J Mater Sci: Mater Electron (2016) 27:2938–2943
DOI 10.1007/s10854-015-4113-x

Green synthesis and characterization of cobalt aluminate nanoparticles and its photocatalyst application

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Received: 2 September 2015 / Accepted: 20 November 2015 / Published online: 26 November 2015

Abstract Nanocrystalline cobalt aluminate ($CoAl_2O_4$) was prepared by novel sol–gel method using aluminum nitrate, copper nitrate and lactose without adding external surfactant. Moreover, lactose plays role as capping agent, reducing agent, and chelate agent in the synthesis $CoAl_2O_4$ nanoparticles. The copper aluminate nanoparticles were characterized by using XRD, SEM, FT-IR, and EDX. The samples indicated a paramagnetic behavior, as evidenced by using vibrating sample magnetometer at room temperature. To evaluate the catalytic properties of nanocrystalline cobalt aluminate, the photocatalytic degradation of methyl orange under ultraviolet light irradiation was carried out.

1 Introduction

Materials at the nanometer scale have been studied for decades because of their unique properties arising from the large fraction of atoms residing on the surface, and also from the finite number of atoms in each crystalline core. Especially, because of the increasing need for high area density storage, the synthesis and characterization of semiconductor nanocrystals have been extensively investigated [1–8]. The search for low cost and efficient photocatalysts is still continuing. Some spinel-type oxides such as $NiAl_2O_4$, $ZnAl_2O_4$ and $CuAl_2O_4$ used as photocatalysts are semiconductor materials with narrow band high and these materials have been proven to be an efficient in the degradation of pollutants and/or the production of photocatalytic hydrogen [9–12]. Among the class of materials, cobalt aluminate ($CoAl_2O_4$) spinel, known as Thenard's blue, is widely used as catalyst, color filter for automotive lamps or pigment layer on luminescent materials because of its thermal, chemical, photochemical stability and peculiar optical properties [13–17]. In recent years, much work has been done on the preparation and the optical properties of $CoAl_2O_4$ spinel materials [18–24]. A variety of techniques such as combustion [18], Pechini [19], sol–gel [20–22], and reverse microemulsion have been successfully used for the preparation of cobalt aluminate oxide. However, most of these methods are either complex or expensive which diminishes preparation of the nano-sized materials in a large scale as compared to the combustion or sol–gel synthesis. Moreover, other disadvantages include the necessity of high temperature, inhomogeneity, and low surface area of the nano-sized products. Generally, smaller particle size results in higher surface area which is required for different catalytic applications. Hence, using a novel sol–gel method at relatively low temperature is a new and good approach to prepare nanosized cobalt aluminate particles suitable for application in the above-mentioned different fields especially the photocatalytic. In this report, for the first time, we had presented the green approach for preparation of $CoAl_2O_4$ nanoparticles by novel sol–gel method in the presence of lactose without adding external capping agent. This approach is simple and friendly to the environment. The photocatalytic degradation was investigated using methyl orange (MO) under ultraviolet light irradiation [23–27].

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2 Experimental

2.1 Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at scan range of $10 < 2\theta < 80$. The electronic spectra of the cobalt aluminate were obtained on a Scinco UV–vis scanning spectrometer (Model S-10 4100). The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. Fourier transform infrared (FT-IR) spectrum was recorded on a magna Nicolet 550 spectrophotometer in KBr pellets. The magnetic measurement of samples were carried out in a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature in an applied magnetic field sweeping between ±10,000 Oe.

2.2 Synthesis of $CoAl_2O_4$ nanoparticles

At first, 0.291 g of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 50 mL of distilled water. Then, 1.00 of lactose was subsequently added to the above solution under magnetic stirring at 80 °C for 30 min. Afterwards, 0.750 g of $Al(NO_3)_3{\cdot}9H_2O$ was dissolved in 50 mL of distilled water and was added to the above solution under magnetic stirring. A solution was obtained and further heated at 100 °C for 1 h to remove excess water. During continued heating at 100 °C for 1 h, the solution became more and more viscous to become a gel. Finally, the obtained product was calcinated at 800 °C for 2 h in a conventional furnace in air atmosphere and then cooled it to room temperature.

