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# Hydrothermal fabrication of $TiO_2$-$MoO_3$ nanocomposites with superior performance for water treatment

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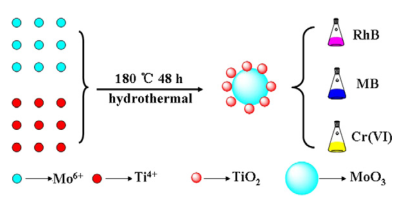
## GRAPHICAL ABSTRACT

A facile one-step hydrothermal method was successfully developed to synthesize TiO2-MoO3 nanocomposites with variable compositions. $TiO_2$-$MoO_3$ nanocomposites have been hydrothermally fabricated at 180 °C using $(NH_4)_6Mo_7O_{24}·4H_2O$ and $TiCl_4$ as the Mo and Ti source, respectively. The TiO2-MoO3 nanocomposites showed good adsorption activity for Rhodamine B (RhB) is approximately 290 mg g-1, Methylene blue (MB) and the Cr(VI) of heavy metal ion are 180 mg g-1 and 59 mg g-1, respectively.

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ABSTRACT

$TiO_2$-$MoO_3$ nanocomposites have been hydrothermally fabricated at 180 °C using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $TiCl_4$ as the Mo and Ti source, respectively. The $TiO_2$ and $MoO_3$ nanocrystalline can be confirmed in the products with the X-ray diffraction (XRD). Transmission electron microscopy (TEM) clear showed that the size of $MoO_3$becomes smaller with the increase of the Ti-doping amount. The $MoO_3$ was embraced by anatase $TiO_2$ nanoparticles with an average size of 10 nm. The $TiO_2$-$MoO_3$ nanocomposites showed good adsorption activity for Rhodamine B (RhB) is approximately 290 mg $g^{-1}$, Methylene blue (MB) and the Cr(VI) of heavy metal ion are 180 mg $g^{-1}$ and 59 mg $g^{-1}$, respectively.


## 1. Introduction

The purification of contaminated water has been extensively studied owing to the rapid development of industry and agriculture and the rapid growth of global population. Several approaches have been adopted to purify the water including different physical, chemical, and biological methods [1–13]. Among these methods, adsorption process has been one of the most popular technologies for water purification and recycling [14–24].

Currently, nano adsorbents for water treatment have gained considerable interest because of their large surface areas and easy surface modification [25–31]. During the past few decades, $TiO_2$ and other photocatalyst nano-materials have been intensively studied as a classic photocatalyst in several fields [32–38]. And it was found that $TiO_2$ nanoparticles are also one of effective adsorbent for the treatment of the water, recently [39,40]. Meanwhile, a large number of studies have been showed that its adsorption performance may be improved by coupling or doping other oxides [41–55]. For example, Sher Bahadar Khan et al. [56], have succeeded synthesis of $Co_3O_4$ co-doped $TiO_2$ nanoparticles for enhance heavy-metal ions of adsorption proprieties in aqueous

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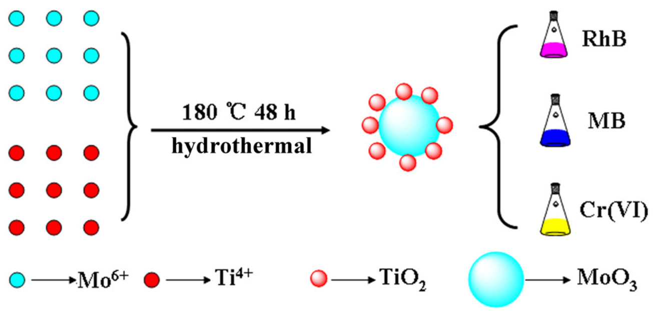


**Fig. 1.** Schematic representation of synthetic strategies for $TiO_2$-$MoO_3$ nanoparticles.

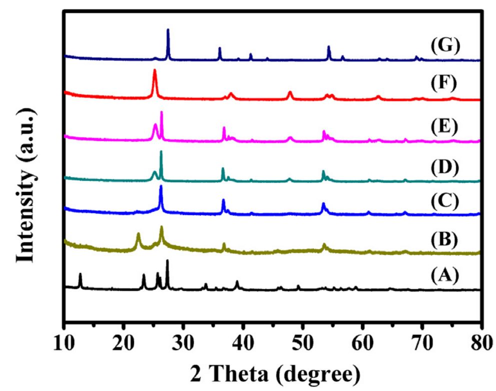


**Fig. 2.** XRD patterns for $TiO_2$-$MoO_3$ composites:(A) pure $MoO_3$; (B) $n_{Ti}$: $n_{Mo}$ = 0.25:1; (C) $n_{Ti}$: $n_{Mo}$ = 0.5:1; (D) $n_{Ti}$: $n_{Mo}$ = 1:1;(E) $n_{Ti}$: $n_{Mo}$ = 2:1; (F) $n_{Ti}$: $n_{Mo}$ = 4:1; (G) pure $TiO_2$.

solution. Maryline Chee Kimling [57] reported that amorphous $TiO_2/ZrO_2$ matrices can be prepared by using a sol–gel templating technique for improved dye adsorption capacity. Recently, Zhuying et al [58] also reported that the $TiO_2$-$WO_3$ nanocomposites are promising materials for adsorption of Methylene blue (MB). Although some work of $TiO_2$-$MoO_3$ composites have been reported [59–61], however, rarely attention has been paid to dye-adsorption and the synthesis methods are always complexity. Therefore, it is necessary to develop a method to synthesize small-sized $TiO_2$-$MoO_3$ composites adsorbent for water treatment.

