Mesoporous Octahedron-Shaped Tricobalt Tetroxide Nanoparticles for Photocatalytic Degradation of Toxic Dyes

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ABSTRACT: The present article reports a facile approach to fabrication of mesoporous octahedron-shaped tricobalt tetroxide nanoparticles (Co3O4 NPs) with a very narrow size distribution for eco-friendly remediation of toxic dyes. Co3O4 NPs were fabricated by a sol–gel process using cobalt chloride hexahydrate (CoCl2·6H2O) and monosodium succinate (C4H5O4Na) as a chelating/structure-directing agent and sodium dodecyl sulfate as a surfactant. Moreover, the phase structure, elemental composition, and thermal and morphological facets of Co3O4 NPs were investigated using XRD, FT-IR, EDS, Raman, XPS, TGA, SEM, and TEM techniques. The face-centered cubic spinel crystalline structure of the Co3O4 NPs was confirmed by XRD and SEM, and TEM analysis revealed their octahedron morphology with a smooth surface. Moreover, the narrow pore size distribution and the mesoporous nature of the Co3O4 NPs were confirmed by Brunauer–Emmett–Teller measurements. The photocatalytic activity of Co3O4 NPs for degradation of methyl red (MR), Eriochrome Black-T (EBT), bromophenol blue (BPB), and malachite green (MG) was examined under visible light irradiation, and the kinetics of the dye degradation was pseudo-zero-order with the rate constant in the order of MR > EBT > MG > BPB.

INTRODUCTION

Today’s major concern is to get clean water owing to fast civilization and industrialization, which is an essential for the survival of living organisms. In recent years, the extensive use of carcinogenic organic dyes in the textile industry has increased gradually and increased amounts of pollutant effluents have been released into aquatic ecosystems.1–6 This causes depletion of the dissolved oxygen content, which has adverse effects on aquatic creatures and mankind.7–9 Toxic dyes such as methyl red (MR), Eriochrome Black-T (EBT), bromophenol blue (BPB), and malachite green (MG) are significantly used in textiles, paper making, and pharmaceuticals10–12 due to their relatively low cost even though they are known to have harmful effects on the reproductive system, genotoxicity, and carcinogenic properties.13–15 These dyes are difficult to eradicate by conventional techniques such as adsorption, coagulation, flocculation, biodegradation, and so forth.7,9,10,16 All these methods are expensive and require extra planning to remove the byproducts. Alternatively, photocatalytic degradation of toxic dyes into nontoxic compounds is the most desirable process to mitigate their environmental impact.17,18 Thus, it is indispensable to develop a possible permanent solution for the degradation of toxic dyes in wastewater streams.

Transition-metal oxide-catalyzed photocatalytic degradation has emerged to be a low-cost, environmentally friendly, and efficient method for dye-based effluent treatments compared to its abovementioned counterparts.19–23 Due to their mixed oxidation states, transition-metal oxides have gained remarkable consideration in cutting-edge days, and due to their unique physicochemical and electromagnetic properties, they show potential applications in diverse areas such as wastewater treatment, lightweight fillers, catalysis, supercapacitors, gas sensors, lithium-ion batteries, and chemical storage.24–27 Among the transition-metal oxides, spinel-tricobalt tetroxide...
Co₃O₄ occasionally symbolized as CoO·Co₂O₃ and analogous to FeO·Fe₂O₃ has emerged rapidly as one of the most popular spinel materials due to its unique properties, chemical stability, and facile synthesis method. Furthermore, Co₃O₄ belongs to three types of cobalt oxide families, and the other two oxides are rock salt (CoO) and hexagonal Co₂O₃. It is well known that Co₃O₄ is a p-type semiconductor, and in its spinel structure, Co²⁺ ions occupy the tetragonal 8(a) sites, Co³⁺ ions occupy the octahedral 16(d) sites, and O²⁻ ions are located at 32(e) sites arranged in a cubic close-packed structure.

Previously, diverse approaches have been adopted for the preparation of spinel-Co₃O₄ nanoparticles (NPs) such as chemical vapor deposition at 550 °C, thermal decomposition of cobalt precursors under oxidizing conditions around 210–815 °C, chemical spray pyrolysis at 350–400 °C, pulsed laser deposition (PLD), and electron beam deposition. However, these routes require severe conditions, relatively high temperatures, and some special instruments. Furthermore, the application of these conventional approaches for the synthesis of Co₃O₄ NPs is limited by their low productivity. Moreover, a number of research groups have reported the preparation of mesoporous Co₃O₄ NPs by electrospinning and calcination of mixed polymeric templates such as poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) for visible light photocatalytic applications.

We have recently developed facile routes for the synthesis of monodisperse CuO, spinel-CuAl₂O₄, and novel γ-Bi₂O₃ microspindles for antioxidant, electrochemical, and photocatalytic applications. In the present study, we have developed a simple protocol for large-scale fabrication of octahedron-shaped Co₃O₄ NPs by a sol–gel method using monosodium succinate (C₄H₅O₄Na) and sodium dodecyl sulfate (NaC₁₂H₂₅SO₄) at a low temperature (50 °C) followed by calcination at 500 °C for 3 h. The as-fabricated Co₃O₄ NPs in the presence and absence of SDS were characterized by an array of analytical techniques for their structural, compositional, and morphological characteristics.

There are a number of reports on the photodegradation of methylene blue, Rhodamine B, and Direct Red 80 using Co₃O₄. Therefore, we here focused on low-temperature fabrication of mesoporous spinel-Co₃O₄ NPs using a sol–gel method and their application for the photocatalytic degradation of toxic organic dyes [methyl red (MR), Erichrome Black-T (EBT), bromophenol blue (BPB), and malachite green (MG)].

Moreover, detection of the trapping species assay was carried out using potassium iodide (KI), potassium bromate (KB), sodium thiosulfate (ST), and benzoquinone (BQ) as scavengers, and a detailed structural fragmentation of MG after degradation was explored by the liquid chromatography–mass chromatography (LC–MS) technique. Finally, the scavenging activity of Co₃O₄ NPs was determined using different scavengers to confirm the free-radical formation.

**RESULTS AND DISCUSSION**

**Formation Mechanism.** An octahedron-shaped Co₃O₄ NPs was fabricated via a sol–gel method, and its formation mechanism is presented in Scheme 1. C₄H₅O₄Na was used as a chelating/structure-directing agent for the fabrication of Co₃O₄. In the initial stage, C₄H₅O₄Na reacts with Co²⁺ ions in solution, forming a cobalt–succinate complex (Figure S1b). After addition of NaC₁₂H₂₅SO₄ as the surfactant, it attaches to the surface of the cobalt–succinate complex, and its morphology turns spherical [Figure S2]. Due to the presence of free oxygenated coordination sites in C₄H₅O₄Na, a lone pair of oxygen electrons coordinates with Co²⁺, which is in agreement with the UV–visible spectra [Figure S1a,b].

The UV–visible spectrum shows the reduced peak intensity of free Co²⁺ ions after the addition of C₄H₅O₄Na, which signifies that interactions took place at the co-ordination site of
C₄H₅O₄Na. Furthermore, the peak intensity remains un-
changed after the addition of NaC₁₂H₂₅SO₄ (Figure S1c),
authenticating the idea that NaC₁₂H₂₅SO₄ does not have
strong interactions with Co²⁺. Thus, as per the proposed
mechanism, NaC₁₂H₂₅SO₄ assembles on the surface of the
C₄H₅O₄Na⁻Co²⁺ complex. The complex formation with
C₄H₅O₄Na at a certain temperature was responsible for the
growth of Co₃O₄ crystals with selective facets. In addition, it
was controlled by the addition of NaC₁₂H₂₅SO₄ that has
inherent physicochemical properties. It adopts differ-
ent morphologies such as micelles, vesicles, etc. through
concentration variation. During the growth of the
C₄H₅O₄Na⁻Co³⁺ complex into a crystal, NaC₁₂H₂₅SO₄ plays
a crucial role in the formation of exclusive octahedron-shaped
Co₃O₄. It deposits on the surface of octahedron Co₃O₄
through self-assembly via hydrophobic interactions among
the long hydrocarbon chains. Co₃O₄ has a tendency to form a
sphere (Figure S2), and NaC₁₂H₂₅SO₄ inhibits the alteration of
octahedral phases to other morphologies.