2.3 Photocatalytic experimental

The methyl orange (MO) photodegradation was examined as a model reaction to evaluate the photocatalytic activities of the cobalt aluminate nanoparticles. The photocatalytic experiments were performed under an irradiation ultraviolet light. The photocatalytic activity of nanocrystalline $CoAl_2O_4$ obtained was studied by the degradation of methyl orange solution as a target pollutant. The photocatalytic degradation was performed with 50 mL solution of methyl orange (0.0005 g) containing 0.1 g of $CoAl_2O_4$. This mixture was aerated for 30 min to reach adsorption equilibrium. Later, the mixture was placed inside the

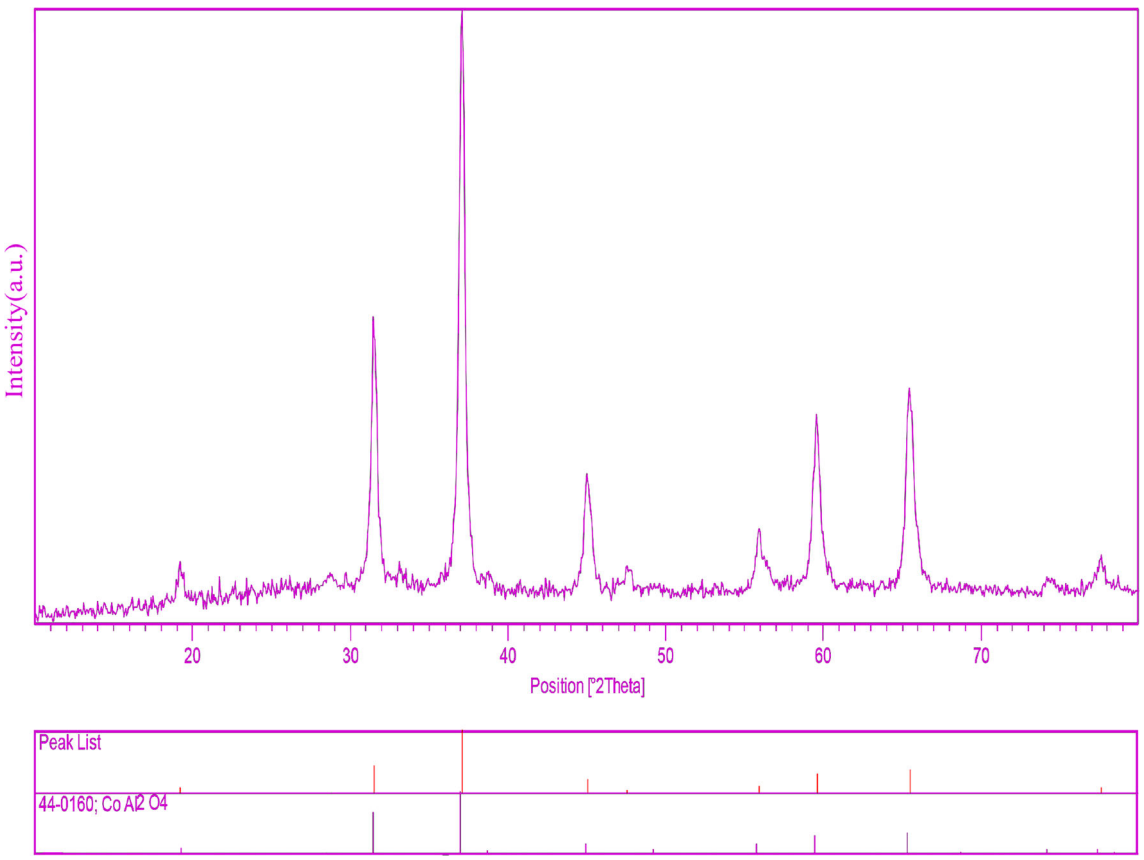


Fig. 1 XRD pattern of $CoAl_2O_4$ nanoparticles calcined at 800 °C

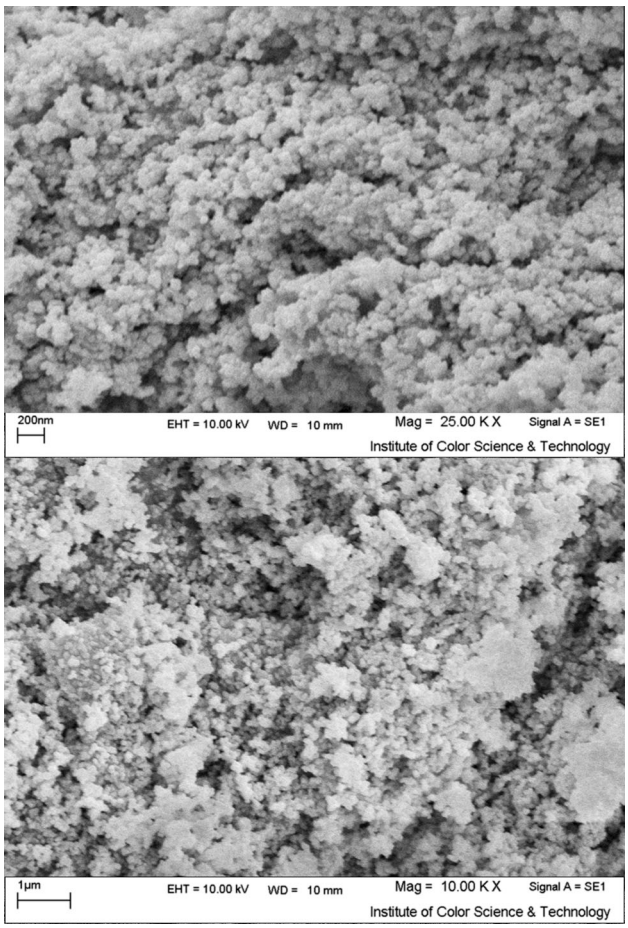


Fig. 2 SEM image of $CoAl_2O_4$ nanoparticles calcined at 800 °C

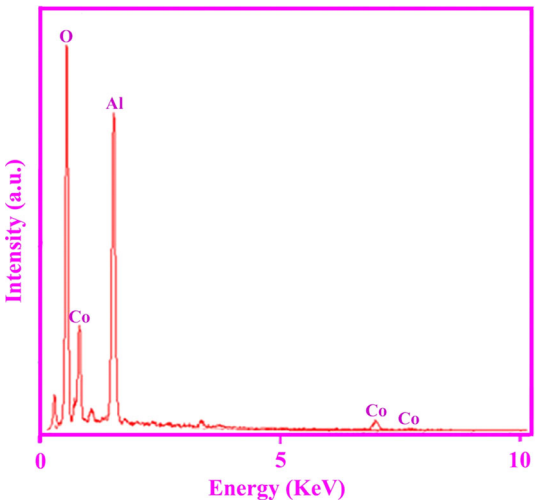


Fig. 3 EDS pattern of $CoAl_2O_4$ nanoparticles calcined at 800 °C

photoreactor in which the vessel was 15 cm away from the visible source of 400 W mercury lamps. The photocatalytic test was performed at room temperature. Aliquots of the

