Applied Surface Science 436 (2018) 562–569

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Fabrication of a temperature-responsive and recyclable MoS_2 nanocatalyst through composting with poly (*N*-isopropylacrylamide)

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ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form 6 December 2017
Accepted 9 December 2017
Available online 11 December 2017

Keywords:
Molybdenum disulfide
Poly (*N*-isopropylacrylamide)
Temperature-responsive
Recyclable
Nanocatalyst

ABSTRACT

A temperature-responsive, recyclable nanocatalyst was fabricated by composting the exfoliated molybdenum disulfide (MoS_2) nanosheets with poly (*N*-isopropylacry lamide) (PNIPAM). The structure and morphology of MoS_2/PNIPAM nanocatalyst was fully characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Thermogravimetry analysis (TGA), Scanning electron microscope (SEM) and Transmission electron microscopy (TEM). The temperature-responsive properties of the MoS_2/PNIPAM nanocatalyst were confirmed by Dynamic Light Scattering (DLS) and Ultraviolet–visible ((UV–vis)) absorption spectroscopy. The catalytic activities of the MoS_2/PNIPAM nanocatalyst were studied using the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as the model reaction. Results showed that the catalytic activity of the MoS_2/PNIPAM nanocatalyst could be regulated by temperature. Furthermore, when the temperature went higher than the low critical solution temperature (LCST) of PNIPAM, the MoS_2/PNIPAM nanocatalyst tended to aggregated to form bulk materials from homogeneous suspension.

1. Introduction

4-Nitrophenol (4-NP), a kind of nitroaromatic compounds, had been widely used as intermediates in the building blocks of many dyes, explosives, pesticides [1,2]. However, it had become one of the major sources of water pollution in environment [3–5]. 4-Aminophenol (4-AP), a reduction product of 4-NP, was a vital reagent in many applications including antipyretic and analgesic drugs, anticorrosion lubricant and so on [6–8]. Converting the harmful 4-NP into useful 4-AP was important that can reduce the pollutant and generate value-added product simultaneously [9,10].

To date, most of the investigations on transformation of 4-NP into 4-AP were based on noble-metal catalysts due to their high catalytic efficiency [11,12]. Unfortunately, the high cost and natural scarcity of noble-metal limited their large-scale applications [13,14]. Intensive efforts had been contributed to the investigation of non-noble-metal catalysts alternatives such as copper alloys [15], metalic oxide [16], two-dimensional (2D) nanomaterials [17,18]. Among them, MoS_2 nanosheets, one of the most important kind of 2D nanomaterials which possessed a structure composted of three stacked atom layers (S-Mo-S) had attracted intense attentions due to its narrow band gap [19], extensive applications including catalysts [20–22], lithium batteries [23] and hydrogen production [24]. Guardia et al. revealed that the chemically exfoliated MoS_2 nanosheet was an inexpensive and easy-prepared nanomaterial which had been widely used as efficient catalysts [25]. However, due to the high dispersion stability of the exfoliated MoS_2 nanosheets in water, it was hardly to recycle the MoS_2 nanosheets after the catalytic reduction reactions [26,27]. The recyclable and reusable properties were the basic properties of nanocatalyst. Recently, many papers had reported that the incorporation with some stimuli-responsive material was an efficient way to endow the nanocatalyst with facility recyclability [28]. Ferroferric oxide (Fe_3O_4) had been widely used to give a magnetic response to nanocatalyst [29]. For example, Wang et al. revealed that the RGO@Fe_3O_4@Au magnetic nanocomposites showed high catalytic activity and excellent recycling performance [30]. Yu et al. revealed that Fe_3O_4@TiO_2-GO magnetic composites had extensive photocatalytic performance [31]. The stimuli-responsive polymers were also considered to be good candidates to endow the nanocatalyst with recyclability [32]. For instance, Ki-Tae Bang et al. revealed a facile template-free synthesis of pH-responsive polyelectrolyte/amorphous TiO_2 composite hollow microcapsules for photocatalysis [33]. Minji Yoon et al. employed PNIPAM to develop a thermo-sensitive photocatalytic Au-PNIPAM-ZnO, which demon-

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https://doi.org/10.1016/j.apsusc.2017.12.080
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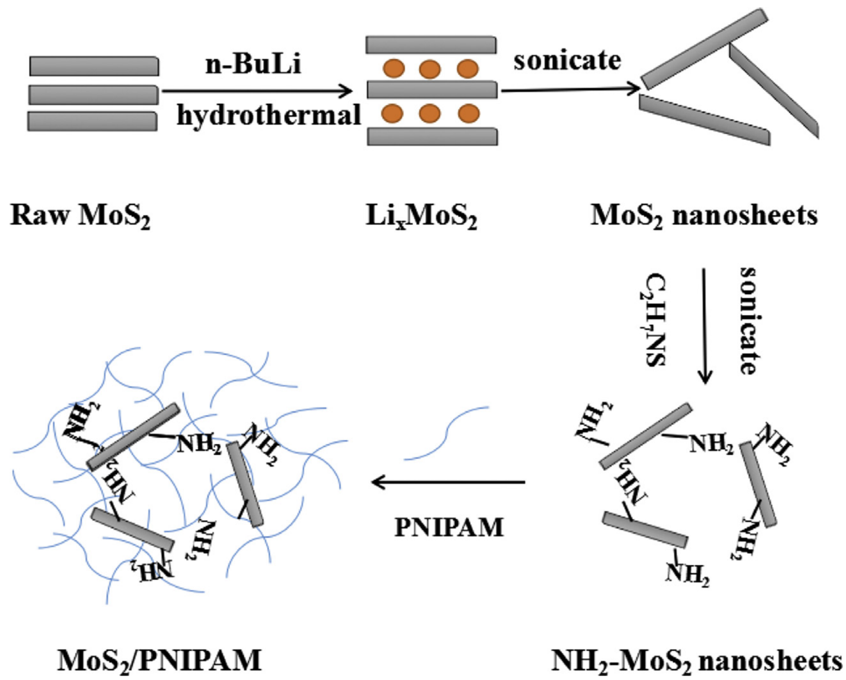