Crystal Structure. The phase and crystal structure of the
synthesized Co₃O₄ NPs were investigated by XRD, and the
XRD pattern of precalcined Co₃O₄ shows weak diffrac-
tion peaks [Figure 1a]. However, the diffraction pattern of calcined
Co₃O₄ NPs [Figure 1b] showed well-defined reflections at 31.30, 36.75, 44.94, 59.53, and 65.38°
corresponding to the (220), (311), (400), (511), and (440)
lattice planes compared to that of precalcined Co₃O₄. With
SDS, Co₃O₄ NPs [Figure 1c] show the presence of well-
defined peaks at 20.11, 31.08, 36.67, 38.57, 44.69, 55.76, 59.24,
and 65.25° corresponding to the (111), (220), (311), (222),
(400), (422), (511), and (440) lattice planes, indicating a more crystalline nature compared to that calcined without SDS and the precalcined Co₃O₄. The patterns were indexed to the face-centered cubic (FCC) spinel structure and well supported by JCPDS (74-2120). Additionally, no extra patterns were observed for the other phases of Co₃O₄, confirming the purity of the material. The lattice parameter of calcined Co₃O₄ was found to be 8.08 Å with the Fd-3m space group, and the average crystallite size of spinel-Co₃O₄ was estimated using Debye–Scherer’s equation, which was in the range of 23–29
nm. Moreover, the presence of only cobalt (Co) and oxygen (O) atoms in the EDS spectrum (Figure S3) confirmed the purity, which is well supported by the XRD study.

Thermal and Pore Size Analysis. The thermal stability of precalcined and calcined Co₃O₄ NPs was examined by TG
[Figure 2a,b]. The detailed thermal degradation pathway of
calcined Co₃O₄ NPs is depicted in Scheme 2. However, a
detailed discussion and the mechanism of precalcined Co₃O₄
NPs is presented in the Supplementary Information (Scheme S1). The thermograph of the calcined Co₃O₄ NPs showed a three-step thermal disintegration process. Initially, Co₃O₄ NPs showed that an insignifi-
cant weight loss (0.23%) took place between 48 and 120°C, corresponding to the removal of the
adsorbed water (Table S1). In the second step, no mass loss
was observed at 120°C, and this was retained up to 798°C
due to the chelate ring of the oxygen ions of succinate with the
Co²⁺ moiety. Furthermore, a fraction of mass loss (7%)
occurred between 798 and 902°C in the third step of thermal
degradation, attributed to the opening of the chelate ring (O₂),
and eventually reaches a constant mass above 900°C, due to
the partial conversion of Co₃O₄ to a stable CoO state, forming
(3Co₃O₄ → 6CoO·Co₃O₄ + O₂), i.e., the CoO·Co₃O₄
adduct. This is well supported by the XRD pattern (Figure S4, calcined at 900°C for 5 h), which displayed the mixed phases of CoO·Co₃O₄ (JCPDS no. 72-1474). The half-
decomposition temperature (HDT), temperature range, and degraded materials at each step are provided in Table S1. The corresponding reaction at 900 °C can be described as

$$3\text{Co}_3\text{O}_4 \rightarrow 6\text{CoO-\text{Co}_3\text{O}_4} + \text{O}_2$$

Our hypothesis sought for the structural changes during heat treatment based on the TG results; the precalcined material has a cobalt complex, i.e., \([\text{Co (II)} \cdot (\text{C}_4\text{H}_4\text{O}_4)^{2-} \cdot (\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\), while the calcined material has pure spinel-Co₃O₄. In conclusion, calcined Co₃O₄ has high thermal stability, and therefore, it was tested for the photocatalytic degradation of organic dyes. Therefore, the surface area, pore size distribution, and pore volume of the prepared material were investigated using the nitrogen (N₂) adsorption/desorption isotherm, and the adsorption isotherm [Figure 2c] is in agreement with the type IV isotherm with an H₃ hysteresis loop typical of an asymmetric, interconnected mesoporous structure. Moreover, the material exhibits a monodisperse pore size of ~7.1 nm and a surface area of 69 m²/g, which are generally favorable for adsorption and catalysis applications.