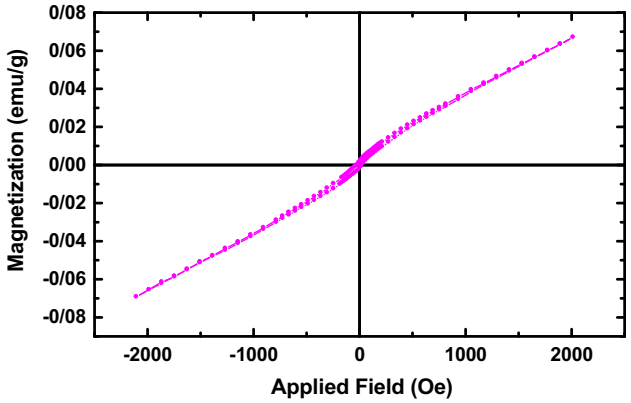


Fig. 4 VSM curves of $CoAl_2O_4$ nanoparticles calcined at 800 °C

mixture were taken at definite interval of times during the irradiation, and after centrifugation they were analyzed by a UV–vis spectrometer. The methyl orange (MO) degradation percentage was calculated as:

$$\text{Degradation rate } (\%) = \frac{A_0 - A}{A_0} \times 100$$

where A_0 and A are the absorbance value of solution at A_0 and A min, respectively.

3 Results and discussion

The XRD pattern of as-prepared $CoAl_2O_4$ nanoparticles is shown in Fig. 1. Based on the Fig. 1, the diffraction peaks can be indexed to pure cubic phase of $CoAl_2O_4$ (space group Fd3m, JCPDS No. 44-0160). No other crystalline phases were detected. From XRD data, the crystallite diameter (D_c) of $CoAl_2O_4$ nanoparticles was calculated to be 27 nm using the Scherer equation:

$$D_c = K\lambda/\beta\cos\theta \qquad \text{Scherer equation}$$

where β is the breadth of the observed diffraction line at its half intensity maximum (400), K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. The morphology of the nanoparticles was investigated using SEM which demonstrates uniform nanoparticles with spherical shape homogenously distributed all over the sample, as it could be clearly observed in Fig. 2. The $CoAl_2O_4$ nanoparticles with particle size of about 30–40 nm were observed. The EDS analysis measurement was used to investigate the chemical composition and purity of $CoAl_2O_4$ nanoparticles. According to the Fig. 3, the product consists of Co, Al, and O elements. Furthermore, neither N nor C signals were detected in the EDS spectrum, which means the product is pure and free of any capping agent or impurity. The VSM magnetic measurements for

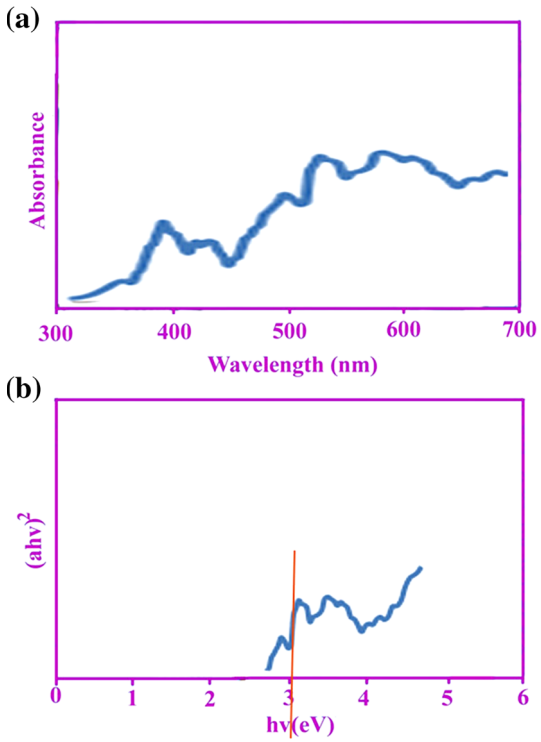


Fig. 5 **a** UV–vis absorption spectra of prepared $CoAl_2O_4$ nanoparticles for 120 min at calcination temperature of 800 °C and **b** plot to determine the direct band gap of $CoAl_2O_4$

