possible growth mechanism was also discussed. It can be found that the MoO_3 nanosheets exhibited significantly enhanced visible light photocatalytic reduction capacity with stable recyclability to Cr(VI). The results show that the MoO_3 nanosheets can be used as a cost-effective and recyclable photocatalyst for the removal of Cr(VI) from water. Our findings provide new inspiration for the design of new types of catalysts.

1. Introduction

Wastewater always contains heavy metals and organic compounds which endanger the environment. As is well known, chromium is widely used in many fields such as mining, chemical manufacturing, electroplating and leather making and processing, and pollution caused by chromium, mainly Cr(VI), has been ranked among the top ten worst toxic contamination issues according to a report released in 2012.[1,2] Thus, the removal of Cr(VI) in water has great significance to our environment.

Environmental friendly catalytic processes are increasingly receiving attention nowadays, and photocatalytic technology provides a method for overcoming the problems.[3] The photocatalysis is a physico-chemical process in which chemical reactions are driven using light energy and photocatalysts.[4] Semiconducting nanomaterials have been widely used as photocatalysts because they are unique in nature of the mechanical, optical, electrical, catalytic and magnetic properties.[5–8]

As a n-type semiconductor, molybdenum trioxide (MoO_3) can be used in catalytic, optical and electrochemical applications, and compared to other metal oxide materials, MoO_3 has low cost, good structural stability and less toxicity.[9–11] For example, assembled-sheets-like MoO_3 was synthesized with a facile heat treatment route and used as an anode for lithium ion batteries, which maintained an improved discharge capacity over 100 cycles with capacity retention of ~100%;[12] Wang *et al.* prepared ultrafine β-MoO_3 from industrial grade MoO_3 powder *via* the method of sublimation and discussed its growth mechanism;[13] Pandeeswari *et al.* fabricated nanostructured α-MoO_3 thin film as a highly selective TMA sensor;[14] by a solution combustion reaction, ultra-porous MoO_3 can be obtained with both excellent photocatalytic and electrochemical properties.[15]

Therefore, the development of MoO_3 nanoparticles has consequently increased in recent years.[16–20] By now, many synthesis processes of MoO_3 are widely investigated using electrodeposition, molten salt, hydrothermal, sol–gel methods *et al.*, and different morphologies including nanofibers, microbelts and flower-like spheres can be fabricated.[21–26]

Nowadays MoO_3 has been widely used as photocatalysts. As reported in ref. 27, three-dimensional MoO_3 nanoflowers assembled with nanosheets were fabricated by the modified hydrothermal method for degradation of RhB under visible light; Liu *et al.* fabricated hierarchical porous monoliths of MoO_3 nanoplates. The as-prepared MoO_3 exhibited strong adsorption performance and excellent photocatalytic activity as well as promising cyclic performance for photodegradation of MB;[28] MoO_3 microrods were synthesized using leaf extract of *Azadirachta indica* and used for the cationic dye degradation;[29] Ma *et al.* prepared MoO_3 nanoflake on conjugated polymer for hydrogen evolution from water solution under solar light.[30]

It is known that two-dimensional materials shows very interesting physical and chemical characteristics.[31–33] In this

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[a] *Testing Center, Yangzhou University, Yangzhou, Jiangsu 225009, China*

[b] *Key Laboratory of Integrated Regulation and Resources Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing, Jiangsu 210098, China*

[c] *Key Laboratory of Advanced Functional Materials of Nanjing, Nanjing Xiaozhuang University, Nanjing 211171, China. E-mail: gangzhou361@163.com; Tel: +86-516-83262091*

work, MoO_3 nanosheets which deposited vertically on the surface of quartz tablet were fabricated by one-step chemical vapor deposition method. The morphology, construction and optical properties of MoO_3 were characterized by XRD, XPS, SEM, HRTEM, UV-Vis methods, respectively. The photocatalytic and recyclable performance of the as-prepared MoO_3 on the degradation Cr(VI) were analyzed. The fabrication process is low energy consumption, easy to operate and environmentally friendly. Meanwhile, the MoO_3 deposited on quartz tablet is easy to be separated from water, which avoids secondary pollution during using process. Thus, the as-prepared MoO_3 exhibits good application prospect for solving the pollution problems in water.