Scheme 1. The synthetic route of the MoS_2/PNIPAM nanocatalyst.

strated the feasible and promising use in the photodegradation of organic pollutants [34]. PNIPAM was a popular thermo-responsive polymer, which can undergo a reversible "coil-to-globule" phase transition in water around its lower critical solution temperature (LCST) [35,36].

In this work, a temperature-responsive and recyclable catalyst MoS_2/PNIPAM nanocatalyst had been successfully prepared. The combination of MoS_2/PNIPAM nanocatalyst had been improved by modified 2-aminoethanethiol on the surface of MoS_2 nanosheets. The catalytic activities of the MoS_2/PNIPAM nanocatalyst were studied using the reduction reaction of 4-NP to 4-AP as the model reaction. The experimental results showed that MoS_2/PNIPAM nanocatalyst had splendid catalytic properties and brilliant recycling performance (Scheme 1).

2. Experimental

2.1. Materials

MoS_2 powders were provided by Sigma–Aldrich. The n-butyllithium (1.6 M in hexane) was bought from Amethyst Chemicals. *N*-Hexane of analytical grade was provided by general-reagent. 2-Aminoethanethiol was provided by Tokyo Chemical Industry. *N*-Isopropylacrylamide (NIPAM), *N,N,N,N*-Tetramethylethylenediamine (TEMED), *N,N*-Methylenebisacrylamide (BIS) and p-Nitrophenol were bought from adamas-beta. Potassium persulfate (KPS) was purchased from Sinopharm Chemical Reagent Co. Ltd. in China. Sodium borohydride ($NaBH_4$) was purchased from Aladdin. Deionized water (DI) was used in all experiments.

2.2. Preparation of MoS_2 and NH_2-MoS_2 nanosheets

The exfoliated MoS_2 nanosheets were synthesized by a hydrothermal method. Briefly, 1.0 g MoS_2 and 30 mL *n*-butyllithium (1.6 M in hexane) were added to a 100 mL Teflon-lined stainless steel autoclave and heated at 100 °C for 4 h. The product (LixMoS_2) was rinsed three times with 100 mL *N*-hexane and dried in a vacuum at 60 °C for 4 h. Successively, LixMoS_2 (0.2 g) was hydrolyzed in deionized water (100 mL), and ultrasonicated at room temperature for 12 h to produce a colloidal suspension of exfoliated MoS_2 layers. Finally, it was purified by dialysis for one week to remove the remaining impurities for the following experiments. Then 2-aminoethanethiol was added to deionized water and ultrasonicated 48 h until dispersed homogeneous and freeze-dried for the following experiments.

2.3. Preparation of MoS_2/PNIPAM nanocatalyst

MoS_2/PNIPAM nanocatalyst was prepared with NIPAM as monomer, MoS_2 (10 mg) nanosheets as additives, BIS as chemical cross-linker, KPS as initiator, and TEMED as an accelerator. Typically, NIPAM (100 mg, 15 mM), BIS (0.231 mg, 0.0015 mM), and KPS (0.027 g) were dissolved in the NH_2-MoS_2 suspension (10 mL) of the desired concentration at 0 °C. Then TEMED (40 μL) was added to the reaction solution, and then, the solution was treated by sonication in an ice bath for 3 min. The resultant slurry was washed with deionized water, centrifuged three times and freeze-dried for the following experiments.

2.4. Characterizations

The morphology of the as-prepared nanocatalyst was observed by SEM (Hitachi S-4800) at an accelerating voltage 5 kV. X-Ray photoelectron spectroscopy (XPS) analysis was performed on an X-ray photo-electron spectrometer using Al Kα radiation (ESCALAB 250, Thermo Fisher Scientific Co. Ltd.). Ultraviolet-solar absorption spectra were measured on a UV-1800 spectrometer (Shimadzu, Japan). Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60H instrument at a heating rate of 20 °C/min under nitrogen atmosphere. Fourier transform infrared (FI-IR) spectra with wavelength resolution of 0.125 cm^{-1} were recorded on a Nicolet Nexus 870 spectrometer in the wavelength range from 4000 cm^{-1} to 5000 cm^{-1} using the KBr pellet technique. The hydrodynamic diameter was determined by a dynamic light scattering (DLS) instrument (Zetasizer Nano-ZS90, Malvern Instruments, UK).