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Normal spinel $CdCr_2O_4$ and $CdCr_2O_4$/Ag nanocomposite as novel photocatalysts, for degradation of water contaminates

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ABSTRACT

In this work $CdCr_2O_4$ and $CdCr_2O_4$/Ag nanostructures were synthesized by a new simple route with chrome nitrate and cadmium nitrate as chromium and cadmium source. N,N′-(bis(salicylidene)-ethylene-1,2-diamine) as new capping agent in the presence of triethylenetetramine (TETA) as alkaline agent were used to fabricate nanostructured cadmium chromite for the first time. The as-prepared nanoparticles $CdCr_2O_4$ and $CdCr_2O_4$/Ag were characterized by UV–Vis diffuse reflectance spectroscopy (DRS), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDX), and scanning electron microscopy (SEM). Results indicated that grain size and morphology of $CdCr_2O_4$ changes by change preparation factors such as kind of capping agent, alkaline agent and temperature. Up to now, this is first effort on the evaluation of photocatalytic efficiency of the cadmium chromite nanoparticles ($CdCr_2O_4$) and $CdCr_2O_4$/Ag in various conditions. In order to investing of photocatalytic properties of the nanoparticles, the effect of various factors such as various type of pollutant, grain size and morphology of cadmium chromite nanostructures, concentration of dyes and pH on photocatalytic behavior of products were studied.

1. Introduction

The chromite compounds have highly regarded due to their interesting properties and applications such as catalysts [1], semiconductors [2], electrochemical sensors and high temperature ceramics [3]. Chromite is used in the production of refractory materials. Adding of chromite as refractory material is due to increase its quality and mechanical strength at high temperatures. The general formula for this compounds is MCr_2O_4, where M = Co^{2+}, Fe^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and Mn^{2+}, which the M-site is tetrahedrally and the Cr is octahedrally coordinated. Most of the chromite crystallizes in the cubic spinel structure such as, $ZnCr_2O_4$ [4], $MgCr_2O_4$ and $CdCr_2O_4$. Generally chromites are subset of spinel compounds. Recently they have been noticed because of their different properties and applications such as super hard materials [5], magnetic materials and high-temperature ceramics [6]. Spinels have been synthesized by various methods such as hydrothermal [7], sonochemical [8], sol-gel [9], thermal decomposition [10], co-precipitation [11] and microemulsion [12] methods. But using the conventional solid-state method at high temperature, spinel particles obtained with low surface areas. Generally, many studies have been done on chromite such as cobalt, copper, zinc [13], but the studies on $CdCr_2O_4$ have been fewer [14].

Chromite is used mainly in catalytic and photocatalytic processes, for example, $CuCr_2O_4$ and $CoCr_2O_4$ spinels are operational and active catalysts that are applied for hydrocarbon oxidation [15,16], $NiCr_2O_4$ can be applied as a catalyst for oxidative dehydrogenation of propane [17] and $ZnCr_2O_4$ can be applied as a photocatalyst.

Here we report the synthesis, morphology and magnetic characterization of $CdCr_2O_4$ and $CdCr_2O_4$/Ag nanostructures by hydrothermal method. Moreover, a new capping agent was used for the first time to prepare of $CdCr_2O_4$ nanostructure. The as-obtained nanostructures were distinguished by Fourier transform infrared (FT-IR) spectrometry, X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM) and vibration sample magnetometer (VSM). At the end, optimized sample was used for the preparation of $CdCr_2O_4$/Ag and photocatalytic process.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were of analytical grade and were used as received without further purification. $Cd(NO_3)_2$, $CrCl_3$, $N(Et)_3$, triethylenetetramine (TETA), PEG and PVP were purchased from Merck Company.

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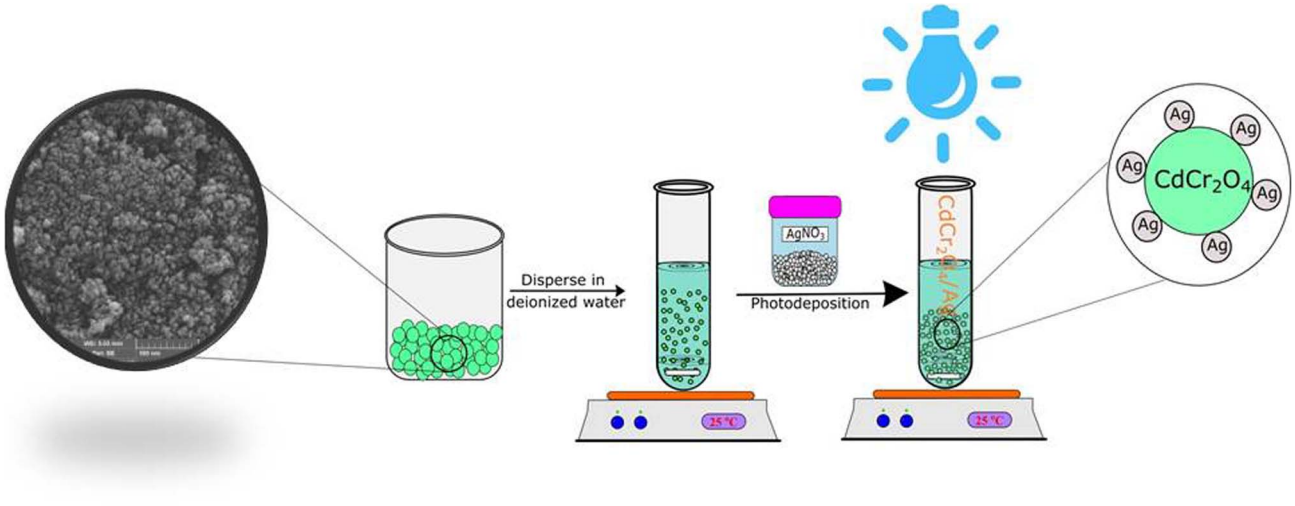

