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Structure and effective visible-light-driven photocatalytic activity of α -NiMoO₄ for degradation of methylene blue dye



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ABSTRACT

 α -NiMoO₄ powders were prepared by the Pechini method. The sample was investigated by X-ray powder diffraction (XRD) measurement, structural refinement, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX). The average size of α -NiMoO₄ powders was measured to be 250 nm. The optical absorption spectrum of α -NiMoO₄ confirmed an efficient absorption in the UV–visible light wavelength region. The sample presents a narrowed band-gap energy of 2.23 eV, and the effective photocatalytic activity was evaluated by the photodegradation of methylene blue (MB). The effective photocatalytic activity was discussed on the base of the crystal structure characteristics such as heavily distorted NiO₆, activated optical centers and good electric conductivity. These results indicate that the hexagonal tunnel-structure alternately connected by MoO₄ and the heavily distorted NiO₆ is the dominated superiority for high photocatalytic capacity.

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1. Introduction

In recent years, photocatalysts driven by visible-light have been intensively investigated in water splitting and solving environmental pollution problems [1–9]. It has been demonstrated that the compounds with Group-VA transition metal ions, such as W, Mo, Ti, et al., usually show efficient photocatalysis because of the efficient optical absorption in visible region [10–17]. Among them, molybdate oxides show an excellent visible-light driven photocatalytic activity for degradation of dyes in water solution [18]. For example, α -Fe₂O₃/Bi₂MoO₆ [19], α -MoO₃ [20], reduced-graphene-oxide/Bi₂MoO₆ [21], Bi₂Mo₃O₁₂ [22] and NaM(MoO₄)₂ (M = Y, Bi) [23]. The other molybdates such as PbMoO₄ and SrMoO₄ [24], Fe₂(MoO₄)₃ [25], Ag₂MoO₄ [26], etc, possess attractive photocatalytic activities due to the interesting structural properties.

NiMoO₄ has two polymorphs at atmospheric pressure, which was firstly identified by Plyasova et al. [27] in 1973, i.e., α -NiMoO₄ (low temperature phase) and β -NiMoO₄ (high temperature phase).

Both of these two phases present monoclinic crystal structure. The most obvious difference between α -NiMoO₄ and β -NiMoO₄ is the coordination of the Mo^{6+} ions, which is octahedral in α -NiMoO₄ and tetrahedral in β -NiMoO₄. Both of the α - and β -phases were reversible. The α-phase when heated to a temperature of 650 °C can convert to the β -phase, and then revert back to the α -phase when temperature decreases [28]. In recent years, NiMoO₄ has been widely investigated due to its very interesting and rich potential applications. NiMoO₄ catalysts have been widely used for oxidation reactions and particularly for the oxidative dehydrogenation (ODH) of alkanes [29]. α -NiMoO₄ has an anti-ferromagnetic ordering. The magnetic structure can be described as a sequence of such cells with alternating signs along the *c*-direction [30]. Both α - and β phases are p-type semiconductors, but as temperature higher than 450–650 °C, they become n-type semiconductors. The α -phase has doubly ionized vacancies, while the β -phase singly ionized vacancies. These materials exhibit lithium ion storage capabilities and thus show promise for battery applications [31]. So far, no reports have been found on the photocatalytic activities of NiMoO₄.

In this work, we selected nickel molybdate, α -NiMoO₄, to investigate its photocatalytic activity, which is composed of Ni and Mo ions in oxygen octahedra and crystallizes in monoclinic system



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with a space group of C2/m. It can be noted that α -NiMoO₄ structure has two color centers, Ni- and Mo-complexes. It is easy to induce the d-d or by charge transfer (CT) transitions from O-2*p* to 3*d* orbital in Ni²⁺- or Mo⁶⁺-groups. Consequently photo-induced exciton can be easily created in this host [32]. Moreover, no photoluminescence can be observed in α -NiMoO₄ in this work. Usually weak luminescence indicates that the composites have a much lower recombination rate of photogenerated charge carriers [33]. This is favorable for the enhancement of photoactivity in degradation reaction.

Nickel molybdate α -NiMoO₄ powders as a new photocatalyst responsive to visible light were developed by the Pechini method. As we all know, this method is based on the formation of a polymeric resin produced by polyesterification between a chelated metallic complex using hydrocarboxylic acids and a polyhydroxy alcohol. The chelated compound obtained from the reaction is polyesterification-hot (polymerization by condensation or polycondensation) with polyethylene glycol. The sources of metallic ions can be nitrates. The sample was investigated by the crystal phase, morphologies, and UV–vis absorption. The efficient optical absorption and photocatalytic activity were confirmed by the degradation of methylene blue (MB) under visible light irradiation.