**FT-IR and Raman Spectroscopy.** The FT-IR spectrum of the Co₃O₄ NPs was recorded from 500 to 4000 cm⁻¹, and the results are shown in the supplementary information (Figure S5). As shown in Figure 3a, the broad IR band at 1097 cm⁻¹ is assigned to the symmetric stretching of the CO₃⁻ ion, and the two sharp peaks at 676 and 571 cm⁻¹ are ascribed to the (Co−O) linkage fingerprint stretching vibrational modes that consequently confirm the formation of Co₃O₄ NPs. In specific, the bands at 676 and 571 cm⁻¹ are characteristic of Co−O bonding vibrations, signifying the occurrence of Co⁵⁺ ions and Co⁵⁺ ions at the octahedral and tetrahedral sites, respectively, of the spinel-Co₃O₄ crystal lattice.

Moreover, Raman shifts were used to analyze spinel-Co₃O₄ along with the Fd3m space group symmetry equation as follows:

$$\Gamma = A_{1g}(R) + E_g(R) + F_{2g}(IN) + 3F_{2g}(R) + 2A_{2u}(IN) + 2E_u(IN) + 4E_u(IR) + 2F_{2u}(IN)$$

where R is the Raman active vibration, IR is the infrared-active vibration, and IN is the inactive mode. The Raman spectrum shown in Figure 3b shows the presence of five prominent peaks at 191.1, 471.8, 514.2, 609.2, and 679.5 cm⁻¹ corresponding to F₁₃g, E₁₃g, F₂₁g, F₁₁g, and A₁₁g, respectively. Co₃O₄ has a normal spinel structure containing Co²⁺(Co³⁺)₂O₄, which was constituted by CoO₆ (octahedra) and CoO₄ (tetrahedra). The A₁₁g mode contributes to the symmetric Co³⁺−O stretching vibration. However, the bands at 471.8 and 514.2 cm⁻¹ correspond to the E₆ and F₂₁g symmetry, and F₂₁g and A₁₁g are attributed to the vibration of the Co₃O₄ tetrahedra. The nonexistence of any extra peaks again confirms the high purity of the synthesized Co₃O₄ NP. Furthermore, all the peaks were shifted toward higher wavelengths compared to the reported peak position due to the size effects or the surface stress/strain.
morphology of uniformly distributed octahedron-shaped Co₃O₄ is obtained by calcination at 500 °C. Furthermore, the TEM images of Co₃O₄ NPs [Figure 4e,f] clearly show the octahedron nature of the single Co₃O₄ NP having a core shell size of 3.2 nm and confined by the face normal projection of the octahedron [Figure 4e], with average sizes of 50−75 nm. Moreover, the measured d-spacing of 0.243 nm is attributed to the (311) plane and 0.204 nm to the (400) plane of Co₃O₄ NPs [Figure 4g], which are consistent with the XRD data. The selected area electron diffraction (SAED) pattern of Co₃O₄ NPs [Figure 4h] reveals a ring-like pattern, indicating the polycrystalline nature of Co₃O₄ NPs.

