



انجمن مهندسی شیمی ایران



دانشگاه صنعتی شریف

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

بدین وسیله گواهی می‌گردد، مقاله تحت عنوان

**Hydrothermal Synthesis of ZnO Nanosheets Using Molybdophosphoric Acid
as a Green and Eco-friendly Catalyst**

به تحریر نویسندگان

**Hamed Rashidi , Ali Ahmadpour, Fatemeh F. Bamoharram ,Seyyed Mojtaba
Zebarjad , Majid M. Heravi ,Ali Ayati**

در چهارم، هفتمین کنفرانس ملی مهندسی شیمی ایران، ۲۵ الی ۲۷ مهرماه ۱۳۹۱، دانشگاه صنعتی شریف، مورد پذیرش قرار گرفته و ارائه گردیده است.

احمد رضائی سعادت آبادی

بهرنگر



Effect of Precursor on Physicochemical Properties and Catalytic Performance of Ni-Co over Mixed Nano-oxides of Al-Mg-Zr Used in Dry Reforming of CH₄

Seved Mehdi Sajjadi^{1,2}, Mohammad Haghighi^{*1,2}, Farhad Rahmani^{1,2}

کد مقاله: ۱۰۲۳۱

Abstract

Ni-Co over mixed nano-oxides of Al-Mg-Zr have been synthesized by sol-gel technique with two different precursors of zirconia i.e. zirconyl nitrate hydrate (ZNH) and zirconyl nitrate solution, 35 wt% solution dilute nitric acid (ZNS) and used in dry reforming of methane. Both nanocatalysts have been characterized by XRD and FESEM analysis. Comparing XRD patterns of synthesized samples revealed that nanocatalyst employed ZNS (NCZNS) has a suitable crystalline structure which improves catalytic activity. In contrast, the amorphous behavior was intensified in the other one which used ZNH (NCZNH). FESEM results of NCZNS indicated uniform, homogeneous and well dispersed particle size. The synthesized nanocatalysts showed high catalytic activity and stability during 1440 min. It was observed that NCZNS has better catalytic performance. The results confirmed the remarkable effect of zirconia precursor on the sample morphology, structure and catalytic activity.

Functionalized magnetic nano-particles for determination and removal of heavy metal ions in environmental samples

کد مقاله: ۱۰۲۳۵

Nader Dizadji¹, *Ghazaleh Armaghan², Omid Sadeghi³, Dariush Bastani⁴

Abstract

In this work Fe₃O₄ nano-particles have been synthesized by co-precipitation method. This nano-particles have been functionalized by amine group using 3-Amino propyl triethoxy silane and characterized by X-ray powder diffraction (XRD), infrared (IR) spectroscopy, scanning electron microscopy (SEM), thermal (TGA-DSC) and elemental analyses. Application of these magnetic nano-particles was investigated in heavy metal determination and removal. Effects of several parameters such as the sample pH, eluent type and concentration and also maximum adsorption capacity of functionalized mesoporous in removal and determination of heavy metals have been studied.

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Research Highlights

- Novel synthesis of ZnO nanosheets using Heteropolyoxomatalates.
- Using new catalytic approach for synthesis of ZnO nanosheets.
- Investigating the photocatalytic activity of the ZnO nanosheets.



1. Introduction

ZnO nanoparticles (NPs) are promising materials to use as catalysts for photo-catalytic degradation [1], gas sensors [2] and catalysts for liquid phase hydrogenation [3]. Therefore, investigations on the synthesis of nanosized and nanostructured ZnO have attracted great attentions.

Different synthesis methods for preparation of ZnO nanostructures have been used including sol- gel technique [4], spray pyrolysis [5] and hydrothermal processing [6]. Controlling the particle shape and size is one main concern for nanostructured material synthesis, because both electrical and optical properties of nanomaterials depend on both size and shape of the particles.

In the past few years, POMs were applied to the morphology-controlled fabrication of nanostructures and has attracted more and more remarkable attentions in the synthesis of nanomaterials [7]. Polyoxometalates (POMs) are a class of inorganic metal-oxygen cluster compounds with unique molecular structure, chemical characters and electronic versatility [8].

