Facile Fabrication of Co$_3$O$_4$ Nanostructures as an Effective Photocatalyst for Degradation and Removal of Organic Contaminants

Ali Abbasi 1,* Mazyar Ahmadi Golsefidi 2, Mehdi Mohammad Beigi 1, Nazanin Sadri 2, Mehdi Abroudi 1

1 Young Researchers and Elite Club, Gorgan Branch, Islamic Azad University, Gorgan, Iran
2 Department of chemistry, Faculty of sciences, Gorgan branch, Islamic Azad University, Gorgan, Iran

ABSTRACT

Co$_3$O$_4$ nanoparticles were synthesized via a simple Co-precipitation reaction between precursors of cobalt and NH$_3$. The effect of different parameters such as concentration of NH$_3$ and precursors of cobalt on the size and photocatalytic activity of the products was investigated. The achieved nanoparticles were characterized by X-ray powder diffraction analysis, field emission scanning electron microscopy, energy-dispersive spectroscopy (EDS) and diffuse reflectance spectroscopy (DRS). The photocatalytic behavior of Co$_3$O$_4$ nanoparticles was evaluated using the degradation of various organic pollutants (rhodamine B and methyl orange) under visible irradiation. Also effect of pH on the photocatalytic performance of Co$_3$O$_4$ nanostructures was investigated. Best concentration of NH$_3$ for degradation of methyl orange and rhodamine B is 3 mol, and most appropriate precursor of cobalt for the demolition of dyes is Co(Hsal)$_2$. Photo-degradation of Rhodamine B and methyl orange (89%) was performed using Co$_3$O$_4$ nanoparticle (band gap 1.7 eV) synthesized by Co(Hsal)$_2$ as precursor of cobalt under visible light irradiation for 4h.

INTRODUCTION

Metal oxides are widely used in the various fields such as; heterogeneous catalysis, protein-purification systems [1], solar energy transformation, electronics devices and etc. Among the metal oxides, copper and cobalt are the most active for the decomposition of organic pollution [2, 3]. Cobalt oxide is one of the most important materials among the transition metal oxides and widely used in anode materials in gas and humidity sensors [4, 5], Li-ion rechargeable batteries, magnetism, and optical devices [6]. catalyst for oxygen evolution and oxygen reduction reaction [7, 8], electrochemical capacitors for high power devices in energy storage systems (supercapacitors) [9, 10] and solar selective absorber, pigment for glasses and ceramics [11]. Also Co$_3$O$_4$ nanoparticles as additive has been used in various fields of material science such as improve temperature-stable BaTiO$_3$-based dielectrics [12]. Various methods have been applied for synthesis of metal oxides such as plasma sputtering [13], laser ablation technique, micro-emulsion [14], sol-gel route [15], spray pyrolysis [16], thermal salt
decomposition [17], powder immobilization and hydrothermal method [18], that the majority of them are synthesized using water as a solvent [19, 20]. But among these methods, Co-precipitation method has been recognized as one of the important and accessible strategies for production of various nanoparticles, also this way has advantages compared to other routes including phase purity, high crystallinity and homogeneity of the materials synthesized.

Elimination of pollutants from water is a challenge for water treatment [21-23]. Amongst various ways for remove pollutants from water, photo-degradation has great importance. In these processes, organic structures decomposed by photo-catalyst material under UV or visible light and finally CO$_2$ and H$_2$O are achieved. The aim of the present work is study the effect of different concentration of NH$_3$ and various precursor of cobalt on the size and morphology of Co$_3$O$_4$ nanoparticles, and then studies obtained products in order to investigation of efficient photocatalyst. Here rhodamine B and methyl orange were used as organic pollution and sample 2 and 5 had the best photocatalytic activity.

**MATERIALS AND METHODS**

Cobalt (II) nitrate, acetylacetonate, NH$_3$, methanol Sodium salicylate (NaHsal) and salicylaldehyde (Sal) were purchased from Merck and used without purification. Deionized water was used as solvent. The prepared Co$_3$O$_4$ samples were characterized using X-ray diffractometer using Ni-filtered Cu Kα radiation, scanning electron microscope (SEM), model 1455VP. Prior to taking images, the samples were coated with a very thin layer of Pt to make the sample surface conducting and prevent charge accumulation. Also UV-vis spectrum of the sample was taken on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan) + visible sources of 400 W Osram lamps.

**Synthesis of Co$_3$O$_4$**

Co$_3$O$_4$ samples were prepared by using various precursor of Cobalt (II), NH$_3$ and de-ionized water as solvent. First 1 mol of various precursor of Cobalt dissolved in deionized water then NH$_3$ as alkaline agent was added to solution. The obtained precipitates were collected, washed and dried at 60 °C, then calcinated at 450 °C for 2 h. The production conditions of Co$_3$O$_4$ nanostructures were summarized in table 1.

