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Facile size-controlled preparation of highly photocatalytically active $ZnCr_2O_4$ and $ZnCr_2O_4$/Ag nanostructures for removal of organic contaminants

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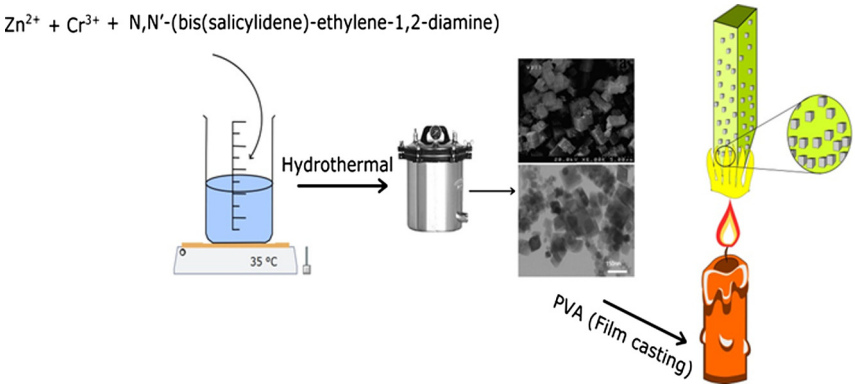
GRAPHICAL ABSTRACT



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ABSTRACT

The $ZnCr_2O_4$ nanoparticles were synthesized and characterized by different techniques such as; XRD, SEM, EDS, VSM, TEM and IR. In order to modify the morphology of structures, various alkaline and capping agents were used. For this work TETA, en and NH_3 as alkaline agents and salicylaldehyde, N,N′-(bis(salicylidene)-ethylene-1,2-diamine) and SDS as capping agents were employed. The cubic morphology for the $ZnCr_2O_4$ nanoparticles were obtained by using TETA and N,N′-(bis(salicylidene)-ethylene-1,2-diamine). When SDS and TETA were used, very uniform spherical zinc chromite nanoparticles with fine grain size were produced. Then on the surface of these nanoparticles, Ag nanoparticles were covered by photodeposition method. For investigation photocatalytic activity of the nanoparticles, several factors such as various azo dyes, temperature, grain size and morphology were investigated. Also by using of $ZnCr_2O_4$/Ag nanoparticles prepared polymer based nanocomposite. Results indicate that, nanoparticles can enhance the thermal stability of the PVA matrix.

1. Introduction

Spinel compounds are highly regarded owing to interesting physico-chemical properties and their applications such as super hard materials [1], magnetic materials [2] and high-temperature ceramics [3]. Oxides with spinel structure (with general formula AB_2O_4, in which the A-site is tetrahedrally and the B-site is octahedrally coordinated) are widely used as utile and cheap sensors for detection of toxic and hazardous materials. One of the most important spinel compounds is $ZnCr_2O_4$ due to their potential application as the efficient catalysts in the number of heterogeneous

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chemical processes such as CO oxidation [4], sensing properties [5], reduction of several organic molecules [6], and catalytic combustion of hydrocarbons [7]. Zinc chromite ($ZnCr_2O_4$) has a normal spinel structure that Non-magnetic Zn^{2+} and magnetic Cr^{3+} ions have a strong preference for the tetrahedral A- and the octahedral B-sites, respectively. A large number of chromites have been prepared in nanocrystal form to date. For instance, Some chromates, such as $CuCr_2O_4$, $NiCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$, have been synthesized using co-precipitation route, by the process of recrystallization from pyridine followed by ignition in the temperature range of 700–1200 °C, $MgCr_2O_4$ nanocrystals have been synthesized when an appropriate mixture of oxides is pressed into bars and sintered for several hours in an electric furnace at 1400 °C [8].

Up to now, many ways were reported for the synthesis of $ZnCr_2O_4$ such as; conventional ceramic way [9], Sol-Gel [10], microwave process [11], solution method [12], spray pyrolysis [13], and mechanical activation [14]. For instance zinc chromite synthesized by Marinkovic et al. with the spray pyrolysis process [15], Niu et al. have synthesized nanocrystalline $ZnCr_2O_4$ via a microemulsion method [16]. Among these methods, hydrothermal route have been known as one of the economical and convenient route to control the compositional, high purity, morphology and crystals [17,18]. $ZnCr_2O_4$ is a geometrically frustrated antiferromagnet compound with a first order transition at 12.5 K from paramagnetic phase with cubic structure to antiferromagnetic phase with tetragonal structure [19–21].

In the present work, the nanocrystalline zinc chromite has been prepared by hydrothermal route by optimizing the alkaline agent, surfactant and capping agent conditions. N,N′-(bis(salicylidene)-ethylene-1,2-diamine was synthesized and used as capping agent to produce cubic-like nanostructure. Also salicylaldehyde and SDS were used as capping agent and surfactant respectively. For investigation photocatalytic activity of nanoparticles were applied of several factors such as various azo dyes (rhodamine B, methylene blue and methyl orange), different temperature and grain size of zinc chromite nanostructures. Also by using of $ZnCr_2O_4$/Ag nanoparticles prepared polymer based nanocomposite. Results indicate that, nanoparticles can enhance the thermal stability of the PVA matrix.