In this article, the authors wish to report the results for the synthesis of ZnO nanosheets hydrothermally, using HPMo as a catalyst. The results suggested that HPMo is a useful catalyst for this reason. Also, photocatalytic activity of nanosheet products is examined with photocatalytic degradation of methylene blue (MB) as one of the most important azo dye and kinetic of reaction was also studied. The major aim described in this work is the design and development of applications for HPMo as a green and eco-friendly catalyst, which is a very important member of keggin type heteropoly acids.

2. Experimental

2.1. Synthesis methodology

Zinc acetate dihydrate, Ethanol (analytical grade) and molybdophosphoric acid (HPMo) were purchased from Merck Company. In a typical experiment, 1 g of Zinc acetate dehydrate was added into 30–40 mL solution of 3×10^{-3} M of HPMo in ethanol under magnetic stirring. After stirring for a few minutes, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, maintained at 120 °C for 48 hr and then cooled to room temperature naturally. The white precipitates were separated by centrifugation, washed several times with distilled water and ethanol, respectively and then dried at 60°C for 8 hr to get a white fine powder. The powder was used for further characterization and for photodegradation of azo dyes.

2.2. Measurements and analysis

FT-IR spectra were obtained with a Bruker 500 scientific spectrometer (KBr powder). The crystal structure of the prepared ZnO nanostructures were characterized by X-ray diffraction (XRD) (Bruker D8 Advance) using Cu-K α radiation ($\lambda=1.5406$ Å). The morphology and size of ZnO nanosheets were determined by transmission electron microscope (TEM, PHILIPS CM-120) with an acceleration voltage of 120 kV.

2.3. Photocatalytic degradation procedure

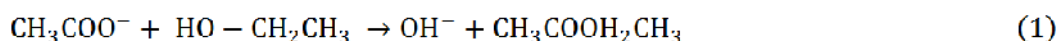
For photocatalytic degradation, the prepared ZnO nanosheets (0.1 g) were dispersed into 25 mL of 3.2×10^{-5} M of MB aqueous solution and then obtained suspension was stirred at dark for 30 min for equilibrium between adsorption-desorption of MB on the surface of nanosheets. Then, the suspension was transferred into the photoreactor in which oxygen was bubbling continuously from the bottom of the reactor. The suspension was then exposed to a



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3. Results and discussion

In this study, ZnO nanosheets were synthesized by hydrothermal method. The ZnO nanosheets were synthesized by the reaction of $\text{Zn}(\text{CH}_3\text{COO})_2$ and ethanol in the presence of HPMo as excellent catalyst under hydrothermal conditions. The chemical equations can be expressed as follows [9]:



The HPMo accelerate the above weak esterification reaction (Eq. (2)), leading to release of OH^- and subsequently, massive ZnO nanoclusters were momentarily formed (Eq. (3)). Hexagonal ZnO crystal has a positively polar zinc face and a negatively polar oxygen face. Therefore, temporary stabilization of ZnO nanoclusters occurs when negative charge $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ was adsorbed at the positive charge zinc face of ZnO [9]. Then, ZnO nanoclusters aggregated in order to minimize the total surface energy and finally self-assembled into metastable plates under hydrothermal conditions. The absorption of POMs on the surface of nanomaterials has been reported and employed for the morphology controlled of various nanomaterials [10]. In the previous work, the ZnO nanorods were synthesized by the forced alcoholysis process of zinc acetate in the presence of Preyssler-type heteropolyanion as bulk and nano forms [8].

Figure 1 shows a TEM image of the ZnO nanosheets formed at 120°C after 48 hr hydrothermal synthesis process.

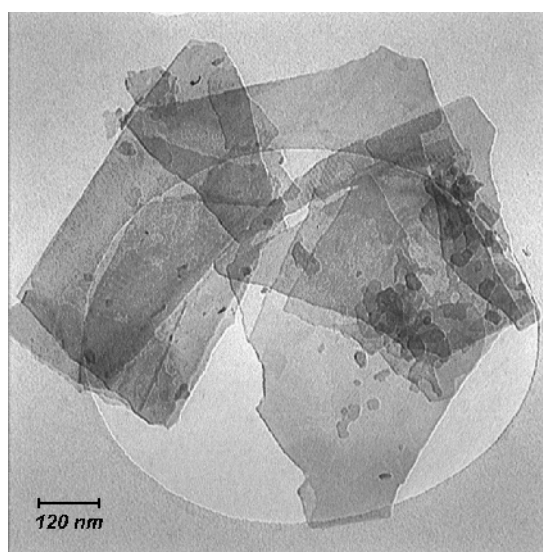


Fig. 1. TEM images of synthesized ZnO nanosheets.