**XPS Analysis and Bad Gap Energy.** The XPS survey and high-resolution C1s, Co2p, and O1s spectra of spinel-Co₃O₄ are depicted in Figure 5. Four notable peaks at 284.7 eV (C1s), 529.9 eV (O1s), 779.7 eV (Co2p), and 794.4 eV (Co2p) were observed in the XPS survey spectrum [Figure 5a]. The peak at 284.7 eV in the C1s HR spectrum shown in Figure 5b is assigned to the adventitious C−C hydrocarbon bond, which is used for the calibration of the binding energy scale. The prominent peak of the Co2p3/2 level is deconvoluted into two peaks at 779.78 and 794.49 eV [Figure 5c], attributed to the Co³⁺2p3/2 (in octahedron site species) and Co²⁺ 2p3/2 (in tetrahedral sites species) conformation, respectively. The exact oxidation state of Co can be induced from the spin−orbit splitting of the Co2p (2p 1/2) peak at 794.35−794.45 and 795.35−795.7 eV, assigned to Co³⁺2p1/2 and Co²⁺2p1/2 configurations, respectively. Moreover, the shake-up peaks of the Co₃O₄ phase are also observed at 789 and 803.8 eV. The energy difference between Co2p3/2 and the main peak of Co2p1/2 is about 14.76 eV, which is characteristic of the Co₃O₄ (mixed Co(II)/Co(III) phase). Consequently, the XPS analysis confirms the Co₃O₄ spinel structure. The O1s core level [Figure 5d] is related to the peak at 529.98 eV with a shoulder close to 531.1 eV corresponding to multiple oxygen species such as surface lattice oxygen, surface adsorbed oxygen,
Figure 5. (a) XPS survey, (b) C1s, (c) Co2p, and (d) O1s spectra of Co3O4 NPs.

Figure 6. (a) UV-DRS spectrum and (b) $(\alpha h \nu)^2$ vs $h \nu$ for Co3O4 NPs.

Figure 7. Effect of catalyst loading on (a) photodegradation and (b) ln($C_t/C_0$) versus irradiation time.
and chemisorbed water in the Co₃O₄ crystal lattice attached to Co.⁴⁴

The as-synthesized Co₃O₄ NPs have a p-type semi-conducting nanostructure, and their diffuse reflectance spectroscopy (DRS) data [Figure 6a,b] reveal the presence of two absorption peaks at 408 and 694 nm due to the ligand–metal charge transfer (LMCT).⁴⁹ The Kubelka–Munk (K–M) model is used to estimate the optical band gaps of Co₃O₄ NPs:

\[ \alpha h\nu = A(h\nu - E_g)^n \]

where \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy, \( A \) is a constant, \( E_g \) is the band gap energy, and the exponent \( n \) is 2 for the direct band gap and \( 1/2 \) for the indirect band gap. Therefore, the band gap \( E_g \) for Co₃O₄ NPs was estimated from the linear fit of \((\alpha h\nu)^2 \) versus \( h\nu \), and it was found to be 1.572 eV [Figure 6b]. This band gap energy is attributed to the charge transfer of O²⁻ to Co(II) and O²⁻ to Co(III) and is expected to provide excellent photocatalytic activities.

**Photocatalytic Performance.** Visible light-induced photocatalytic degradation of MG, EBT, BPB, and MR was investigated using the mesoporous octahedron-shaped Co₃O₄ NPs. In order to study the influence of the catalyst dose on dye degradation efficiency, different doses (50, 100, and 150 mg) of Co₃O₄ NPs were used while keeping all other characteristics constant. Figure 7 shows the influence of catalyst dose on the degradation efficiency and reaction kinetics. A sharp decrease of the concentration of the corresponding dyes was observed [Figure 7a], which was supported by the UV–visible spectra of...
dyes before and after treatment with Co₃O₄ NPs (Figure S7). Moreover, the reaction kinetics is pseudo-zero-order [Figure 7a] after 40 min of visible light irradiation. Initially at 50 mg, they show less degradation due to limited access to the catalyst surface and absorption of light. However, in 100 mg catalyst loading, significantly higher degradation was observed than in 50 and 150 mg loading owing to the availability of more effective active sites along with more interactions with dyes and the catalyst surface, which were more responsible for the enhanced deterioration of the corresponding dye.