2. Experimental section

2.1 Materials

All chemicals including molybdenum disulfide (MoS_2) and potassium dichromate ($K_2Cr_2O_7$) are analytically pure and used as received without further purification. Deionized water was used for all procedures.

2.2 Preparation of MoO_3 nanosheets

MoO_3 nanosheets were prepared by chemical vapor deposition. As shown in Fig. 1, 0.2 g MoS_2 were placed in a combustion boat on the middle of the tube furnace, and then a piece of quartz tablet (1 × 1 cm) was placed behind the MoS_2 with a distance of about 15 cm, and 517 sccm argon gas was pumped for 40 min. After that, the tube furnace was vacuum pumping till 7.5×10^{-2} Torr, and then heated to 900 °C with the heating rate of 10 °C min^{-1}. The reaction was kept for 20 min with Ar flow of 26 sccm and O_2 flow of 4 sccm. Finally the system was cooled to room temperature and the quartz tablet coated with products was taken out for further analysis.

2.3 Characterization

Scanning electron microscope (SEM) images were obtained using a HITACHI S-4800 microscope (Japan). High-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI Tecnai G2 F30 microscope (USA). The phase purity of the product was characterized by X-ray diffraction (XRD, German Bruker AXSD8 ADVANCE X-ray diffractometer) using an X-ray diffractometer with Cu KR radiation ($\lambda = 1.5418$ Å). The ultraviolet-visible (UV-Vis) diffuse reflectance spectra were obtained on an America Varian Cary 5000 spectrophotometer. Raman spectra were measured using a Britain Renishaw inVia Raman spectrometer at room temperature.

2.4 Photocatalytic experiments

The degradation of $K_2Cr_2O_7$ was proceeded using the as-prepared MoO_3 nanosheets as photocatalysts with visible lights. Cr(VI) stock solution (10 mg L^{-1}) was prepared by dissolving $K_2Cr_2O_7$ in distilled water. After the a piece of MoO_3-coated quartz tablet was immersed in 20 mL of Cr(VI) solution, the resulting solution was magnetically stirred in the dark for 30 min at room temperature. Then the photocatalytic experiments were carried out in a GHX-2 photochemical reactor as report in ref. 34 and 35, which includes mainly four parts: light source system including a 300 W xenon lamp with a 420 nm cut-off filter and cooling attachments such as electric fan; reactor (two-layer Pyrex glass bottles of 400 mL capacity, the space between the two layers is filled with circulating water to cool the reactor); magnetic stirrer; and temperature controller. In each experiment, the distance between the xenon lamp and the reactor was set to be 5.8 cm, and the reaction temperature was 25 °C. At an interval of 10 min, 3 mL of the solution was extracted and monitored *via* UV-Vis spectrometer.

The photocatalytic efficiency of Cr(VI) could be calculated according to the following equation: % degradation $= (1 - A_t/A_0) \times 100\%$, where A_0 and A_t are the initial absorbance and absorbance at time '*t*' of Cr(VI).[36]

Besides, as referential photocatalysts, 0.8 mg TiO_2 (P25) and 0.8 mg MoS_2 nanosheets were respectively used for degradation of Cr(VI).

3 Results and discussion

3.1 Characterizations

Fig. 2(a) displayed XRD patterns of the as-prepared MoO_3. Diffraction peaks of the product is in good agreement with orthorhombic α-MoO_3 (JCPDS card no. 05-0508) and the main peaks observed at 12.9°, 23.5°, 26.1°, 27.4° and 39.2° are corresponding to the (020), (110), (040), (021) and (060) planes. No other peaks of impurities were detected. The sample exhibits sharp peaks which ascribable to its highly crystalline nature.

Fig. 2(b) shows the typical Raman spectra of MoO_3 nanosheets. The Raman peaks at 819 cm^{-1} and 995 cm^{-1} should be induced by the symmetric and asymmetric stretching vibration modes of terminal bond Mo=O. The asymmetric stretching vibration mode of O–Mo–O was assigned at 665 cm^{-1}, while the

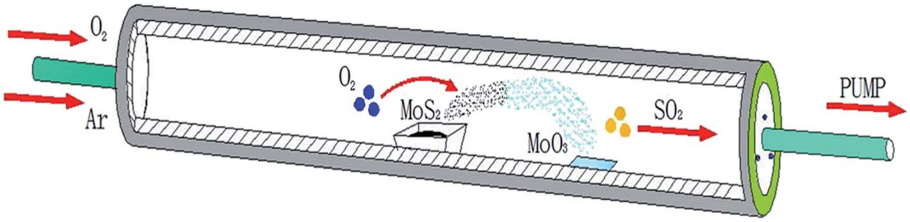

Fig. 1 The fabrication process for MoO_3 using CVD method.

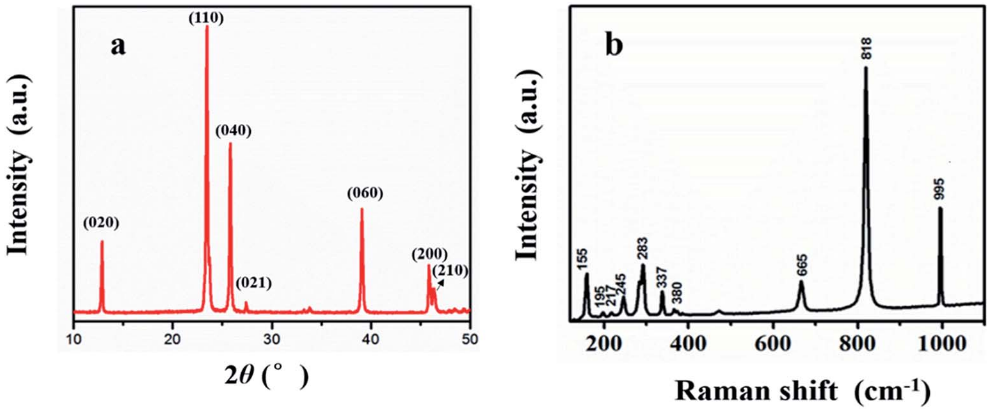

Fig. 2 (a) XRD and (b) Raman spectra of MoO_3.

Raman peaks at 380 cm^{-1}, 337 cm^{-1}, 283 cm^{-1} and 245 cm^{-1} indicated the vibrating bending modes in MoO_3.[11]

According to XRD and Raman analytical results, it can be found that the product is well-crystallized MoO_3.

XPS analysis was performed in further to confirm the presence of elements of Mo. Fig. 3(a) shows that the peaks in the spectra were assigned to Mo, O, and C. From Fig. 3(b), two peaks located at 233 eV and 236 eV can be respectively due to Mo $3d_{1/2}$ and Mo $3d_{3/2}$ signals, ensuring the Mo^{6+} valence state.[28] Besides, the atom ratio of Mo and O is about 1 : 3, in further proving the formation of MoO_3.

The morphology of the as-prepared MoO_3 was characterized *via* SEM and TEM respectively and the results can be found in Fig. 4(a)–(d).

From SEM images, it can be found that MoO_3 nanosheets were uniformly grown vertically on the surface of the substrate,

