Original Research Paper

Effect of surfactants and precipitation agents on the morphologies of Nd_6MoO_{12} nanostructures for enhancing photocatalytic activity

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ABSTRACT

In this study, Nd_6MoO_{12} nanostructures were prepared via a facile coprecipitation-calcination method. Results of this study display that morphology and particle size of the Nd_6MoO_{12} nanostructures can be controlled by altering the precipitators and surfactants. Neodymium molybdenum oxide nanostructures with different morphologies such as unique sphere-like, rod-like and hierarchical were successfully synthesized. The as-prepared Nd_6MoO_{12} nanostructures were characterized by energy dispersive X-ray microanalysis (EDX), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) and UV–Vis diffuse reflectance analysis. The photocatalytic degradation of the methylene blue as water pollutant was performed to investigate the photodecomposition properties of various particle sizes and morphologies of neodymium molybdenum oxide samples.

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1. Introduction

The rare earth molybdates are an interesting family of compounds that have been extensively investigated owing to their specific catalytic, optical, magnetic and electronic properties [1–3] as well as potential applications, including solid-state laser host materials [4], low loss microwave dielectric ceramics [5], white light-emitting diodes (w-LEDs) [6], fast oxide-ion conductors [7] and photocatalysts for degradation of organic water pollutants [8].

Among the rare earth molybdenum oxides, neodymium molybdates have interesting chemical, physical, thermoelectric and photoluminescence properties as well as anomalous Hall effect [9–12]. Neodymium molybdenum oxides can have multiple absorption of photons, effective charge separation and restrain the recombination rate of the photo-induced carriers to achieve higher photocatalytic performance [13]. Therefore, neodymium molybdates compounds can be used to remove organic pollutants from industrial wastewater.

So far, a variety of routes have been employed to provide neodymium molybdate compounds with controlled morphologies and particle sizes including metathesis reaction [8], molten salt [9] spark plasma sintering [10], hydrothermal [14] and solid state

[15]. It is well-known that the co-precipitation method as a facile, convenient, low-cost and repeatable route can control the morphology and particle size of nanostructures, especially by utilizing various precipitating agents and surfactants.

In this work, Nd_6MoO_{12} nanostructures were prepared by a simple coprecipitation-calcination approach. To our knowledge, it is the first time that Nd_6MoO_{12} nanostructures with different morphologies such as uniform sphere-like, rod-like and hierarchical have been prepared utilizing various precipitating agents and surfactants. Moreover, the effect of particle size and morphology of Nd_6MoO_{12} samples on the photodegradation efficiency of methylene blue were investigated and the results show a high activity for methylene blue photodegradation under illumination of ultraviolet light by using neodymium molybdate photocatalysts.

2. Experimental

2.1. Materials and characterization

Nd_6MoO_{12} nanostructures were prepared by a simple coprecipitation method utilizing the following chemicals purchased from Merck Company: $Nd(NO_3)_3 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, liquor ammonia solution containing 25% ammonia (NH_3), ethylenediamine (en), triethylenetetramine (trien), cetyl-trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and polyethylene glycol

6000 (PEG-6000). Powder X-ray diffractions (XRD) were carried out with a Philips diffractometer equipped with X'PertPro and the monochromatized Cu Kα radiation ($\lambda = 0.154$ nm). The Fourier transform infrared (FTIR) spectroscopic study was performed on a Magna-IR, 550 Nicolet FTIR spectrometer in the 400–4000 cm^{-1} range. GC-2550TG (Teif Gostar Faraz Company, Iran) was used for all chemical analyses. The field-emission scanning electron microscopy (FESEM) images of neodymium molybdenum oxide samples were taken by a Tescan mira3 field emission scanning electron microscopes that embedded with an energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) images were taken on a JEM-2100 with an accelerating voltage of 200 kV equipped with a high resolution CCD Camera. The UV–Vis diffuse reflectance spectra of samples were obtained on a UV–Vis spectrophotometer (Shimadzu, UV-2550, Japan). Thermogravimetric-differential thermal analysis (TG-DTA) of the as-prepared Nd_6MoO_{12} nanostructures was performed by using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min^{-1} and a heating rate of 10 °C min^{-1}.