The Co₃O₄-catalyzed photoactivity of dyes was monitored by the changes in the absorption spectrum of the dye solution as a function of time (Figure S8). As the irradiation time increases, the absorption peak height decreases for the corresponding dyes and reaches a flat pattern within 40 min of visible light irradiation, indicating degradation of more than 95% of the MR, EBT, BPB, and MG dyes. In addition, this was confirmed by the rapid change in the color of the dye solution (Figure S9). The rapid photocatalytic degradation of toxic dyes in the presence of Co₃O₄ NPs reflects the enhanced light harvesting, charge transfer, and separation. The time-dependent dye degradation under visible light irradiation is displayed in Figure 8. In contrast to very rapid degradation in the presence of Co₃O₄ NPs, it can be clearly seen that no degradation takes place in the dark or under visible light in the absence of Co₃O₄ NPs.

It is clearly seen that the patterns of the dye concentration profile of all dyes were almost identical and the dyes were fully degraded within 40 min in the presence of Co₃O₄ NPs, indicating the high catalyst activity for the degradation of the tested dyes.

As shown in Figure 8, there is near linear dependence of C₈/C₀ on irradiation time, which suggests that the process kinetics is pseudo-zero-order (rate = -dC₈/dt = k). Solving this equation leads to C₈ = C₀ - kt or C₈/C₀ = 1 - (k/CO)t. Therefore, the slope of the linear fit of C₈/C₀ versus t is -k/C₀, where C₀ is the initial dye concentration (mol/m³), C₈ = C₀ (ppm)/M, M is the dye molecular weight, and k is the zero-order degradation rate constant (mol/m³/min). Figure 9a,b shows the fitting of normalized dye concentration versus time for the various dyes under visible light illumination in the absence (Figure 9a) and presence of Co₃O₄ NPs (Figure 9b). Moreover, the reaction rate constant and the % dye degraded after 40 min are provided in Table 1. The present study shows more rapid Co₃O₄ NP-catalyzed photodegradation for all dyes including MG compared to previously reported Co₃O₄ and Co₃O₄–ZrO₂ nanocomposites. Additionally, we examined the Co₃O₄ NP catalysis activity on the EBT-based effluent collected from industries, and the results are presented in Figure S10.

**Catalyst Reusability.** Recyclablility of Co₃O₄ NPs was performed after complete deterioration of the corresponding dye; the NPs were recovered by filtration, washed multiple times, dried at 80 °C, and reused again. This was repeated for 4 cycles, and the result of the Co₃O₄ NP reusability in terms of % degradation in each cycle is presented in Figure 10. The results indicated no loss of photocatalytic efficiency up to the first 2 cycles, and a slight decrease in efficiency was observed during cycles 3 and 4. Moreover, the XRD pattern Figure S11) shows no changes in the structure and architectural stability of reusable Co₃O₄ NPs after 4 cycles compared to when calcined with Co₃O₄ NPs [Figure 1c].

**Photodegradation Mechanism.** A probable Co₃O₄ NP-catalyzed photodegradation mechanism under visible light irradiation is presented in Figure 11. The electrons (e⁻) in the valence band were excited to a higher-energy conduction band along with the holes (h⁺) of the corresponding Co₃O₄ NPs. The SDS-mediated Co₃O₄ NPs were treated under visible light, resulting in the migration of e⁻ from the valence band to the conduction band via a suitable band gap energy (Eᵥ), which generates electron-deficient h⁺. Due to this, the e⁻–h⁺ phenomenon occurs. The e⁻–h⁺ pairs were present on the surface of the active Co₃O₄ catalyst, which was trapped by oxygen and water molecules, respectively, along with the corresponding dye molecules. Thus, surface-active Co₃O₄ permits the photogenerated charge carriers from the inside of the bulk to transfer to the surface to prevent the hole–electron recombination. Generally, the mesoporous nanostruct-

Table 1. Percentage of Degradation, Rate Constant (k), and R² of Co₃O₄-Catalyzed Dye Degradation under Visible Light Irradiation

