Green synthesis and possible applications of MoO$_2$ nanoparticles

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Abstract. This work reports the green hydrothermal synthesis of MoO$_2$ nanoparticles and their applications in Cr$^{6+}$ adsorbent and MoO$_3$ precursor. A green hydrothermal method, which was based on the autoclave-sealed reactions of (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O and glucose in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours, was proposed for the synthesis of MoO$_2$ nanoparticles. The characterization results from X-ray diffraction and transmission electron microscopy suggested the successful preparation of pure monoclinic phase MoO$_2$ (m-MoO$_2$) nanoparticles. The m-MoO$_2$ nanoparticles exhibited a good adsorption capacity for Cr$^{6+}$ (for example, 300 mg of m-MoO$_2$ nanoparticles can adsorb the whole Cr$^{6+}$ in 300 mL of 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution after mixing for 280 minutes). Besides, the m-MoO$_2$ nanoparticles can be completely converted to orthorhombic phase MoO$_3$ nanoflakes after heating in air at 400 °C for 5 hours.

1. Introduction
The oxides of molybdenum (MoO$_3$ and MoO$_2$) are important functional materials, because they have promising uses in catalysis[1, 2], supercapacitor[3], photoconductor[4], field emission[5], anode materials for lithium-ion batteries[6], adsorption[7], and sensing[8], etc. However, the properties and applications of MoO$_3$ and MoO$_2$ are related to their structures (such as phase, size and morphology), which in turn depend on their synthesis methods and synthesis conditions[1-8]. Therefore, it has great scientific and practical significance to explore alternative methods to synthesize MoO$_2$ nanomaterials for improved performance, novel applications, and less economic and environmental cost.

Nowadays, priority attention has been paid to green synthesis chemistry, which aims to eliminate or at least minimize the use and generation of hazardous substances[9]. The choice of renewable and environmentally benign reactants and solvents, and no generation of toxic byproducts and pollution are the primary issues that deserve consideration in a green synthesis strategy[9]. Herein, a green hydrothermal method, which was based on the autoclave-sealed reactions of (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O and glucose in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours, was proposed for the synthesis of pure m-MoO$_2$ nanoparticles. The possible applications of the as-synthesized m-MoO$_2$ nanoparticles as Cr$^{6+}$ adsorbent and MoO$_3$ precursor were also studied.

2. Experimental
K$_2$Cr$_2$O$_7$ was a guaranteed reagent, whereas all the other reagents were of analytical reagents. 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution was prepared by the dissolution of 250 mg of K$_2$Cr$_2$O$_7$ in 5.0 L of deionized water.
2.1. Synthesis
0.809 mmol \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) was placed into a 50 mL Teflon jar, and 35 mL of deionized water and 5 mL of acetic acid were added and stirred until the dissolution of \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\). Then, 1.618 mmol glucose was added to the above solution and stirred until the dissolution of glucose. The Teflon jar was sealed into stainless steel autoclaves and heated in an electric oven at 190 °C for 12 hours. After the autoclaves cooled down to room temperature naturally, the resultant precipitates were centrifuged, washed with absolute ethanol and deionized water, and dried in vacuum at 105 °C for 5 hours.

2.2. Characterization
The composition and structure of the obtained products were characterized by X-ray diffraction (XRD, German Bruker AXS D8 ADVANCE X-ray diffractometer), transmission electron microscopy (TEM, The Netherlands Philips Tecnai-12 electron microscope) and scanning electron microscopy (SEM, Hitachi S-4800 Field Emission Scanning Electron Microscopy). The adsorption property of the as-synthesized m-MoO\(_2\) nanoparticles (300 mg) was tested by adsorbing the Cr\(^{6+}\) in 300 mL of 50 mg/L \(\text{K}_2\text{Cr}_2\text{O}_7\) aqueous solution under the dark condition at room temperature.

3. Results and discussion

Fig. 1(A) shows the XRD pattern of the product synthesized via the hydrothermal reactions of glucose and \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) in (a) acetic acid (12.5 vol%) aqueous solution, and Fig. 1(A)-(b) deionized water at 190 °C for 12 hours, Fig. 1(B) the product obtained by heating the as-synthesized m-MoO\(_2\) nanoparticles in air at 400 °C for 5 hours.

