Structural and morphological properties of Co₃O₄ nanostructures: Investigation of low temperature oxidation for photocatalytic application for waste water treatment

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ABSTRACT

The shape and incomparable size of synthesized Co₃O₄ nanostructures demonstrated using high resolution FESEM and HRTEM. The synthesized nanomaterials were considered by XRD and FTIR spectroscopy. Co₃O₄ nanostructures were investigated for different applications, such as, photocatalytic degradation of hazardous waste water from dyeing industry. Remarkably, the toxicity of Co₃O₄ have been described earlier, the toxicity is reduced by modified cost effective material through biosynthesis. Possible reaction mechanism pathways during photocatalyst into the dye solution over Co₃O₄ nanostructures have been proposed. In this view, the result shows, economic and green synthesis of Co₃O₄ nanostructures have a high applicability for the removal of waste water treatment application widely. This could be attribute to a novel Co₃O₄ nanostructures that favorably significant in the present environment for the removal of hazardous chemicals.

1. Introduction

Textile industries have grown up to meet the need of growing population and synthetic dyes give color to the fashion technology. Similarly, the effect of these dying factories is of great concern and effluent treatment requires immediate attention as it affects river water and water storages [1]. Many methods have been employed such as activate carbon adsorption, membrane filtration, biological treatment and so on. The above methods provide less effect in removing the dye effluent from the textile industries which lead researchers to search the new material for effective removal of the dyes [2]. Advanced heterogeneous photo-catalytic oxidation process such as Fenton method has proven quite successful for the effluent treatment [3]. Heterogeneous photo-catalytic dye degradation method received more interest as it is eco-friendly and provides high efficiency in effluent treatment [4].

Recently, synthesis of metal oxide nanoparticles using plant parts, marine algae, fruits and microorganisms as simple and possible alternative technique is highly preferential instead of using poisonous chemicals becomes the environmental hazard [5]. Well-defined Co₃O₄ Nps with a variety of morphologies have been successfully synthesized by several methods. Angel et al., However, it seems that either complex process controls or long synthesis time might be required for this greener method [6]. However, Synthesis of A. linearis leaf extract using eco-friendly routes received much attention by the researchers because they are clean, non-toxic, eco-friendly, free from unwanted byproducts, non-hazardous, require ambient reaction temperature, etc. [7]. Fuku et al., have synthesized using plant extracts, microorganisms and enzymes adopting green protocol for the physical and chemical routes while presenting a potential electrode for energy applications [8]. Raja et al., have suggested that the obtained Tabernaemontana divaricata as bioactive compound have proposed the interactions of steroids, terpenoids, flavonoids, phenyl propanoids, phenolic acids and enzymes present in the Tabernaemontana divaricata leaf extract [9]. Fuku et al., have mentioned clearly the synthesize of punica granatum peel extract approaches for the mixture of metal oxide nanoparticles, in aqueous bio-reductive polyphenols from punica granatum peel extract and the
2.1 Synthesis of Co₃O₄ nanostructures

In a typical procedure, an aqueous solutions of cobalt nitrate [Co(NO₃)₂]₉ A.linearis leaf extract were used to synthesize the Co₃O₄ nanostructures by hydrothermal method. A.linearis plant leaf was prepared by taking 50 g of thoroughly washed and finely cut leaves in 100 ml sterile distilled water in a beaker. The aqueous A.linearis plant leaf were deposited onto a freshly cleaved mica substrate. The sample aliquot was left for 1 min and then washed with deionized water and left to dry for 15 min the mixture was boiled for 1 h and filtered using Whatman filter paper no 1. During this process, 2.3 g of [Co(NO₃)₂] was dissolved in 50 mL of distilled water and magnetically stirred for 60 min with constant stirring then allowed to achieve a homogeneous solution for another 30 min. As prepared homogeneous suspension placed in a hot plate (Barnstead Thermolyne, SP46925) and uniformly heated up to 300 °C for 15 min in the hydrothermal method shown in the illustrate plate (Barnstead Thermolyne, SP46925) and uniformly heated up to constant stirring then allowed to achieve a homogeneous solution for in 50 mL of distilled water and magnetically stirred for 60 min with basic of magnetic moment and magnetic crystal structure. Numerous degradation of organic pollutants [10]. In this attention, A.linearis leaf extract not only acts as a fuel, but also as capping agents and renders a coordination action capturing the metal ion in the amylose helix in well-defined sites. Currently, efforts were focused on the synthesis of size and shape controlled Co₃O₄ Nps by diverse methods. Though, the production of eco-friendly, low cost Co₃O₄ Nps in large scale by the existing routes remain difficult. However, cobalt oxide utilized in various field for the invention of wide frameworks in view of their mixed electronic valence state of cobalt, stoichiometric, non-stoichiometric oxides and the presence of oxygen vacancies. Cobalt oxide is a suitable transition metal oxide, owing to its multi nature than the other 3d metal oxides [11].