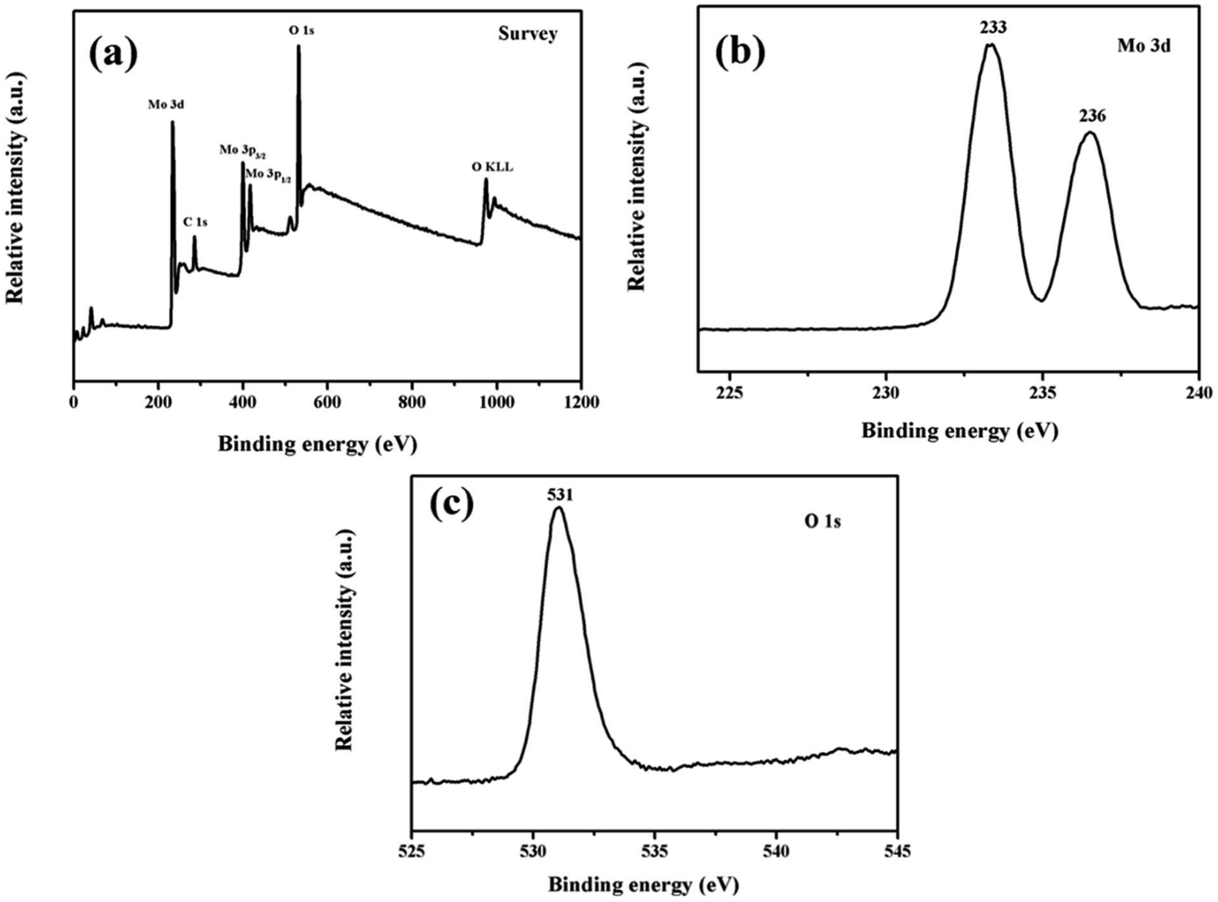

Fig. 3 XPS spectra of the MoO_3 (a) a typical survey spectrum (b) Mo 3d core level (c) O 1s core level.