**Syntheses of various precursors**

For the synthesis of various precursors, 0.4mol cobalt (II) nitrate dissolved in methanol then 0.8 mol acetylacetonate was added to above solution at 60°C. The obtained precipitates were washed and dried. For the synthesis of Co(Sal)$_2$ and Co(Hsal)$_2$ in above method salicylaldehyde and Hsal (salicylate) were replaced to acetylacetonate.

**Photocatalytic measurements**

The photocatalytic performance of the as-synthesized Co$_3$O$_4$ nanostructures was evaluated by applying of the various contaminants solution. 0.05 g Co$_3$O$_4$ nanoparticles were used for demolition of 40 ml dye solution (10 ppm) then solution was mixed by a magnet stirrer for 1 h in darkness. The solution was irradiated by a 400 W visible lamp which was placed in a quartz vessel in a reactor. After each 20 minutes, sampling (about 5-10 ml) was performed and was centrifuged to separate the catalyst and then was analyzed with the UV–Vis spectrometer.

**RESULTS AND DISCUSSION**

Co$_3$O$_4$ nanostructure is characterized by X-Ray Diffraction Analysis (XRD), Energy Dispersive analysis of X-rays (EDS), Diffuse Reflectance Spectroscopy (DRS) and Scanning Electron Microscopy (SEM).

Fig. 1 present the XRD patterns of the Co$_3$O$_4$ powder with different precursor of cobalt. The X-ray diffractograms were scanned between 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alkaline agent</th>
<th>Ratio of ammonia</th>
<th>Ligand (capping agent)</th>
<th>Figure of SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH$_3$</td>
<td>1</td>
<td></td>
<td>3a and b</td>
</tr>
<tr>
<td>2</td>
<td>NH$_3$</td>
<td>3</td>
<td></td>
<td>3c and d</td>
</tr>
<tr>
<td>3</td>
<td>NH$_3$</td>
<td>3</td>
<td>Acetylacetonate</td>
<td>4a and b</td>
</tr>
<tr>
<td>4</td>
<td>NH$_3$</td>
<td>3</td>
<td>Salicylaldehyde</td>
<td>4c and d</td>
</tr>
<tr>
<td>5</td>
<td>NH$_3$</td>
<td>3</td>
<td>Sodium salicylate</td>
<td>4e and f</td>
</tr>
</tbody>
</table>
angles of 15-75°. Each spectrum indicate the peaks characteristic for the Co₃O₄ crystal with 2 values of ~19°, 31.1°, 36.9°, 38.5°, 45°, 55.8°, 59.5° and 65.3° that the related to h k l planes of (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), respectively. The XRD spectra of as-prepared Co₃O₄ nanoparticles were demonstrated a pure cubic phase (space group: Fd-3m) which was quite close to the literature amounts (JCPDS No. 76-1802). It can be seen that the highest intensity of the diffraction peak for all powders is (3 1 1) and crystallite size, by using the Scherrer equation and full with at half maximum (FWHM) was obtained about 30 nm.

To confirm the chemical composition of the synthesized powders, the sample was examined by EDS analysis (Fig. 2). This spectrum confirms that the targeted chemical composition could achieve in the final product. Obviously, the sample is composed of Co and O.

The effect of concentration of NH₃ on the particle size was investigated. The various amount of NH₃ (1 and 3 mol that were named sample 1, 2) as alkaline agent were used for study effect of concentration on the particle size. As can be seen by increasing concentration of NH₃ to 3 mol, particle size was decreased (Fig. 3c and d) compared to concentration of 1 mol (Fig. 3a and

Fig. 1. XRD patterns of Co₃O₄ produced by Co-precipitation method.

Fig. 2. EDS curve of Co₃O₄ nanostructure (sample 5)
b). In the next step, for investigate the effect of ligand, were used of Co(acac)$_2$, Co(Sal)$_2$, and Co(Hsal)$_2$ as various precursors of cobalt (samples 3, 4 and 5 respectively). Based on the FESEM micrographs of the Co$_3$O$_4$ samples prepared with the aid of different capping agents (Fig. 4a-f), it is suggested that Hsal has a great impact on the preparation of uniform spherical Co$_3$O$_4$ nanostructures. As it can be seen in Fig. 4 e and f nanoparticles synthesized by Co(Hsal)$_2$ are very uniform compared to nanoparticles prepared with Co(acac)$_2$ (Fig. 4a and b) and Co(Sal)$_2$ (Fig. 4c and d). Hence, the use of Hsal is favourable to form uniform spherical Co$_3$O$_4$ nanostructures.

The photocatalytic activity of a material is controlled by absorption coefficient and optical band gap that which these features are related to the electronic structure of the material. Fig. 5 shows the UV–Vis absorption spectrum of the Co$_3$O$_4$ nanoparticles. In this spectrum can be seen the absorption peaks at 207, 245 and 385 nm.