Due to its properties, cobalt has capability to offer in different spin states in the oxide forms: low energy, high energy, as well as intermediate spin. These cedible spin states create the physics of the cobalt oxides engaging from a fundamental view point in spintronic applications so that the cobalt ion in cobalt oxides is of the identical range of magnitude as the intra-atomic exchange energy and the 3d-orbital band width according to the crystal field splitting of the 3d energy level of complexity in spins state [12]. Generally, Co₃O₄ is an important candidate for anti-ferromagnetic p-type semiconductor with superior properties such as electrochemical properties [13], gas-sensing [14] and catalytic properties [15, 16] and has been study the applications in various fields like heterogeneous catalysts, solid-state sensors, lithium ion batteries as well as electrochemical operational devices. Furthermore, due to their magnetic character cobalt oxide has been used as equipment for recording and medical diagnostics as a contrast agent for MRI (magnetic resonance imaging). Varieties of hybrid photocatalysts can produce the fast recombination of photoexcited electron-hole pairs through different mechanism.

In our understanding, semiconductor metal oxide electrons can be transferred easily than respective metal NPs via Schottky contact due to Fermi energy of metals usually being lower than that of the semiconductor [17]. Despite, ferromagnetic nature of Co₃O₄ conflict on the basic of magnetic moment and magnetic crystal structure. Numerous effects have been made to fabricate the nanostructures of Co₃O₄ to improve its applications in the field of biology [18]. Apart from the effluent treatment, the spinel shows significant biomedical application which is studied in recent years [19]. To provide greener environment, researchers engaged with plants part to synthesis different materials which produce less damage to the environment [20]. At present there is few literatures regarding various applications of Co₃O₄ nanoparticles. These exposures increased an interest in us to employ Co₃O₄ nanostructures in different field [21].

2. Experimental section

2.1 Synthesis of Co₃O₄ nanostructures

In a typical procedure, an aqueous solutions of cobalt nitrate [Co(NO₃)₂]₉ A.linearis leaf extract were used to synthesize the Co₃O₄ nanostructures by hydrothermal method. A.linearis plant leaf was prepared by taking 50 gm of thoroughly washed and finely cut leaves in 100 ml sterile distilled water in a beaker. The aqueous A.linearis plant leaf were deposited onto a freshly cleaved mica substrate. The sample aliquot was left for 1 min and then washed with deionized water and left to dry for 15 min the mixture was boiled for 1 h and filtered using Whatman filter paper no 1. During this process, 2.3 g of [Co(NO₃)₂] was dissolved in 50 mL of distilled water and magnetically stirred for 60 min with constant stirring then allowed to achieve a homogeneous solution for another 30 min. As prepared homogeneous suspension placed in a hot plate (Barnstead Thermolyne, SP46925) and uniformly heated up to 300 °C for 15 min in the hydrothermal method shown in the illustrate Fig. 1. The resulting black precipitate was centrifuged at 8500 rpm for 15 min and washed several times with deionized water. The dried obtained black powder was further annealing in air at 500 °C for 2 h to obtain Co₃O₄ nanostructures.