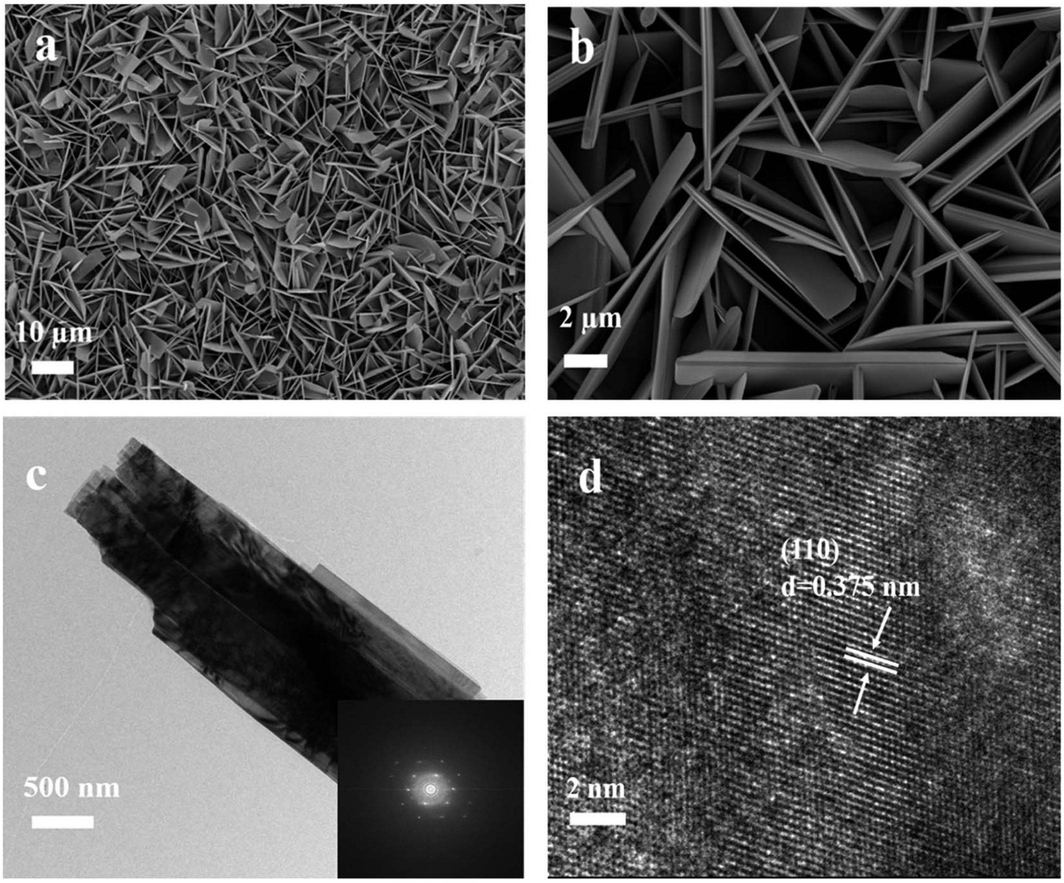

Fig. 4 (a and b) SEM and (c and d) TEM images of MoO_3 nanosheets.

which form 3D network structure and possess large surface area. Fig. 4(c) is the TEM image of MoO_3 nanosheet and Fig. 4(d) is the HRTEM image. It can be found that the as-prepared MoO_3 is well-crystallized and the lattice spacing is 0.375 nm, which belongs to the (110) plane.

To investigate the light absorption properties of the as-prepared MoO_3, the UV-Vis absorption spectra of the MoO_3 was recorded and displayed in Fig. 5. It can be seen that there is a broad absorbance peak during 200–450 nm, and band gap is estimated to be 2.9 eV from the plots of $(\alpha h\nu)^2$ *versus* photon energy $h\nu$.[37]

3.2 Growth mechanism

In this work, the MoO_3 nanosheets which grown vertically on the surface of quartz tablet were fabricated *via* CVD method. During the CVD process, MoS_2 was steamed up in the high-temperature area. Then it was reacted with oxygen and meanwhile driven by Ar, then deposited gradually on the surface of the quartz tablet in the low-temperature area. Therefore, the growing mechanism of the morphology is based on the vapor-solid (VS) mechanism. According to VS mechanism, the size of the nanosheet is proportional to the time and growth rate, which is depend on the evaporation rate and pressure. According to $P = B\exp\left\{\frac{-\pi\sigma^2}{(kT)^2\ln(\alpha)}\right\}$, P is the probability of nucleation, B is a constant, σ is the surface energy of solid whiskers, k is the boltzmann constant, T is the absolute temperature, α is the supersaturation ratio (defined as: $\alpha = p/p_0$, p and p_0 are the initial pressure and equilibrium pressure at the corresponding ambient temperature respectively). Evaporation rate and system pressure may increase by affecting the

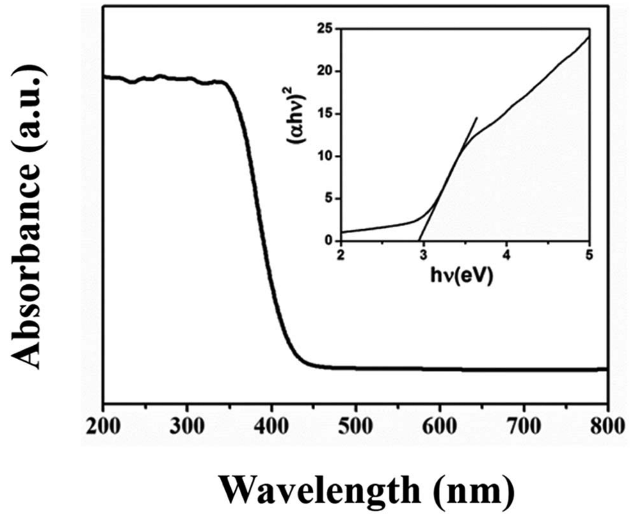

Fig. 5 UV-Vis spectra of MoO_3.

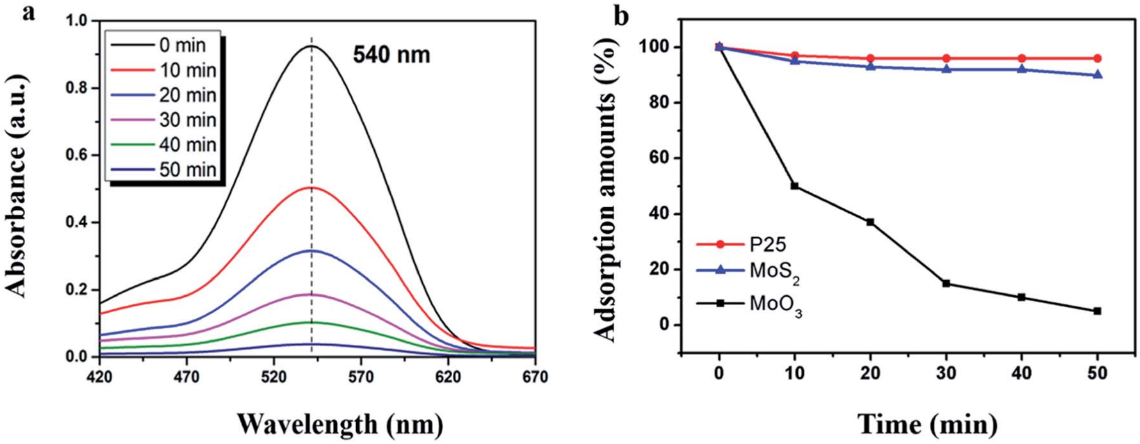

Fig. 6 (a) Photocatalytic efficiency of MoO_3 and (b) degradation performance of the referential photocatalysts.

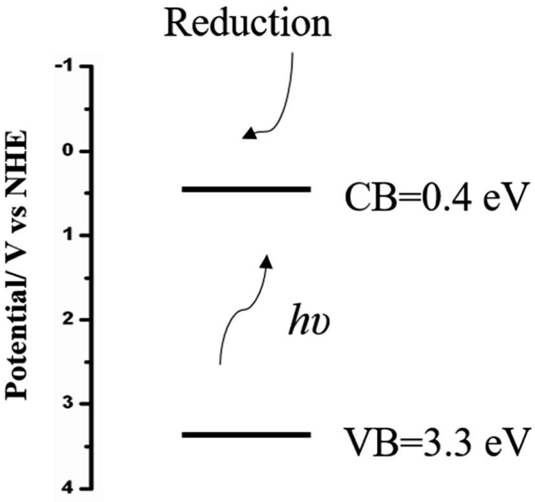

Fig. 7 Photocatalytic mechanism of the as-prepared MoO_3 nanosheets.

supersaturated vapor pressure. Thus, MoO_3 nanosheets were more easily formed under higher temperature and supersaturation.

3.3 Photocatalytic activity of Cr(VI)

Fig. 6(a) displays the photocatalytic efficiency of Cr(VI) under visible light with MoO_3 as photocatalyst. It can be found that the intensity of characteristic peak of Cr(VI) gradually weakens as the irradiation time goes on, indicating the degradation of the Cr(VI), which proves that the as-prepared MoO_3 can be used to degrade Cr(VI).

P25 and MoS_2 nanosheets were used as referential photocatalysts for degradation of Cr(VI), and it can be found that both the P25 and MoS_2 nanosheets have little photocatalytic performance on the degradation of Cr(VI) as shown in Fig. 6(b).