The band gap of nanoparticles was determined by Diffuse Reflectance spectroscopy (DRS) that estimated by Tauc's equation;

\[
\alpha = \alpha_0 \left( \frac{\hbar \nu}{E_g} \right)^n / \hbar \nu
\]

where \(\alpha\) is absorption coefficient, \(\hbar \nu\) is the photon energy, \(E_g\) is the optical band gap, \(\alpha_0\) and \(h\) are the constants and \(n\) related to the type of electronic transition and can have any value between 0.5 to 3 eV. The energy gap \(E_g\) of the sample was determined by extrapolating the linear section of the plots of \((\alpha h \nu)^2\) vs. \(h \nu\) to the energy axis (1.7 eV) as show in Fig. 6, in result the nanoparticles are photoresponsive in the visible ranges, and as has been shown, Co$_3$O$_4$ has absorption in the visible area.

The photo-catalytic activities of the Co$_3$O$_4$ nanoparticles were measured by monitoring the degradation of rhodamine B and methyl orange in an aqueous solution under visible irradiation. In this section was surveyed the effect of various parameters including; kind of pollutant, particle size and pH on the photocatalytic activity of nanostructures. As depicted in Fig. 7, after applying visible irradiation, a photon produce electron and hole in the conduction band (CB) and valence band (VB) of Co$_3$O$_4$, respectively.

![SEM images of Co$_3$O$_4$ prepared in various concentrations of NH$_3$: (a and b) 1 mol, (c and d) 3 mol.](image-url)
Fig. 4. SEM images of Co$_3$O$_4$ prepared by (a and b) Co(acac)$_2$, (c and d) Co(Sal)$_2$, and (e and f) Co(Hsal)$_2$.

Fig. 5. UV–Vis diffuse reflectance spectrum of Co$_3$O$_4$ (sample 5)
The rhodamine B and methyl orange demolition percentage in time of t (DP (t)) were calculated as follows:

\[
DP (t) = \frac{A_0 - A_t}{A_0} \times 100
\]  

(2)

Where \( A_t \) and \( A_0 \) are the absorption value of the solution at 0 and t minute [24-28].

The presented mechanism of the demolition of pollutants can be displayed as:

\[
\text{Co}_3\text{O}_4 + h\nu \rightarrow \text{Co}_3\text{O}_4^* + e^- + h^+
\]

\[h^+ + \text{H}_2\text{O} \rightarrow \text{OH}^-
\]

\[2e^- + \text{O}_2 + 2 \text{H}^+ \rightarrow \text{O}_2^-\]

\[
\text{OH}^- + \text{O}_2^- + \text{pollutants} \rightarrow \text{Degradation products}
\]

No dye demolition after 60 min without using visible light irradiation or nanocatalysts. Hence, the degradation efficiency of methyl orange and
rhodamine B by Co$_3$O$_4$ nanoparticles produced with different concentration of NH$_3$ and various precursors of cobalt is determined as shown in Fig. 7 under visible light irradiation. Also the irradiation time was 4 h. In the case of methyl orange pH was adjusted at 5, while pH for rhodamine B was 7. Since the methyl orange is an anionic combination, as result decreasing pH value results in a higher adsorption amount of methyl orange on the photocatalyst surface. As shown in Fig. 8, in acidic condition the surface of nanostructure is covered by more positive charge and subsequently anionic molecules can be more adsorbed on the surface. The most appropriate samples for demolition of rhodamine B were achieved sample 2 and sample 5 with demolition percentage - 87% and 89% respectively. The most appropriate samples for degradation of methyl orange were achieved sample 2 and sample 5 with demolition percentage - 86% and 89% respectively. Sample 2 and 5 have higher surface area duo to smaller particle size. Therefore more dye molecules are affected in same time. With the decrease of particle size, the ratio of surface area to volume increases, therefore the catalytic performance is better.

CONCLUSION

Co$_3$O$_4$ nanostructures were prepared by a Co-precipitation process at room temperature. The effects of concentration and precursors of cobalt were studied and for optimization size, after completing each step, SEM analyses were taken from the produced nanoparticles. The influence concentration of NH$_3$ and precursors of cobalt on the photocatalytic properties Co$_3$O$_4$ nanoparticle was studied. Hereon was used of rhodamine B and methyl orange as organic pollutants. Results indicated that the best concentration of NH$_3$ for destruction of methyl orange and rhodamine B was achieved 3mol, and most appropriate precursor of cobalt for the demolition of dyes was achieved Co(Hsal)$_2$.

ACKNOWLEDGEMENTS

The authors are grateful to Islamic Azad University (IAU) for providing financial support to undertake this work.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCE