Facile Synthesis of Spinel CoCr$_2$O$_4$ and Its Nanocomposite with ZrO$_2$: Employing in Photo-catalytic Decolorization of Fe (II)-(luminol-Tyrosine) Complex

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Abstract

In this project, the deep green power from spinel cobalt chromite (CoCr$_2$O$_4$) nano-crystals carried out using the co-precipitation method and then calcinated at 600 °C for 4 hours. This produced nano-crystal (spinel CoCr$_2$O$_4$) fabricated using the ultrasonic technique to link it with zirconium dioxide (ZrO$_2$) in ratios 1:2 and 1:3, respectively. The X-ray diffraction (XRD), scan electron microscopy (SEM), and energy-dispersive X-rays (EDX), as well as ultraviolet-visible spectrophotometry used to describe the characterizations of prepared materials. The XRD analysis demonstrated that the spinel CoCr$_2$O$_4$ synthesis and their composites were found to be nanoparticles. XRD spectra indicated that the spinel CoCr$_2$O$_4$ is successfully loaded on ZrO$_2$ because, the 2θ of ZrO$_2$ is shifted toward a high 2θ value after spinel CoCr$_2$O$_4$ loaded. This case is attributed to the tiny Co$^{2+}$ and Cr$^{3+}$ ions combined with Zr$^{4+}$ in crystal lattice. The SEM images and EDX spectra of these obtained nanomaterials were found to be spherical agglomerations with an enhanced degree of surface roughness after surface fabrication. On the other side, the bandgap of spinel CoCr$_2$O$_4$ nanocrystals elevated from 3.2 to 4.8 eV with increasing the ZrO$_2$ dose. Under UV-A light, the photocatalytic decolorization efficiency of Fe (II)-(luminol-Tyrosine) complex utilizing spinel CoCr$_2$O$_4$ nanocrystals was tested, and it increases from 17.57 % to 30.67% and 41.97% when its nanocomposite was used in 1:2 and 1:3 ratios, respectively. The elevated efficiency after modified the spinel CoCr$_2$O$_4$ surface with ZrO$_2$ as nanocomposite, due to increasing the acidity of the spinel CoCr$_2$O$_4$ surface that enhances the adsorption of hydroxyl on its surface then generality of the hydroxyl radical, and reducing the recombination. The photo-reaction using spinel CoCr$_2$O$_4$ nanocrystals, ZrO$_2$ and their composites were followed pseudo-first-order kinetics depended on the complex concentration.

Keywords: Spinel CoCr$_2$O$_4$; Spinel CoCr$_2$O$_4$ / ZrO$_2$ nanocomposite; Co-precipitation; Facile Synthesis; Photo-catalytic decolorization; and Fe(II)-(luminol-Tyrosine) complex.

1. Introduction

Many researchers who worked in the nanoscience and nanotechnology field, and found the basic science and technical breakthroughs abound in this field. In the last several decades, many novel materials with dimensions in the nanoscale were synthesized and characterized, which including nanoparticles, nanobelts, like-flower nanostructure, nanowires, Quasi-spherical nanoparticle, and nanotubes, were prepared.[1-3]. Though the design and synthesis of nanoscale materials with controllable qualities is a continuous difficulty in the area of nanoscience and nanotechnology, however, it remains important materials, that have good electrical, optical, and physical characteristics[7]. The use of nanotechnology in wastewater treatment that is produced by scientific labs or industry can make the wastewater treatment is better[8-12]. Spinel CoCr$_2$O$_4$ nanomaterial is a distinctive material that has a low bandgap, used as a pigment to colorant of ceramic, porcelain, plastic, and solar absorber coatings. Moreover, the conventional spinel cubic structure shows up with two kinds of cation sublattice. In the A sub-lattice, there are Co$^{3+}$ ions that occupy the tetrahedral (A) sites, and in the B sub-lattice, Cr$^{3+}$ ions are occupying the octahedral (B) sites[13-15]. Magnetic characteristics of the spinel CoCr$_2$O$_4$ greatly rely on the number of cations that are grouped at sites A and B in the aAaAaAaAsssxxxx spinel lattice. NP-influenced magnetic characteristics also differ between single NPs and their counter bulk material[16], which is consistent with their lattice distortion, surface imperfections, and the existence of interactions between NPs. When it comes to the family of chromites, cobalt chromite nanoparticles (CoCr$_2$O$_4$ NPs) have become popular because of their