2.2. Characterization studies

The crystallinity and phase purity of the synthesized photocatalyst was performed by XRD (PAN analytical Pro-Diffractometer) using CuKα radiation (λ = 0.154 nm). The UV-vis DRS was recorded using UV-visible spectrophotometer (Hitachi, Japan), using BaSO₄ as a reflectance sample to estimate the energy band of synthesized sample. To monitor the shape and morphology of the nanoparticles were obtained with field emission scanning electron microscopy (FESEM) (LEO microscope) and transmission electron microscopy (TEM) (Philips Model Tecnai F30). The sample was coated with gold by a gold sputtering device for better visibility of the surface morphology. FTIR spectra were used to study the presence of the functional groups of the synthesized Co₃O₄ nanostructures. Dried Co₃O₄ nanostructures samples ground with KBr to produce pellet, which was examined in a wavelength range of 400–4000 cm⁻¹ by the Perkin Elmer infrared spectrophotometer.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity of synthesized Co₃O₄ nanostructures was determined by degradation of hazardous dye waste water under multilamp photocatalytic reactor. In a typical experiment, the prepared photocatalyst (0.50 g) were dispersed in dye waste water (100 mL), which was kept in the dark 30 min to achieve adsorption/desorption equilibrium between the waste water and the photocatalyst. After that, the solution gently stirred under ambient condition was irradiated with visible light. The light was turned on and 3 mL of the reaction mixture was set out at suitable time intervals and centrifuged to confiscate the solid. Then, the strength of the waste water was determined by UV–Visible spectra on the basis of the absorption intensity. The degradation of dye solution without catalyst also carried and the dye degradation percentage of photocatalyst at various time intervals is plotted against time to compare photodegradation efficiency of photocatalyst. All the photocatalytic degradation experiment was performed in neutral medium (pH ~7).

3. Results and discussion

3.1. Crystalline size and phase identification

The crystalline arrangement of synthesized Co₃O₄ nanostructures were studied by recording powder XRD pattern was shown in Fig. 2. The observed XRD data were entirely indexed via PAN analytical Pro-Diffractometer. The sample exhibit a clear monoclinic structure with characteristic 2θ at 19.7°, 25.6°, 28.5°, 36.6°, 38.6°, 42.5°, 48.2°, 50.4°, 53.2°, 54.9°, 56.5°, 64.5°, 69.8° and their resultant (hkl) planes were predictable such as (111), (211), (200), (220), (311), (222), (500), (422), (511), (411) respectively. It can clearly be seen that all diffraction peaks can be indexed to [JCPDS card number 15–0774]. From the XRD results, we observed that the synthesized cobalt oxide diffraction peaks with other unknown impurities also have notice from the figure and their crystallite values are seemed to be less. The average crystallite size of synthesized samples was determined by using Scherrer formula d = 0.89λ/βCosθ; where ‘d’ is the average crystallite size, ‘λ’ is the X-ray wavelength (0.154 nm), ‘β’ is the Bragg’s angle and ‘β’ is FWHM [9]. The average crystallite size of Co₃O₄ nanostructures was determined to be 21.8 nm. However, the size is explained by the influence of preparation method, calcined at high temperature of the material results in the dipole change of the polar molecules with the steady temperature, this fact leads to the molecular distribution and friction, thereby; resultant product has smaller particle size.
3.2. FT-IR analysis

The chemical bonding information; *A. linearis* plant leaf of Co$_3$O$_4$ nanoparticles was evaluated using Fourier transform Infrared Spectroscopy (FTIR) at room temperature and the characteristic IR bands are plotted in the range of $500 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$ as showed in Fig. 3. FTIR is a tool for ascertaining the various bands to characterize the functional groups and bonds present in the as synthesized Co$_3$O$_4$ nanoparticles were performed to detect the surface modification of the materials. Further this analysis provides significant information about the presence of intercalated anions between the Co$_3$O$_4$ NPs which exhibits the synthesized *A. linearis* plant leaf of Co$_3$O$_4$ nanostructures. In the IR spectrums of Co$_3$O$_4$ nanoparticles treated with plant extract of coupling agent with the red frequency shift of the LO mode of crystalline from $698 \text{ cm}^{-1}$ to $913 \text{ cm}^{-1}$ is a consequence of the presence of cobalt nanograins. In this analysis, according to the intensity of the band which is assigned to LO mode of crystalline cobalt phase shows an increase with the increase in *A. linearis* plant leaf content in the nanoregime [20]. While the absorption peaks at $1613 \text{ cm}^{-1}$, $1391 \text{ cm}^{-1}$ & $1196 \text{ cm}^{-1}$ in the spectrum were carried out in the range of $500 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$ and the corresponding results are shown in Fig. 3, the weak absorption bands around $3408 \text{ cm}^{-1}$, that are corresponds to the stretching vibration of $3020 \text{ cm}^{-1}$ O–H and to the deformation vibration of water molecules respectively. The absorption band at $1613 \text{ cm}^{-1}$ is according to bending vibration of hydroxyl group [18]. The synthesized Co$_3$O$_4$ nanostructure shows the strong absorption band at $698 \text{ cm}^{-1}$ indicates the Co–O stretching vibrations. As the broad band absorbed at $1196 \text{ cm}^{-1}$ and $913 \text{ cm}^{-1}$ gives the evidence of crystalline phase of the Co$_3$O$_4$ nanostructures [10]. Overall, the vibrational stretching frequencies of M-O functional groups which also in addition to this say that there are no other peaks which were attributed at any different frequencies [19]. This additional information supportively says about that our as prepared sample doesn’t encounter any impurities within it. The strong absorption at $698 \text{ cm}^{-1}$ attributes to $\nu$(Co-O) mode and peaks at $1613 \text{ cm}^{-1}$ and $3408 \text{ cm}^{-1}$ was assigned to water present in the Co$_3$O$_4$ nanostructures [11].
3.3. **FESEM measurement**

Morphological analysis and particle size of prepared Co₃O₄ nanostuctures were well investigated based on the studies of FESEM analysis shown in Fig. 4(a–f). The average diameter of the as prepared sample was found to be less in Fig. 4(a–c). Thus, the SEM image at high magnification implements the high crystalline nature of the nanoparticles [19]. The images clearly display that the composite of synthesized plant extract of Co₃O₄ nanostructures have spherical like structure for Co₃O₄ at 20 nm as shown in Fig. 4(d,e). The HRTEM results confirm the XRD and SEM analysis in the terms of both structure and crystalline shape as in Fig. 5(d). In fact, the crystalline nature discussed above at high magnification level relates to the data obtained with XRD. Fig. 4(f) illustrates the evident further confirms the strong histogram of particle and the average size of the standard distribution formation of Co₃O₄ nanocomposites.

3.4. **Morphology identification**

The morphology and crystalline nature of the Co₃O₄ nanostructures was observed in TEM descriptions and selected area electron diffraction (SAED) patterns are proved in the Fig. 5(a–h), which shows that the result consists of cluster-like nanocrystal were grown-up at narrow size distribution. The shape and particles size distribution of sample estimated from those images at different magnifications [11, 12]. High level agglomeration is appeared in the different magnification due to the association of cobalt oxide nanostructure obtained from concentrated sample used in the analysis. The TEM representation of the nanostructure describes the irregular morphology of the particles. In the porous nanomaterials randomly, distributed particle sizes are in the range from 20 nm - 40 nm with the irregular shape and highly accumulated crystalline nature [13], which is consist with XRD data. The selected area diffraction (SAED) pattern of Co₃O₄ sample shows the high crystallinity nature. The SAED pattern shown the crystalline structure of prepared sample and that the nanoparticles are not consisted of single crystals, instead of aggregates of several crystals as shown in Fig. 5(h). In addition, Diffraction patterns were identically, diffused which suggesting the surface is comparatively polycrystalline nature.

3.5. **UV absorption studies**

In Fig. 6 shown the absorption spectrum of Co₃O₄ nanostructures contains various bands in the UV and visible regions. The UV absorption band centered at 450 nm–650 nm is assigned to the quantum confinement effect [17]. The peaks obtained around 350 nm due to the structural defects and estimated bandgap determined using Tauc’s relation for direct band gap semiconductor as; $\alpha h v = B (h v - E_g)^{1/2}$; where $\alpha$, $h$ and $v$ are the absorption coefficient, Planck’s constant, photo frequency respectively. $B$ is matter reliant adsorption coefficient and $E_g$ is bandgap of the matter to determined, which is 2.54 eV. The bandgap energy indicates that the photocatalyst will be dynamic in irradiation of visible light [18].