the cobalt aluminate (Fig. 4) show the magnetic properties of nanoparticles calcined at 800 °C. The synthesized $CoAl_2O_4$ indicates a paramagnetic behavior, a saturation magnetization of ~ 0.07 emug^{-1} was determined for the $CoAl_2O_4$ nanoparticles. The room temperature UV–vis absorption spectra of $CoAl_2O_4$ nanoparticles were also measured in the range of 300–700 nm. Figure 5a shows the diffuse reflection absorption spectra of the $CoAl_2O_4$ nanoparticles calcinled at 800 °C. The figure indicates that the $CoAl_2O_4$ nanoparticles shows absorption maxima at 530 nm, the direct optical band gap estimated from the absorption spectra for the $CoAl_2O_4$ nanoparticles is shown in Fig. 5b. An optical band gap is obtained by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ where α is the absorption coefficient and $h\upsilon$ is photon energy. Extrapolation of the linear portion at $(\alpha h\upsilon)^2 = 0$ gives the band gaps of 3.05 eV for $CoAl_2O_4$ nanoparticles. Photodegradation of methyl orange under UV light irradiation (Fig. 6a–c) was employed to evaluate the photocatalytic activity of the as-synthesized $CoAl_2O_4$. No methyl orange was practically broken down after 1 h without using Ultraviolet light irradiation or nanocrystalline $CoAl_2O_4$. This observation indicated that the contribution of self-degradation was insignificant. The probable mechanism of the photocatalytic degradation of methyl orange can be summarized as follows:

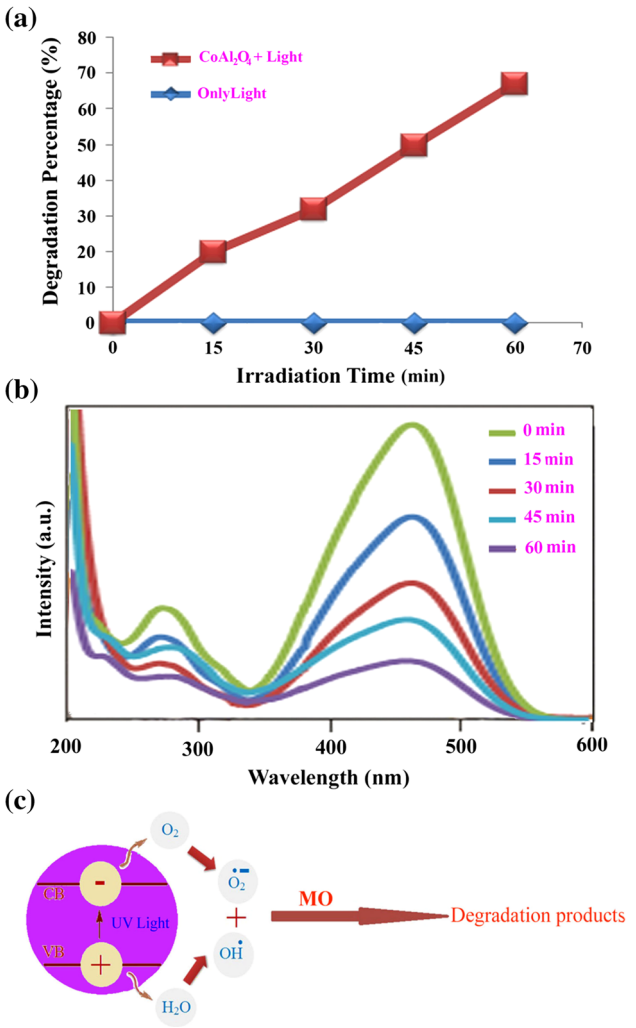


Fig. 6 **a** photocatalytic methyl orange degradation of $CoAl_2O_4$ nanoparticles under ultraviolet light, **b** fluorescence spectral time scan of methyl orange illuminated at 510 nm with $CoAl_2O_4$ nanoparticles and **c** reaction mechanism of methyl orange photodegradation over $CoAl_2O_4$ nanoparticles under ultraviolet light irradiation