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multiferroic characteristics. The spinel CoCr$_2$O$_4$ has a cubic spinel structure with multiferroicity, and a conical spin ordering has been discovered in this material. [17] Due to the conflicting Co-Co, Cr-Cr, and Co-Cr interactions, cobalt chromate nanoparticles undergo three sequential magnetic transitions: At temperature collinear ($T_c$) 95 K, the magnetic transition from paramagnetic to ferromagnetic (FIM) phase happens; at temperature non-collinear spiral ($T_s$) 26 K, the magnetic transition from FIM to an incommensurate conical-spiral phase happens; and at temperature long-range collinear ($T_l$) 14 K, the magnetic transition from ferromagnetic (FIM) to an incommensurate conical-spiral phase happens [18]. Kind-II multiferroic materials, such as pristine spinel CoCr$_2$O$_4$ nanoceramics, are a type of material that manifests magnetoelectric coupling as well as two or more ferroic features. Storing charges in electronic memory devices are made much more efficient using these nanoceramics [19].

The goal of this work project is to focus on the facile synthesis of spinel CoCr$_2$O$_4$ nanocrystals using co-precipitation and then modified with ZrO$_2$ in 1:2 and 1:3 ratios using ultrasonic waves, to reduce the recombination and increase the surface acidity. The structural, morphological, and optical characteristics are determined to conform to this synthesis, as well as its photocatalytic characteristics, which have also been examined on a colored solution from Fe (II)-(luminol-Tyrosine) Complex.

2. Experimental

A. Materials

The powdered ore of zirconium dioxide was obtained from Riedel-De-Haen AG, Seelze, Hanover, Germany. Using cobalt nitrate hexahydrate (Co (NO$_3$)$_2$·6H$_2$O), chromium nitrate nonahydrate (Cr (NO$_3$)$_3$·9H$_2$O), and ammonia solution (25 percent) were supplied from Merck. Cetyltrimethylammonium bromide (CTAB) was supplied by Interchimiques SA. Ferrous chloride trihydrate FeCl$_2$·2H$_2$O, absolute ethanol (C$_2$H$_5$OH), iron (III) sulfate hydrate (Fe$_2$(SO$_4$)$_3$·H$_2$O), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were supplied from BDH. The organic chemistry lab teams at the University of Babylon, college of science, department of chemistry, provided the Fe (II)-(luminol-Tyrosine) complex.

B. Synthesis of Spinel CoCr$_2$O$_4$ nanocrystals

Spinel CoCr$_2$O$_4$ nanocrystals were synthesized via the co-precipitation method. At the outset, cobalt nitrate (0.5 M) and chromium nitrate (1M) was prepared and transferred to an ultrasonic bath at 75 °C for 1 hour. In the second step, the chromium nitrate solution was put in a beaker with size 500 mL, and then cobalt nitrate solution was slowly added to chromium nitrate solution using an ultrasonic bath at 75 °C, and thrown for 1 hour. In the third step, the generated mixture was stirred and heated at the same temperature for a further two hours using a magnetic stirrer. Following that, 1% CTAB is added to the mixture as a capping agent to prevent metal hydroxide formed. 25% aqueous ammonia solution was dropwise added to the last solution until a pH makes it 9.