<table>
<thead>
<tr>
<th>dye</th>
<th>molecular formula</th>
<th>WC at 40 min (%)</th>
<th>rate constant (k, mol m⁻³ h⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR</td>
<td>C₁₉H₁₅N₃O₂</td>
<td>33.9</td>
<td>0.16</td>
<td>0.97</td>
</tr>
<tr>
<td>EBT</td>
<td>C₂₂H₂₂N₂O₆SNa</td>
<td>22.6</td>
<td>1.12</td>
<td>0.95</td>
</tr>
<tr>
<td>BPP</td>
<td>C₂₄H₆Br₄O₅S</td>
<td>26.7</td>
<td>0.39</td>
<td>0.94</td>
</tr>
<tr>
<td>MG</td>
<td>C₁₉H₁₀Br₄O₅S</td>
<td>1.81</td>
<td>0.30</td>
<td>0.96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>dye</th>
<th>molecular formula</th>
<th>PC at 40 min (%)</th>
<th>rate constant (k, mol m⁻³ h⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR</td>
<td>C₁₉H₁₅N₃O₂</td>
<td>95.3</td>
<td>8.2</td>
<td>0.98</td>
</tr>
<tr>
<td>EBT</td>
<td>C₂₂H₂₂N₂O₆SNa</td>
<td>94.3</td>
<td>2.9</td>
<td>0.95</td>
</tr>
<tr>
<td>BPP</td>
<td>C₂₄H₆Br₄O₅S</td>
<td>89.8</td>
<td>2.8</td>
<td>0.97</td>
</tr>
<tr>
<td>MG</td>
<td>C₁₉H₁₀Br₄O₅S</td>
<td>93.7</td>
<td>7.0</td>
<td>0.99</td>
</tr>
</tbody>
</table>

WC: without catalyst; PC: presence of light and Co₃O₄ NPs. 

A probable Co₃O₄ NP-catalyzed photodegradation mechanism under visible light irradiation is presented in Figure 11. The electrons (e⁻) in the valence band were excited to a higher-energy conduction band along with the holes (h⁺) of the corresponding Co₃O₄ NPs. The SDS-mediated Co₃O₄ NPs were treated under visible light, resulting in the migration of e⁻ from the valence band to the conduction band via a suitable band gap energy (Eᵥ), which generates electron-deficient h⁺. Due to this, the e⁻–h⁺ phenomenon occurs. The e⁻–h⁺ pairs were present on the surface of the active Co₃O₄ catalyst, which was trapped by oxygen and water molecules, respectively, along with the corresponding dye molecules. Thus, surface-active Co₃O₄ permits the photogenerated charge carriers from the inside of the bulk to transfer to the surface to prevent the hole–electron recombination. Generally, the mesoporous nanostruct-

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**Photodegradation Mechanism.** A probable Co₃O₄ NP-catalyzed photodegradation mechanism under visible light irradiation is presented in Figure 11. The electrons (e⁻) in the valence band were excited to a higher-energy conduction band along with the holes (h⁺) of the corresponding Co₃O₄ NPs. The SDS-mediated Co₃O₄ NPs were treated under visible light, resulting in the migration of e⁻ from the valence band to the conduction band via a suitable band gap energy (Eᵥ), which generates electron-deficient h⁺. Due to this, the e⁻–h⁺ phenomenon occurs. The e⁻–h⁺ pairs were present on the surface of the active Co₃O₄ catalyst, which was trapped by oxygen and water molecules, respectively, along with the corresponding dye molecules. Thus, surface-active Co₃O₄ permits the photogenerated charge carriers from the inside of the bulk to transfer to the surface to prevent the hole–electron recombination. Generally, the mesoporous nanostruct-