It is seen in Fig. 1 that a large amounts of ultra thin ZnO nanosheets were synthesized after 48 hr. Also, Fig. 2 shows the typical X-ray diffraction (XRD) pattern of these ZnO nanostructures.

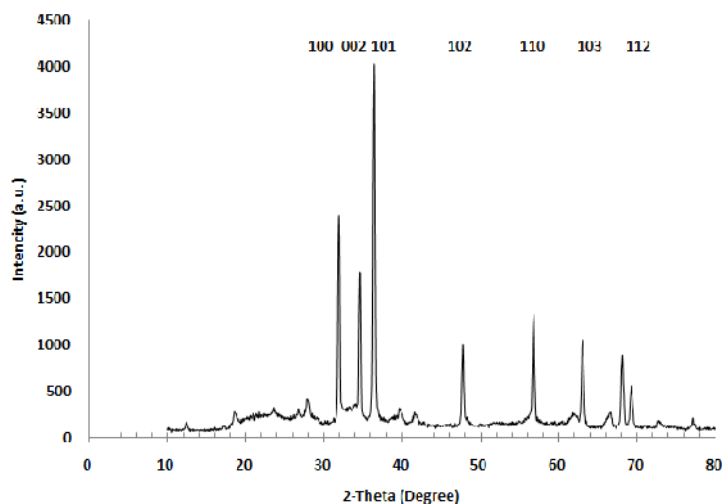


Fig. 2. XRD pattern of prepared ZnO nanostructures.

A Zincite structure can be assigned to samples by comparing the diffraction peak positions with those reported in the International Crystallographic Data Table.

Figure 3a shows typical time-dependent UV-Vis spectrum of MB during photoirradiation with ZnO nanosheets.

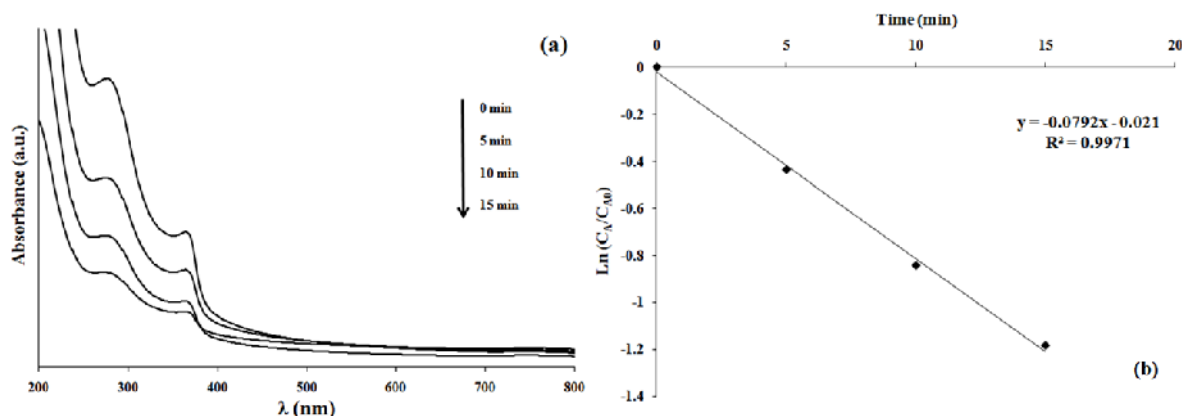


Fig. 3. Photocatalytic degradation of methylene Blue, (a) UV absorption spectra, (b) Kinetic study of degradation reaction for MB.

The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in the visible region. The prominent peak was decreased gradually indicating that the dye has been degraded. Almost 70% decolorization was observed when experiments were carried out under UV light in the presence of ZnO nanosheets for 15 min.



Fig. 3b shows the kinetic of degradation of MB. The results show that the photocatalytic decolorization of MB in aqueous ZnO solutions can be described by the first-order kinetic model, $\ln(C_A/C_{A0}) = kt$, where C_{A0} and C_A are initial and final concentrations, respectively. The semi-logarithmic plots of the concentration data gave straight lines showing the first order kinetics of the reactions. The correlation constants (R^2) of the fitted lines is 0.9971. The rate constants was also estimated to be 0.0792 min^{-1} .