The produced deep green precipitate was filtered and washed with distilled water many times until the filtrate reached to pH of around 7 to ensure all contaminants are removed, and then washed with ethanol to remove the water humidity. The deep green precipitate was dried overnight in a desiccator, then calcinated for 4 hours at 600 °C. Equations 1 and 2 were suggested the chemical reaction of spinel CoCr$_2$O$_4$ formed.

Co(NO$_3$)$_2$·6H$_2$O + 2Cr(NO$_3$)$_3$·9H$_2$O + 8NH$_4$OH → Co(OH)$_2$·Cr(OH)$_6$ + 8NH$_4$NO$_3$ + 15H$_2$O ... (1)

Co(OH)$_2$·Cr(OH)$_6$ → CoO·Cr$_2$O$_3$ + 4H$_2$O ... (2)

2.2 Synthesis of spinel CoCr$_2$O$_4$/ZrO$_2$ nanocomposite

The preceding procedures were carried out with the used ultrasonic technique to like two photocatalysts as a nanocomposite[2,3]. The 1:2 and 1:3 ratios from spinel CoCr$_2$O$_4$/ZrO$_2$ were created as nanocomposites employing an ultrasonic wave at 75 °C for 1 h. As a result, it is acceptable to provide sufficient energy to combine ZrO$_2$ and spinel CoCr$_2$O$_4$ into the crystal lattice. The spinel CoCr$_2$O$_4$ solution was added step by step to incorporate with ZrO$_2$ solution in two ratios 1:2 and 1:3 via ultrasonic bath (60 kHz) for 2 hours at 75 °C. The generated mixture was stirred with heated at the same temperature for a further two hours using a magnetic stirrer, and then dried at a temperature of 75 °C to produce a deep green suspension from the spinel CoCr$_2$O$_4$/ZrO$_2$ nanocomposite that filtered and stored overnight in a desiccator using silica gel. The chemical equation for spinel CoCr$_2$O$_4$/ZrO$_2$ nanoparticles synthesis in different ratios was suggested using equation 3.

CoCr$_2$O$_4$ + ZrO$_2$ → CoCr$_2$O$_4$·ZrO$_2$ ... (3)

2.3 Application of the Spinel CoCr$_2$O$_4$ and spinel CoCr$_2$O$_4$/ZrO$_2$ nanocomposites are used to decolorize Fe (II)-(luminol-Tyrosine) dye solution.

In figure 1, the photoreaction was carried out using a handmade photoreactor. This photoreactor includes 400 watts of UV-lamp power. The reactor's body is constructed from a wooden box to prevent hazardous light, which contains a magnetic stirrer, a Pyrex glass beaker (500 mL), a Teflon bar, and two various fans[20-22].

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At a temperature of 20 °C, exact 0.01g of spinel CoCr$_2$O$_4$ or ZrO$_2$ or spinel CoCr$_2$O$_4$/ZrO$_2$ nanocomposites were added to 100 ppm from Fe (II) - (luminol-Tyrosine) complex solution as a chocolate colored solution with pH 7.3 that dissolved in DMSO. Without irradiation, the suspension solution was magnetically agitated for 30 minutes to allow for the establishment of an equilibrium adsorption condition[23-27]. Following the adsorption stage, the suspension was exposed to UV light, and about 3 mL of aliquots were collected at 10-minute intervals until 40 minutes. The collected suspensions were centrifuged twice at 4000 rpm for 30 minutes, and the absorbance of the resulting filters was measured at 475 nm using a UV-Vis spectrophotometer (AA-1800, Shimadzu). Equations 4 and 5 were used to get the rate constant of this photoreaction and the efficiency of decolorization:[28-34.]