The photocatalytic mechanism of the as-prepared MoO_3 nanosheets were discussed as shown in Fig. 7. The conduction band and valence band potentials of the semiconductor were

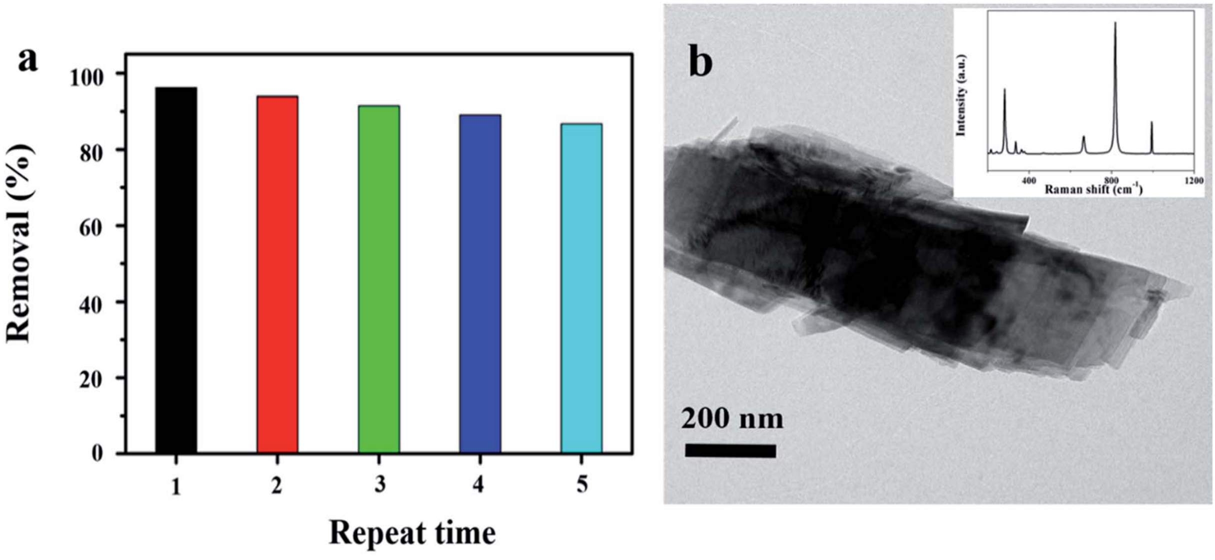

Fig. 8 (a) Recycling of MoO_3 for the photocatalytic degradation of Cr(VI) and (b) TEM of MoO_3 after reusing. Inset is the Raman spectra.

calculated by $E_{CB} = \varepsilon - E_H - 0.5E_g$ and $E_{VB} = E_{CB} + E_g$. ε is the absolute electronegativity of an atom semiconductor, which is defined as the arithmetic mean of the atomic electro affinity and the first ionization energy; E_H is the energy of free electrons of hydrogen scale (4.5 eV); E_{CB} and E_{VB} are the potentials of the conduction and valence bands, respectively, while E_g is the band gap between the conduction and valence bands.[28,38] Therefore, the conduction and valence band positions of MoO_3 were calculated to be 0.4 eV and 3.3 eV, respectively.

The photo-excited electrons converge on the conduction band of the MoO_3 and reduce the absorbed oxygen molecules on the MoO_3 surface, inducing a chain of reactions as follows:[34]

$$MoO_3 + h\nu \rightarrow MoO_3\ (h^+ + e^-) \tag{1}$$

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \tag{2}$$

The recycling of MoO_3 nanosheets used for photocatalytic degradation of Cr(VI) under visible-light irradiation was investigated and the results can be found in Fig. 8.

The recycling test showed that the photocatalytic activity did not exhibit obvious reduction during the recycling, and the Cr(VI) removal of 85% can still be achieved even after recycling for five times. According to the TEM and Raman analysis, it can be found that there was almost no change of the morphology and structure of MoO_3, which meant the recyclable of the as-prepared photocatalyst.

4. Conclusions

MoO_3 nanosheets were fabricated and deposited vertically on the surface of quartz tablet by one-step CVD method. The MoO_3 nanosheets exhibited good photocatalytic efficiency for degradation of Cr(VI). The catalyst was easy to be separated from water and almost retained the catalytic efficiency after reused five times. Thus, the as-prepared MoO_3 has a clear advantage for applications in environmental fields.

Conflicts of interest

There are no conflicts to declare.

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