3.6. **Magnetic studies**

The room temperature filed dependencies of the magnetic curve (hysteresis loops) for the Co₃O₄ NPs under applied field of 10 kOe are shown in Fig. 7. Co₃O₄ nanoparticles shown obvious magnetic hysteresis loops and magnetic parameters like saturation magnetization ($M_s$), coercively ($H_c$) and permanent magnetization ($M_r$) of the samples were obtained. Hysteresis loop exhibit soft ferromagnetic behavior. From the VSM measurement saturation magnetization ($M_s$) and the remnant magnetization ($M_r$) of the sample to be 32.313 emu/g and 2.54 emu/g respectively. The coercivity field was 15.53 Oe, it is evidently implictating that had ferromagnetic behavior, with slender hysteresis curve. It is well known that the magnetic properties of synthesized sample strongly dependent on shape, oxygen vacancies [22]. The precursor's stoichiometric ratio and preparation method also affects the shape of the loops of the nanoparticles. The S-shaped hysteresis curve
Fig. 5. (a-h). HRTEM image of synthesized plant extract of Co$_3$O$_4$ nanostructures.

Fig. 6. UV absorption spectra of synthesized plant extract of Co$_3$O$_4$ nanostructures.

Fig. 7. Magnetic property of synthesized plant extract of Co$_3$O$_4$ nanostructures.
basically indicates the distinctive ferromagnetic behaviour [23].

3.7. Organic dye degradation

The photocatalytic activity of Co₃O₄ nanostructures is evaluated by degradation of hazardous textile dye waste (congo red) irradiating visible light shown in Fig. 8. In Table 1, shows the comparison of Co₃O₄ nanostructures and their photocatalytic activity. The degradation of contaminated waste water (CWW) from the industry with Co₃O₄ nanostructures under the wavelength $\lambda =$ 360 nm is proved in the Fig. 8. The degradation 100 ml of 20 ppm congo red was examined with 30 mg of prepared nanostructure on enlightenment of visible light at neutral medium. The broad band at 498 nm reduced constantly for the decomposition of congo red dye. The degradation rate was estimated from the initial and final concentration of contaminated waste water from industries after photodegradation, from the experiment the C/C₀ is calculated and plotted versus time is shown in Fig. 9. It indicates that after exposing the mixed solution of contaminated waste water and cobalt oxide photocatalyst under visible light irradiation for 240 min, degrade the dye upto 96% (Fig. 10). Without photocatalyst of CWW degradation is almost negligible. Moreover, CWW was degraded in the presence of prepared Co₃O₄ nanomaterials due to hydroxyl radical. Many organic compounds oxidize during photocatalytic reaction occur by the formation of main reactive species of hydroxyl radical reported by Magdalane et al. [24] observed the fast generation of hydroxyl radical was main reason for the efficient degradation CWW by metal oxide nanoparticles. Co₃O₄ nanomaterials have high dense and large pore structure, thus providing a large surface area for dye adsorption [25]. The photocatalytic efficiency is ascribed to the surface area and improved crystallinity in the present material [26].

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<th>Catalyst</th>
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<td>Co₃O₄ nanopowders</td>
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<td>Rhodamine-B</td>
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<td>Present work</td>
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Fig. 8. Decomposition of congo red dye solution (20 ppm) with catalyst (30 mg/100 ml) at neutral medium on illumination of visible light at assorted time intervals.

Fig. 9. The plot of C/C₀ against time for the photocatalyst.

Fig. 10. Efficiency of decomposition of congo red dye by using the catalyst.