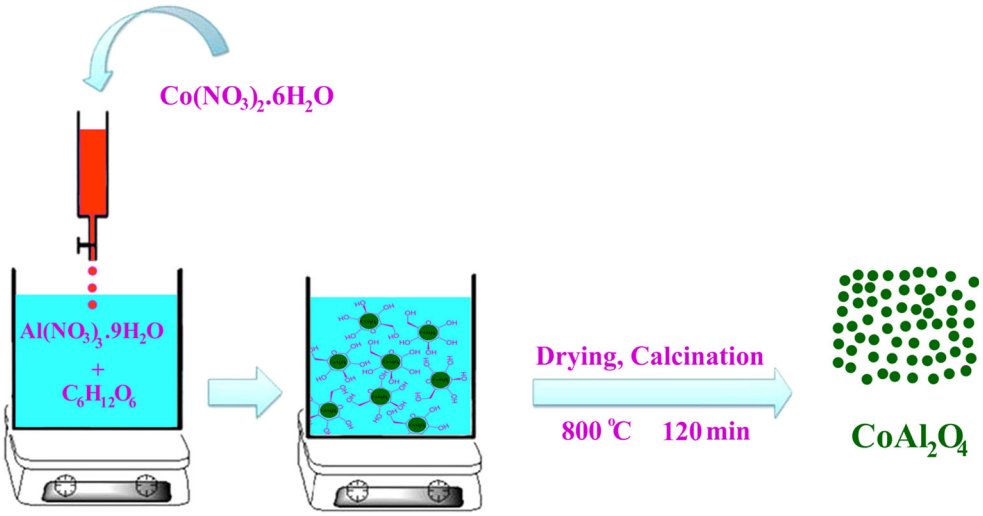
$$CoAl_2O_4 + h\nu \rightarrow CoAl_2O_4^* + e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow OH^{\cdot} \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (3)$$

$$OH^{\cdot} + O_2^{\cdot -} + \text{methyl orange} \rightarrow \text{Degradation products} \quad (4)$$

Using photo catalytic calculations by Eq. (1), the methyl orange degradation was about 68 % after 60 min irradiation of ultraviolet light, and nanocrystalline $CoAl_2O_4$ presented high photocatalytic activity (Fig. 6a). The spectrofluorimetric time-scans of methyl orange solution illuminated at 510 nm with nanocrystalline $CoAl_2O_4$ are depicted in Fig. 6b. shows continuous removal of methyl



Scheme 1 Schematic diagram illustrating the formation of $CoAl_2O_4$ nanoparticles

orange on the $CoAl_2O_4$ under ultraviolet light irradiation. It is generally accepted that the heterogeneous photocatalytic processes comprise various steps (diffusion, adsorption, reaction, and etc.), and suitable distribution of the pore in the catalyst surface is effective and useful to diffusion of reactants and products, which prefer the photocatalytic reaction. In this investigation, the enhanced photocatalytic activity can be related to appropriate distribution of the pore in the nanocrystalline $CoAl_2O_4$ surface, high hydroxyl amount and high separation rate of charge carriers (Fig. 6c). Furthermore, this route is facile to operate and very suitable for industrial production of $CoAl_2O_4$ nanoparticles. The synthesis pathway of $CoAl_2O_4$ nanoparticles is shown in Scheme 1.

4 Conclusion

$CoAl_2O_4$ nanoparticles were synthesized successfully via a novel sol–gel method in the presence of lactose as capping agent, reducing agent, and chelate agent. When as-prepared nanocrystalline cobalt aluminate was utilized as photocatalyst, the percentage of methyl orange degradation was about 68 after 60 min irradiation of UV light. This result suggests that as-obtained nanocrystalline cobalt aluminate as favorable material has high potential to be used for photocatalytic applications under UV light. High purity of the as-prepared nanocrystalline sample was proved by FT-IR, XRD, and EDS analyses. The optical properties of as-formed nanocrystalline products were also studied. VSM analyzes indicates a paramagnetic behavior for the synthesized nanoparticles.

Acknowledgments Authors are grateful to council of University of Central Tehran for providing financial support to undertake this work.

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