2.2. Preparation of Nd_6MoO_{12} samples

Neodymium molybdenum oxide nanostructures were prepared via a facile co-precipitation-calcination approach. In a typical synthesis procedure, 0.1 mmol of $Nd(NO_3)_3 \cdot 6H_2O$ and 0.01 mmol of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in 10 ml hot distilled water (60 °C) separately. After mixing the solutions, the pH of the resultant solution was adjusted to 10 by adding trien drop-wise and final solution was heated at 60 °C for 1 h under constant stirring. The final precipitate was collected by filtration, washed with absolute ethanol and distilled water for several times, dried at 60 °C and subsequently calcined at 800 °C for 4 h (sample No. 3). Schematic diagram of the preperation of Nd_6MoO_{12} nanostructures is showed in Scheme 1. To examine the influence of surfactant on the morphology of the Nd_6MoO_{12} samples, 0.2 mmol of the surfactant was added after mixing $Nd(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions. The effects of precipitator and surfactant on the

Table 1
The reaction conditions for preparation of Nd_6MoO_{12} nanostructures.

| Sample No.	Precipitator	Surfactant	Figure of SEM images
1	NH₃	–	4a
2	en	–	4b
3	trien	–	4c
4	trien	CTAB	5a
5	trien	SDS	5b
6	trien	PEG 6000	10b

morphology and particle size of the Nd_6MoO_{12} samples were studied and the results presented in Table 1.

2.3. Photocatalytic performance of Nd_6MoO_{12} samples

The photocatalytic activity of as-prepared neodymium molybdenum oxide nanostructures was studied by monitoring the photodegradation of methylene blue as cationic dye in an aqueous solution. The photocatalytic reaction was carried out by applying 1 mg of methylene blue aqueous solution (initial concentration of MB dye was about 6.25×10^{-5} M) including 30 mg of as-obtained Nd_6MoO_{12} samples (sample Nos. 1–6) at room temperature. For reaching adsorption-desorption equilibrium, this mixture was aerated for 30 min. Afterward, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the ultraviolet light from the 400 W Osram lamp. Photocatalytic processes were carried out at high UV photon flux irradiation about 3.13×10^{-6} einstein cm^{-2} s^{-1} (approximately UV intensity is equal to 1000 mW cm^{-2}) in the ultra-violet range from 280 to 400 nm. In the following, aliquots of the mixture were taken at certain interval of times during the irradiation, and after centrifugation, they were analyzed by a UV–Vis spectrometer. The methylene blue decomposition percentage was calculated as follow:

$$D.P.(t) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$
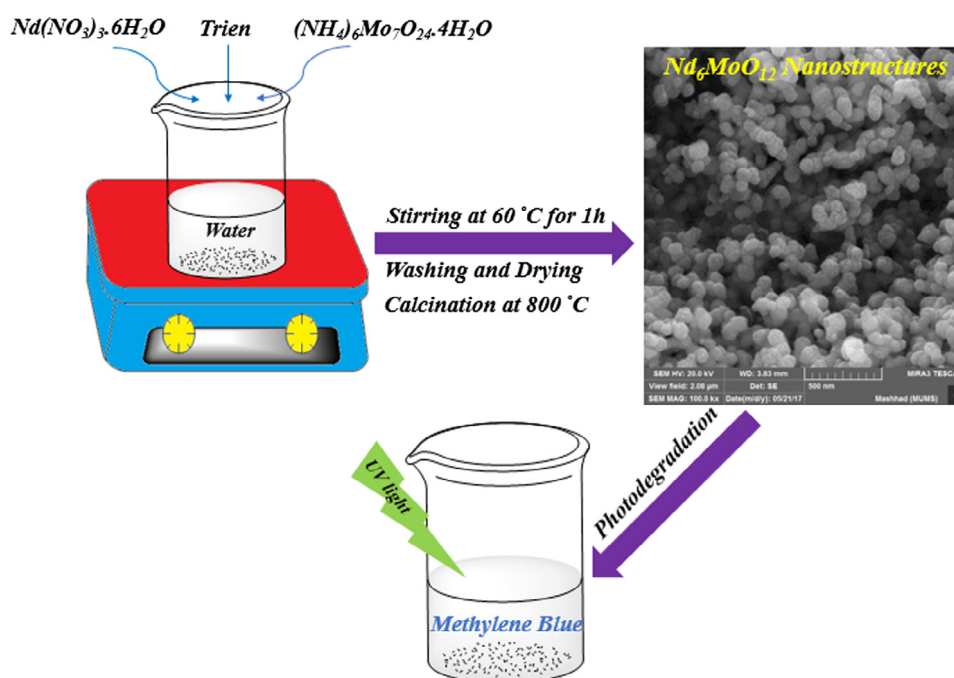
Scheme 1. Schematic diagram of the formation of ultrafine Nd_6MoO_{12} nanostructures (sample No. 3).