Hereby, a facile one-step hydrothermal method was successfully developed to synthesize $TiO_2$-$MoO_3$ nanocomposites with variable compositions. In the synthesis process, alcoholic solutions of titanium tetrachloride as the source of Ti was added into $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution under magnetic stirring in the ice-water bath in order to prevent particle aggregation. The $TiO_2$-$MoO_3$ nanocomposites showed an outstanding adsorption activity for Rhodamine B (RhB) and MB of organic dye. Furthermore, the $TiO_2$-$MoO_3$ nanocomposites have higher adsorption activity for the Cr(VI) of heavy metal ion, and the entire process as shown in Fig. 1. We believe that this will present a facile and more practical alternative to the existing methodologies for the synthesis of small-sized $TiO_2$-$MoO_3$ nano-adsorbents.

## 2. Experimental

### 2.1. Materials

Titanium tetrachloride ($TiCl_4$, P99%) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were of analytic grade from Tianjin Forever Chemical and Shanghai Co. Ltd. China, respectively. All other reagents were received as analytical grade without further purification.

### 2.2. Preparation of $TiO_2$-$MoO_3$ nanocomposites

In a typical synthesis, alcoholic solutions of titanium tetrachloride as added to $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ aqueous solution under mighty stirring in ice water bath, forming white precipitate solution, then above obtained solution was transferred into a 100 mL of Teflon-lined stainless steel autoclave, it was filled with deionized water up to approximately 60% of the total volume, sealed and hydrothermally treated at 180 °C for 48 h. After cooling to room temperature, the obtained precipitate were centrifuged and washed several times with deionized water, and finally samples were dried at 80 °C in the electric-oven for 4 h.

### 2.3. Materials characterization

The structural properties were determined by an X-ray diffractometer (XRD) using a Bruker D8 X-ray diffractometer at scanning of 6° $min^{-1}$ in $2\theta$ from 5° to 80° with Cu Ka radiation ($\lambda$ = 1.54178 Å). Transmission electron microscope (TEM) image was carried out on a Hitachi H-600 with an accelerating voltage of 75 kV.

### 2.4. Adsorption experiment

#### 2.4.1. Removal of RhB and MB dyes

RhB ($C_{28}H_{31}ClN_2O_3$), a kind of synthetic dyes with fresh peach universally used in the textile industry, which was elected as a model organic pollutant. RhB was used for the adsorption test with the concentration of 1000 mg $L^{-1}$ of aqueous solution in the volumetric flask. We select the batch equilibration method to study adsorption of samples. 20 mg of composite materials($TiO_2$-$MoO_3$) with different proportions were well-dispersed into 20 mL of foregone concentration of RhB solution in a 30 mL testing pipe and stirred for 12 h at ambient temperature. The solid and liquid phases of above solution were immediately separated by centrifugation, and the remaining solutions of testing pipe were analyzed by UV–Vis spectroscopy (Shimadzu 2550) at $\lambda_{max}$ = 553 nm. 20 mg of the as-prepared $TiO_2$-$MoO_3$ samples were well-dispersed into 50 mL of an RhB solution with a concentration of 10 mg $L^{-1}$ were used to study the adsorption rate. In order to evaluate the adsorption capacity of above samples, 20 mg of adsorbent was decentralized to 20 mL of the RhB solutions with different concentrations (25 to 400 mg $L^{-1}$) with stirring in the darkness. To study the adsorption isotherm, this experiment was conducted out the initial RhB concentrations with stirring for 12 h at ambient temperature. Besides, the adsorption experiments of MB was performed under the same experimental conditions of RhB.

#### 2.4.2. Removal of the selected heavy metal ion

The Cr(VI) salt for adsorption test was prepared via water serial dilution to the standard solution (1000 mg $L^{-1}$). The adsorption studies were conducted with the same to above method, namely batch equilibration. 20 mg of adsorbents ($TiO_2$-$MoO_3$) were well-dispersed to 20 mL of given concentration of Cr(VI) solution in a 30 mL of cylindrical glass tube and magnetic stirring for 24 h at room temperature. The solid and liquid phases were complete separated by centrifugation, and the residual Cr(VI) concentrations of the test tube were determined though the method described in the reference by spectrophotometer after complication with diphenylcarbazide ($\lambda_{max}$ = 540 nm). To investigate the adsorption capacity, 20 mL of the Cr(VI) solutions with different concentrations (20 to 300 mg $L^{-1}$) was added the 20 mg of $TiO_2$-$MoO_3$ adsorbent with stirring in the dark. The adsorption isotherm was acquired by varying the initial Cr(VI) concentrations with the same stirring speed for 24 h at room temperature.