2. Experimental

 α -NiMoO₄ powders were prepared by the Pechini method. Firstly, the stoichiometric raw materials Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O, were dissolved in some deionized water. Citric acid (HOC(CO₂H)(CH₂CO₂H)₂, CA) with double molar weight of Ni²⁺ contents was used as the chelating agent for the process. The solution was neutralized by ammonium hydroxide and promoted by heating treatment at 85–95 °C for 2–5 h. Then, a certain amount of aqueous polyvinylalcohol (PVA) solution was dropwise added to adjust the viscoelastic of the solution. By keeping the solution under constant stirring, the solution became viscous. The obtained sticky solutions were carefully spin-coated on several clean glasses to prepare the thin film. The wind-dried thin film can be obtained by natural withering on the coated glasses. Finally, the spin-coated films containing the Ni²⁺, Mo⁶⁺ and the organic components were obtained. Then the precursor films were calcinated at 700 °C to decompose the organic components and got the desired target α -NiMoO₄ powders.

The XRD pattern was collected on a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry using Cu-K α radiation (λ = 1.5405 Å). Structural refinements of X/ ray diffractogram were made using the GSAS (general structure analysis system) program. The UV–visible diffuse reflectance spectra of the sample were recorded at room temperature in the range of 200–800 nm using a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan) equipped with an integrating sphere attachment. The microstructure morphology of the samples was investigated using scanning electron microscopy (JSM-6700F, JEOL). X-ray photo-electron spectroscopy (XPS) measurements were carried out using a VG Escalab 200 MKII spectrometer. An aluminum anode (K $_{\alpha}$ = 1486.6 eV) was used to generate the X-ray radiation (240 W, 20 mA; 12 kV).

The photocatalytic experiment was performed in a 0.5 L cylindrical glass photocatalytic reactor with a 500 W Xe lamp as the visible light source. A cut filter (420 nm) was inserted between the xenon lamp and reactor to eliminate ultraviolet light. The flow rate of air was kept at 500 mL min⁻¹. Typically, 300 mL of methylene blue (10 mg L⁻¹) solution containing 0.05 g of photocatalyst was mixed in a beaker. Prior to the photocatalytic reaction, the suspension was allowed to reach adsorption/desorption equilibrium by maintaining the solution in dark for 1 h. At a defined time interval, 5 mL of methylene blue was taken out from the reactor. After centrifuged, the solution was analyzed using the UV–vis spectrophotometer. The percentage of degradation was calculated by the formula of $[1 - (A/A_0)] \times 100\%$, where A_0 is the absorbance of original methylene blue solution before irradiation and A_i is the absorbance of methylene blue solution measured every 15 min in the process of photodegradation.

3. Results

3.1. Crystal formation

The observed diffraction peaks of α -NiMoO₄ **p**owders match well with the standard card PDF#33-0948 selected in the International Centre for Diffraction Data (ICDD) database. The powders show a pure phase formation. Based on the experimental XRD pattern of α -NiMoO₄ powders, the structural refinement was investigated by the GSAS program as shown in Fig. 1. The refined structural data and the atomic coordinates of α -NiMoO₄ are given in Table 1 and **2**, respectively. The sample crystallizes in a monoclinic structure with the space group of *C2/m* (12). The unit parameters are *a* = 7.5638(19) Å, *b* = 8.7320(19) Å, *c* = 7.6483(10) Å, α = 90°, β = 114.26(1)°, γ = 90°, *Z* = 8 and *V* = 582.32(16) Å³. The refined parameters are in agreement with the previous results [26,31].

Fig. 2 displays the structure maps for α -NiMoO₄, which was drawn by the Diamond Crystal and Molecular Structure Visualization software according to the atomic coordinates' refinements shown in Table 2. The structure is composed of metal-oxygen octahedral (Mo and Ni reside) in Fig. 2(a). There are two types of MoO₆ exist in the structure, the distorted Mo(1)O₆ (Mo-O dis-1.6670 Å (2×), tances in: Mo(1) - O(3)_ $M_0(1)$ O(1) = 2.7109 Å (2×), Mo(1)-O(4) = 1.9084 Å), and Mo(1)-O(4) = 1.9084 Å), Mo(1)-O(4) = 1.9084 Å) O(5) = 1.9456 Å); and the ideal $Mo(2)O_6$ (Mo(2)-O(1) = 1.9184 Å $(2\times)$, Mo(2)–O(2) = 1.8440 Å $(2\times)$, and Mo(2)–O(5) = 2.4525 Å $(2\times)$). At the same time, the Ni atom also have two octahedral positions of Ni(1) (Ni-0 = 1.8961 - 2.2216 Å) and Ni(2) (Ni-O = 1.9613 - 2.4361 Å).

The adjacent MoO_6 and NiO_6 octahedra in α -NiMoO₄ are connected by sharing edge with each other in Fig. 2(b). The Mo–O band length ranges from 1.6670 to 2.7109 Å. Coordinations of the molybdenum atoms were confirmed by Rietveld refinement of XRD, which showed Mo atoms are in octahedral environment in α -NiMoO₄.



Fig. 1. A representative experimental (crossed) and calculated (red solid line) X-ray diffraction profiles of α -NiMoO₄. The difference profile is located at the bottom of the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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