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ZnO nanosheets were successfully synthesized by hydrothermal method using zinc acetate dihydrate and ethanol in the presence of molybdophosphoric acid (HPMo) as a catalyst. The results of XRD demonstrated that the synthesized products are single crystalline with zincite phase. The experimental results indicated that the ZnO nanosheets are good photocatalysts for decolorization of MB. The photocatalytic decolorization followed first order kinetic with constant rate of 0.0792 min^{-1} .

References:

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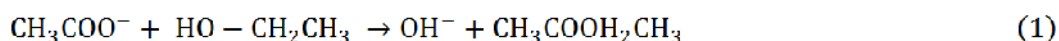
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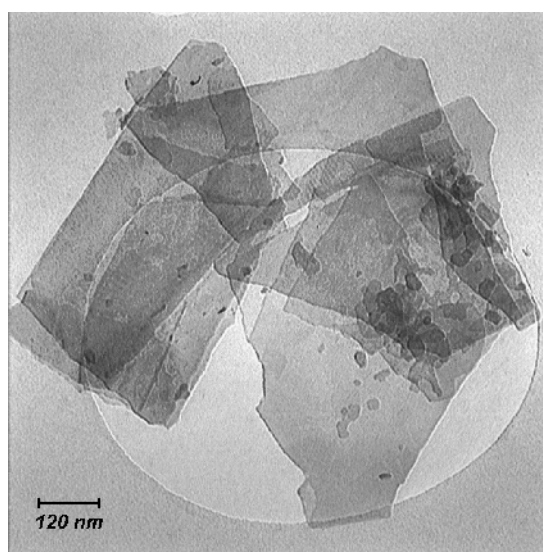


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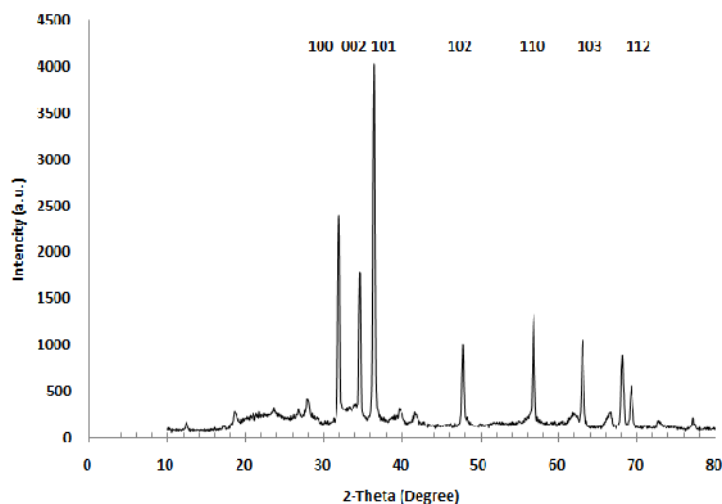


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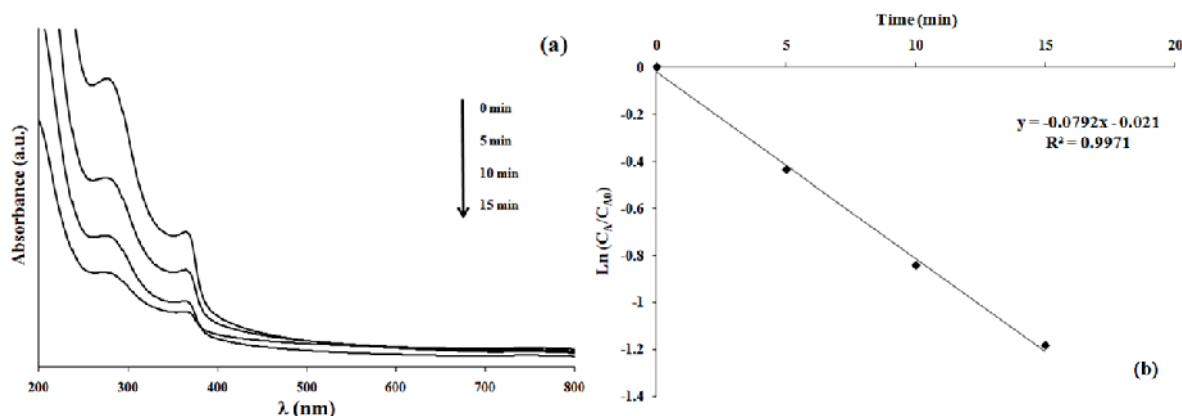


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