2. Experimental

2.1. Materials and characterizations

Materials used in the present study were zinc nitrate ($Zn(NO_3)_2{\cdot}4H_2O$), Merck, 99.9%), chromium chromate ($CrCl_3{\cdot}6H_2O$, Merck, 99.9%), $AgNO_3$, salicylaldehyde, ethylenediamine, triethylenetetramine abbreviated TETA, methanol and NH_3. All chemicals were used without further purification. Also de-ionized water was used as solvent. The XRD of products was recorded by Philips, X-ray diffractometer using Ni-filtered Cu Kα radiation. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The EDX analysis with 20 kV accelerated voltage was done. FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a Nicolet-Impact 400D spectrophotometer. SEM images were taken using an LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor, to prevent charge accumulation, and to obtain a better contrast. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran). Transmission electron microscope (TEM) images of the as-obtained zinc chromite nanostructures were taken on a JEM-2100 with an accelerating voltage of 200 kV. The UV–vis diffuse reflectance spectrum of the as-produced zinc chromite nanostructures was obtained on a UV–vis spectrophotometer (Shimadzu, UV-2550, Japan). Thermogravimetric analysis (TGA) was carried out using an instrument (Shimadzu TGA-50H) with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

2.2. Synthesis of N,N′-(bis(salicylidene)-ethylene-1,2-diamine)

The stoichiometric amount of salicylaldehyde (0.02 mol, 2.44 g) in dissolved methanol (25 ml) was added dropwise to 1,2-ethylenediamine solution (0.01 mol, 0.61 g) in 25 ml methanol. The contents were refluxed for 3 h and a bright yellow precipitate of symmetrical Schiff-base ligand was obtained. The yellow precipitate was separated by filtration, being washed and dried in the vacuum.

2.3. Preparation of zinc chromite nanostructures

$ZnCr_2O_4$ nanoparticles were synthesized by the interaction between $CrCl_3{\cdot}6H_2O$ and $Zn(NO_3)_2$ precursors as starting materials with molar ratio equal to 2:1, respectively. In a typical method, 1 mmol of $Zn(NO_3)_2{\cdot}4H_2O$ and 2 mmol of $CrCl_3{\cdot}6H_2O$ were dissolved in de-ionized water and solution was stirred to achieve a homogeneous solution. An appropriate amount of N,N′-(bis(salicylidene)-ethylene-1,2-diamine), as a new capping agent, was added to the above solution and stirred for 40 min. Then, the pH of prepared mixture was adjusted to 10 through drop-wise addition of triethylenetetramine solution under magnetic stirrer. Finally, the prepared solutions were heated in autoclaves for 48 h at 220 °C individually and the formed precipitates were washed with double distilled water and methanol and dried at 60 °C for 4 h, afterwards the dried powder specimen was calcined at 800 °C for 10 h (sample number 4). The production conditions of zinc chromite structures contain kind of stabilization agent and alkaline agent that effect on the shape, purity and grain size were summarized in Table 1. Schematic diagram of the synthesis of the nanoparticles zinc chromite has been illustrated in Scheme 1.

2.4. Synthesis of $ZnCr_2O_4$/Ag nanocomposite

$ZnCr_2O_4$/Ag nanocomposite was prepared by photodeposition route. 0.006 g $AgNO_3$ was dissolved in 40 ml deionized water and then 0.1 g $ZnCr_2O_4$ was added to the above solution. The mixture was stirred on magnetic stirrer for 40 min and 0.5 ml methanol Merck added. Deoxygenation was also conducted simultaneously. Then the solution was transferred to quartz tube and stirred under UV irradiation for 5 h. Eventually, the product was separated and washed with deionized water and ethanol three times and dried at 60 °C.

2.5. Photocatalytic tests

In order to test the photocatalytic activity of the as-prepared nanoparticles, the photocatalytic decomposition of rhodamine B, methylene blue and methyl orange pollutants (the concentration of all dyes are 10 ppm) in suspension of as-prepared nanostructure under UV light have been performed. Also maximum absorbance wavelength for rhodamine B, methylene blue and methyl orange are 543, 664 and 507 nm respectively. A 400 W high-pressure mercury lamp (GYZ-250) was fixed at a distance of 40 cm above the surface solution. The measured luminous intensity was 1 kWm^{-2} and whole instrument was set in an occluded light box. 0.04 g photocatalyst was dispersed into 50 ml azo dyes aqueous solution. Subsequently, the aqueous suspension was magnetically stirred for 45 min in 20–25 °C. Finally, a 400 W halogen lamp was