Fig. 11. Effect of photocatalyst on degradation for congo red dye solution (20 ppm) at neutral medium on irradiation of visible light at assorted time intervals.
3.7.1. Effect of photocatalyst loading

Photocatalytic studies were carried out by keeping concentration of dye constant at 20 ppm, via changing the amounts of catalyst. Effect of photocatalyst on degradation for congo red dye solution at neutral medium on irradiation visible light at assorted time intervals shown in the Fig. 11. It was observed that the percentage of degradation of dye increases up to 30 mg/100 ml of the dye waste water solution, further it shows an unreasonable decrease [27]. The degradation efficiency of congo red dye solution found to be increases with increase in the quantity of catalyst [28]. The active sites on the surface of catalyst increases, which helps for the higher degradation of dye waste water in the reaction. Beyond 30 mg/100 ml in the reaction, the degradation efficiency of congo red dye solution found to be decreases, may be due to reduction in light penetration and light scattering through the solution [29].

3.7.2. Effect of initial dye concentration

Experiment was carried out by changing the initial concentration of congo red dye waste water from 10 to 30 ppm, keeping the catalyst (30 mg/100 ml) constant shown in Fig. 12. The percentage of decomposition of dye waste water was originated to be reducing with raise in the initial dye concentration. The active site on the catalyst accessible for the reaction is vital for the degradation to carry-out [30]. Active site on the surface of the catalyst becomes same when the dye concentration is increased with enhance in the dye molecules. The intensity of the dye was more and the path of the photons inflowing the solution reduces [31]. Due to the higher concentration of dye molecules, very few excited photons reach the catalyst surface and generates few hydroxyl and superoxide radicals [32]. The optimal concentration of dye was found to be 20 ppm.

3.7.3. Reusability of cobalt oxide nanostructure

To investigate the stability and competence of the catalyst in the photodecomposition process, the reusability of a photocatalyst is a very essential factor. The catalyst was separated from the resultant suspension washed with ethanol and dried at 120 °C, the retrieved catalyst was re-dispersed again in dye waste water for next cycle [33] it was used up to 4 cycles as shown in Fig. 13. After all the cycles the retrieved catalyst showed almost same photo decomposition of dye solution which is shown therefore, the catalyst can be without problems gained from the reaction mixture, which could significantly assist the practical organization of an industrial pollutant clean-out [34].

3.7.4. Mechanism of decomposition of congo red via cobalt oxide nanostructure

The degradation of congo red dye may be due to the creation of excitons on the surface of cobalt oxide. These electrons and holes interact with oxygen molecule and water to generate reactive oxygen species (ROS) is capable for the effective degradation of waste water contains congo red dye [35]. As we all well known that the excitons are generated on the surface of the metal oxide nanoparticles on photoexcitation under visible light illumination is shown in Fig. 14. The mixed solution of (CWW) and photocatalyst is exposed under visible light, the separation of electron hole pair can be attributed by the $e^{-}$ from valence band is excited to the conduction band, when it has enough energy like photon ($h \nu > E_g$). Superoxide radicals ($O_2^{-}$) are generated by the reaction of electron in the conduction band and absorbed O$_2$ molecules on the surface of the cobalt oxide nanomaterials [36]. The more active hydroxyl radical (OH) are also created via the reaction between h$^+$ and OH$^-$ ions in solution. The hydroxyl radical, which are strong oxidizing agents can decompose the CWW from the industry. ROS generated in the reaction (OH, O$_2^{-}$ and h$^+$) can participate in the photo oxidation reaction. Influence of light illumination conditions, CWW solution was decomposed in to CO$_2$, H$_2$O and other small molecules due to the effective separation of photoexcited e$^+$/hole [37].

4. Conclusion

In this summary, Co$_3$O$_4$ nanostructures were successfully prepared by cost-effective and green synthesis by hydrothermal method. A ferromagnetic behavior is observed for the synthesized Co$_3$O$_4$ NPs, upon annealing, followed by oxygen vacancies. Subsequently, the application of the A. linearis plant leaf of Co$_3$O$_4$ NPs in catalytic degradation of TDW analysis was examined. Therefore, multifunctional Co$_3$O$_4$ NPs can be used for self-cleaning and waste water treatment applications.

Declaration of Competing Interest

This manuscript or a very similar manuscript has not been published, nor is under consideration by any other journal. All authors have seen and approved the final, submitted version of this manuscript. The authors declare no competing financial interest. There are no conflicts of interest to declare.

All authors declare that there is no conflict of interest.
Supplementary materials


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