$$\ln \left( \frac{c_t}{c_i} \right) = k_{appt}$$  

$$PDE \% = \left( \frac{c_o - c_t}{c_o} \right) \times 100$$  

3. Results and Discussion

A. Structural Properties

According to figure 2, XRD analysis was used to determine the structure of all photocatalyst samples utilizing two angles ranging from 20° to 80° on a Lab X XRD 6000-Shimadzu. In Figure 2, XRD analysis was utilized to detect the structure and phase of spinel CoCr$_2$O$_4$ powder and a produced spinel CoCr$_2$O$_4$/ZrO$_2$ nanocomposite. The CoCr$_2$O$_4$'s key diffraction peaks are located at 30.3779°, 35.8022°, 43.3839°, 57.5052°, and 63.1014° with Miller indexes (220), (311), (400), (511), and (440) planes, respectively (ICPDS Card No. 00-022-1084), and are in strong agreement with findings from references [35,36]. On the other hand, the ZrO$_2$ peaks exist at diffraction angles (111), (200), (220), and (311) with four locations of 2θ that equal to 30.2973°, 35.0778°, 50.4580°, and 59.9693°, respectively (ICPDS card No.00-049-1642) [36,37].

The XRD analysis for the prepared composites confirms this findings match with the standard diffraction data for CoCr$_2$O$_4$ and ZrO$_2$[2,38]. The essential peaks of m-ZrO$_2$ shift toward high diffraction angle (2θ) after incorporating the crystal lattice, which indicates the formation of a metallic connection between Zr and Co in the spinal structure because both have a coordination number of six [38]. This case is an attitude to Co$^{3+}$ and Cr$^{3+}$ in spinel have less ionic radii compared with Zr$^{4+}$ and equal to 0.709 Å, 0.615 Å, and 0.747 Å respectively [2,39]. On the other hand, the mean crystal sizes (L) for all samples were found using Scherer's equation [40-45]. Where k, denotes the shape constant, λ is Cu's wavelength using as a source of x-ray, 2θ is a Bragg diffraction angle, and (FWHM) is meaning a full width at half maximum intensity.

$$L = \frac{k \lambda}{\beta \cos \theta}$$  

The mean crystalline diameters of the spinel CoCr$_2$O$_4$, ZrO$_2$, and the 1:2, and 1:3 ratios spinel CoCr$_2$O$_4$/ZrO$_2$ composites were found equal to 15.5823 nm, 8.1785 nm, 9.6355 nm, and 9.0929 nm respectively. The addition of ZrO$_2$ in varied ratios to spinel CoCr$_2$O$_4$ leads to reduce the mean crystal size.
by elevating the ratio of ZrO$_2$ that will enhance the surface and optical characteristics.

B. Morphology of studied photocatalyst surfaces

1. SEM analysis was used to determine the morphology of the sample's surface using (FESEM FEI Nova Nano SEM 450). The SEM images of spinel CoCr$_2$O$_4$, ZrO$_2$, and their nanocomposites surfaces in Figure 3 demonstrate that the shape of the synthesized spinel CoCr$_2$O$_4$ is nanocrystals, which is consistent with the XRD and literature results [46]. The spinel CoCr$_2$O$_4$-ZrO$_2$ composites and ZrO$_2$ appear quasi-spherical shapes, that due to the high proportion of ZrO$_2$ in comparison to spinel CoCr$_2$O$_4$, which is used to increase the lightness of spinel CoCr$_2$O$_4$ during prepared composites, this vital step to improve their optical properties when used as a photocatalyst. ZrO$_2$ is a commercially available substance having a micron-scale structure because it is having a high ability to agglomerate with fine powder.

EDX analysis was used to validate the sample's components. As seen in Figure 4, the spinel CoCr$_2$O$_4$ contains Co, Cr, and O, ZrO$_2$ contain Zr and O, and its composites spinel CoCr$_2$O$_4$-ZrO$_2$ also contain Co, Zr, Cr, and O, without any impurities, this is a good agreement with reported in references [19, 47].