Fig. 1(A) shows the XRD pattern of the product synthesized via the hydrothermal reactions of \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) and glucose in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours. All the XRD peaks in Fig. 1(A)-(a) can be indexed to monoclinic phase MoO\(_2\) (m-MoO\(_2\)) (PDF 86-0135), suggesting pure m-MoO\(_2\) was obtained via the hydrothermal reactions of \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) and glucose in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours. However, in the absence of glucose, no solid product can be obtained via hydrothermal treatment of \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours; whereas in the absence of acetic acid (12.5 vol%), a mixture of major hexagonal phase MoO\(_2\) (h-MoO\(_2\)) (PDF 50-0739) and minor m-MoO\(_2\) were obtained via the hydrothermal reactions of \((\text{NH}_4)_3\text{MoO}_4\cdot4\text{H}_2\text{O}\) and glucose in deionized water at 190 °C for 12 hours (Fig. 1(A)-(a)). The above results suggest that both the reducing agent (glucose) and acid conditions are essential to the current hydrothermal preparation of pure m-MoO\(_2\).

Fig. 1(B) shows the XRD pattern of the product obtained by heating the as-synthesized m-MoO\(_2\) nanoparticles in air at 400 °C for 5 hours. All the XRD peaks in Fig. 1(B) can be indexed to orthorhombic phase MoO\(_3\) (o-MoO\(_3\)) (PDF 76-1003), suggesting that the as-synthesized m-MoO\(_2\) nanoparticles can be converted completely into o-MoO\(_3\) when they were heated in air at 400 °C for 5 hours.
The TEM image of the as-synthesized m-MoO$_2$ is shown in Fig. 2(A), which reveals that this product consists of 8–20 nm nanoparticles. Fig. 2(B) shows the SEM image of the o-MoO$_3$ obtained by heating the as-synthesized m-MoO$_2$ nanoparticles in air at 400 °C for 5 hours. As can be seen from Fig. 2(B), the o-MoO$_3$ comprises nanoflakes with the thickness of about 50–160 nm.

Fig. 2. (A) TEM image of the as-synthesized m-MoO$_2$, and (B) SEM image of the o-MoO$_3$ obtained by heating the as-synthesized m-MoO$_2$ nanoparticles in air at 400 °C for 5 hours.

Fig. 3 shows the adsorption of the Cr$^{6+}$ in 300 mL of 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution by 300 mg of the as-synthesized m-MoO$_2$ nanoparticles under the dark condition at room temperature. It can be seen from Fig. 3 that the as-synthesized m-MoO$_2$ nanoparticles exhibited a good adsorption capacity for Cr$^{6+}$, for example, 300 mg of m-MoO$_2$ nanoparticles can achieve the complete adsorption of the Cr$^{6+}$ in 300 mL of 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution after mixing for 280 minutes.

Fig. 3. The adsorption of the Cr$^{6+}$ in 300 mL of 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution by 300 mg of the as-synthesized m-MoO$_2$ nanoparticles under the dark condition at room temperature. Note: C0 and Ct denote the Cr$^{6+}$ concentrations at the adsorption times of 0 minute (that is, just when 300 mg of m-MoO$_2$ nanoparticles and 300 mL of 50 mg/L K$_2$Cr$_2$O$_7$ aqueous solution were mixed) and t minutes, respectively.

4. Summary

Pure m-MoO$_2$ nanoparticles were synthesized via the hydrothermal reactions of (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O and glucose in acetic acid (12.5 vol%) aqueous solution at 190 °C for 12 hours. The proposed synthesis method uses inexpensive, nontoxic and renewable glucose as the reducing agent and acetic acid (12.5
vol%) aqueous solution as the solvent (it is also worth mentioning that (NH$_4$)$_6$Mo$_7$O$_{24}$$\cdot$$4$H$_2$O is also a common and inexpensive reactant), thus it is viable for scale-up production of m-MoO$_2$ nanoparticles. The as-synthesized m-MoO$_2$ nanoparticles exhibited a good adsorption capacity for Cr$^{6+}$, thus they have potential application in treating Cr$^{6+}$-contaminated wastewater. Besides, the as-synthesized m-MoO$_2$ nanoparticles can be completely transformed into o-MoO$_3$ nanoflakes after heating in air at 400 ºC for 5 hours, thus they may also be used as a precursor to prepare o-MoO$_3$ nanoflakes.

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