Scheme 1. Schematic diagram of the synthesis of $CdCr_2O_4$/Ag nanostructures.

Table 1
The reaction conditions for synthesis of $CdCr_2O_4$ via a hydrothermal method.

Sample no	Alkaline agent	Stabilizer agent	Figure of SEM	Temperature reaction	Temperature calcination	Ag-doped
1	$N(Et)_3$	–	5a and b	200	800	No
2	TETA	–	5c and d	200	800	No
3	TETA	–	–	200	–	No
4	TETA	–	6a and b	180	800	No
5	TETA	–	6c and d	150	800	No
6	TETA	–	–	180	600	No
7	TETA	N,N′-(bis(salicylidene)-ethylene-1,2-diamine)	7a and b	180	800	No
8	TETA	PEG	7c and d	180	800	No
9	TETA	PVP	7e and f	180	800	No
10	TETA	N,N′-(bis(salicylidene)-ethylene-1,2-diamine)	8a and b	180	800	Yes

The crystal phases of the sample were analyzed by X-ray diffraction using Ni-filtered Cu Kα radiation. FT-IR spectra were recorded on samples embedded in KBr pellets in the range of 400–4000 cm^{-1} with a Nicolet-Impact 400D spectrophotometer. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. SEM images were recorded by using an LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Au (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 measurement was carried out in a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) at room temperature. The UV–Vis spectra of the samples were taken on a UV–Vis spectrophotometer (Shimadzu, UV-2550, Japan) + visible sources of 400 W Osram lamps. 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. Preparation of N,N′-(bis(salicylidene)-ethylene-1,2-diamine)

The stoichiometric amount of salicylaldehyde (0.02 mol) was dissolved in methanol (25 ml) and added drop by drop to 1,2-ethylenediamine solution (0.01 mol) 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. Synthesis of $CdCr_2O_4$ nanoparticles

$CdCr_2O_4$ nanoparticles were prepared by the reaction of cadmium nitrate with chrome chloride and deionized water as solvent. Here N $(Et)_3$ and TETA were used as alkaline agents. For the investigation of capping agent effect, PVP, PEG and N,N'-(bis(salicylidene)-ethylene-1,2-diamine) were applied. In a typical synthesis, 1 mmol of $Cd(NO_3)_2$ and 2 mmol of $CrCl_3$ powders were dissolved in 50 ml of distilled water. The mixed solution was subsequently added into 50 ml distilled water containing capping agent under stirring. Then, TETA as alkaline agent was added dropwise to the aqueous solution containing Cr and Cd. Next, the mixture was putted in an autoclave for 11 h at 180 °C. The formed precipitates were collected and washed with double distilled water and methanol and dried at 60 °C. Finally, calcination of the product was carried out at 800 °C for 3 h.

2.4. Synthesis of $CdCr_2O_4$/Ag nanocomposite

For the preparation of $CdCr_2O_4$/Ag nanocomposite a photodeposition method was used. First $Ag(NO)_3$ dissolved in 50 ml deionized water to obtain 0.1 mM solution and then 0.1 g $CdCr_2O_4$ was added to above solution. The mixture was dispersed by ultrasound bath and then stirred for 30 min. Then the solution was shifted to quartz tube and stirred under UV irradiation for 3 h. Finally the solid was separated, washed with ethanol and water three times and dried at 70 °C. Schematic diagram of the synthesis of the $CdCr_2O_4$/Ag is depicted in Scheme 1. The detailed preparation conditions are summarized in Table 1.

2.5. Measurement photocatalytic activity

Photocatalytic activity of $CdCr_2O_4$ and $CdCr_2O_4$/Ag nanoparticles were measured by the decomposition of rhodamine B, methyl blue (MB) and murexide solution in water under UV light irradiation. Each time, 0.05 g photocatalyst was dispersed into 50 ml dye aqueous solution