C. Optical property of studied photocatalyst

The optical energy bandgaps (E$_g$ in eV) were determined for all photocatalyst samples using the Tauc equation [20,48], as seen in equations 7 and 8.

$$\alpha h\nu = k(h\nu - E_g)^m$$  \hspace{1cm} ... (7)

$$\alpha = \frac{(2.303 \Delta)}{t}$$  \hspace{1cm} ... (8)

Where, absorption coefficient(\(\alpha\)), Plank's constant(\(h\)), light, frequency(\(\nu\)), optical constant(k), thickness(\(t\)), absorbance(A), and constant value (m) is maybe equal to 1/2 or 2 for direct (allowed) transitions and indirect (forbidden) transitions, respectively.

According to the plotted Tauc equations in Figures 5, 6, 7, and 8, the bandgap of spinel CoCr$_2$O$_4$ elevates with elevated the dose of ZrO$_2$ in spinel CoCr$_2$O$_4$/ZrO$_2$ (1:2), spinel CoCr$_2$O$_4$/ZrO$_2$ (1:3), due to ZrO$_2$ has a maximum bandgap (5 eV) with the direct transition. The bandgap of spinel CoCr$_2$O$_4$ and it's composite 1:2 and 1:3 found to be direct transition also with magnitudes equal to 3.2 eV, 4.7 eV, 4.8 eV, respectively.

D. Photo-decolorization of Fe(II)-(luminol-Tyrosine) dye

After determining the effectiveness of the obtained spinel CoCr$_2$O$_4$ nanocrystals and their nanocomposite as a spinel CoCr$_2$O$_4$-ZrO$_2$, they were applied in decolorization of Fe (II)-(luminol-Tyrosine) complex as a chocolate-colored solution.
that disappearance its color after irradiation for 1 h. After used composite, the apparent rate constant has elevated, and the photo-decolorization efficiency increases also from 17.57% using spinel to 30.67% and 41.97% using 1:2 and 1:3 composite ratios, respectively.

This attitude increases the lightness and acidity of spinel CoCr$_2$O$_4$ nanocrystals' surface through the manufacture of their composites that leads to an increase in the adsorption of hydroxyl ions [2,5]. Hence, the hydroxyl radicals will generate when the solution is exposed to UV or visible light [49-51]. Additionally, this modification surface increase the spacing of changes on the photocatalyst and the electron-hole recombination time will reduce [3,48].

**Figure 5:** Tauc plot for ZrO$_2$ as a direct bandgap

**Figure 6:** Tauc plot for spinel CoCr$_2$O$_4$ as a direct bandgap

**Figure 7:** Tauc plot for spinel CoCr$_2$O$_4$/ZrO$_2$ (1:2) nanocomposites as a direct bandgap

**Figure 8:** Tauc plot for spinel CoCr$_2$O$_4$/ZrO$_2$ (1:3) nanocomposites as a direct bandgap

**Figure 9:** The relation between the apparent rate constant for Fe(II)-(luminol-Tyrosine) complex decolorization in studied photocatalyst solution

**Figure 10:** The relation between PDE% for Fe(II)-(luminol-Tyrosine) complex decolorization in studied photocatalyst solution

4. Conclusion

Spinel CoCr$_2$O$_4$ nanocrystals created using a one-step co-precipitation method. The 1:2 and 1:3 ratios of spinelCoCr$_2$O$_4$ /ZrO$_2$ were successfully synthesized as nanocomposites that were accomplished using ultrasonic waves as an environmentally friendly approach. The produced photocatalysts were confirmed using XRD, SEM, and EDX measurements. Additionally, there is an optical bandgap. The XRD data suggest the production of spinel CoCr$_2$O$_4$ as a nanocrystalline orthorhombic phase, which agrees with miller's XRD study. SEM images and EDX spectra acquired show that the synthesis spinel CoCr$_2$O$_4$ is nanocrystals. Spinel CoCr$_2$O$_4$'s optical band gap was increased after integrating with ZrO$_2$ to form nano-composites. Spinel CoCr$_2$O$_4$'s photoreaction activity rose as well after the modification to produce the nanocomposites.
5. Conflicts of interest

“There are no conflicts to declare”.

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8. References