Figure 10. Reusability of Co₃O₄ NP-catalyzed dyes under visible light irradiation.
ture, high surface area, and photoactive semiconductor catalysts facilitate faster electron relocation from the core to the surface of the corresponding catalyst.\textsuperscript{51,52} In the valence band portion, H\textsubscript{2}O molecules were attached and converted themselves into active OH\textsuperscript{−} radicals via tricking H\textsubscript{2}O molecules.\textsuperscript{52} Concurrently, the electrons in the conduction band of the corresponding Co\textsubscript{3}O\textsubscript{4} interacted with the dissolved molecular oxygen present in H\textsubscript{2}O to produce a superoxide radical anion, which was further allowed to react with the H\textsubscript{2}O molecule to produce OH\textsuperscript{−}, which has powerful oxidizing ability. Due to the presence of such strong oxidizing agents, the corresponding dyes were oxidized and turned colorless.\textsuperscript{12} It is highly notable that the morphology of metal oxide plays a key role in reducing the probability of electron–hole pair recombination, which is vital for efficient photocatalysis.\textsuperscript{53–56} Photocatalytic semiconductor materials with 0D-, 1D-, 2D-, and 3D-like morphologies provide better photocatalytic activity compared to those with other disordered morphologies.\textsuperscript{48,52} Apart from other effects of semiconductor materials, the band gap of the corresponding metal oxide is a key factor for enhanced photocatalytic activity. Therefore, in this manuscript, multiple parameters including mesoporosity, surface area, morphology, and tuned band gap energies collectively contribute to the enhanced visible light photocatalytic activity of octahedron-shaped Co\textsubscript{3}O\textsubscript{4} NPs.

**MG Degradation Study by LC–MS.** The Co\textsubscript{3}O\textsubscript{4} NP-catalyzed photodegradation products of MG after 5, 15, 25, 35, and 45 min of exposure to visible light were examined by LC–MS, and the mass spectra are presented in Figure 12. Before irradiation, i.e., at zero time, a sharp peak corresponding to MG at m/z = 364 was seen [Figure 12a]. After 5 min of exposure, the degraded MG residue shows a base peak at m/z = 329 [Figure 12b] due to loss of the chloride (Cl\textsuperscript{−}) ion. The other smaller peaks at m/z = 149, 181, and 212 are attributed to the split parts of MG (C\textsubscript{6}H\textsubscript{5}COCHOCH\textsubscript{3}\textsuperscript{+}, C\textsubscript{6}H\textsubscript{5}COC\textsubscript{6}H\textsubscript{5}\textsuperscript{+}, and C\textsubscript{6}H\textsubscript{5}COC\textsubscript{6}H\textsubscript{4}NH(CH\textsubscript{3})\textsubscript{2}\textsuperscript{+}, respectively). Visible light exposure to the MG dye solution [Figure 12c] for 15 min gave a base peak at m/z = 287, which arises due to the loss of three CH\textsubscript{2} molecules.

![Figure 11. Possible mechanism of photoexcitation and dye decomposition using Co\textsubscript{3}O\textsubscript{4} NPs.](image1)

![Figure 12. LC–MS spectra of the photodegradation products of MG at (a) 0 min (before degradation) and after (b) 5 min, (c) 15 min, (d) 25 min, (e) 35 min, and (f) 45 min.](image2)
Moreover, the mass spectrum for the degradation products after 15 min shows peaks at \( m/z \) 136, 183, and 212, which correspond to \( C_6H_5COClH_2N^+ \), \( C_6H_5COHCH_2H^+ \), and \( C_6H_5COCH_2H_2NH(CH_3)_2^+ \); respectively, in addition to the base peak at \( m/z \) 287 corresponding to tridesmethyl malachite green [Figure 12c], which is formed due to the N-demethylation of MG. After 25 min, the base peak was found to be at \( m/z \) 198, and the other peaks belong to \( C_6H_5COCHOH_2N^+ , C_6H_5COHCl^+ , C_6H_5COHCH_2H_2NH(CH_3)_2^+ \), and \( NH_2CH_2C_6H_5C_6H_4NHCH_2^+ \) for \( m/z \) 149, 160, 212, and 287, respectively [Figure 12d]. At this stage, 62.74% of the dye was degraded. For complete dye degradation, irradiation was continued to 35 min [Figure 12e], and 90.45% of the MG dye was degraded; the product spectrum shows a base peak at \( m/z \) 105 due to the presence of benzyl ketone, and smaller peaks were observed at \( m/z \) 121, 141, 173, 187, and 315, which were attributed to \( C_6H_5N(CH_3)_2^+ \), \( C_6H_5COHCl^+ \), \( C_6H_5CO- (CH_2)_4NH_3^+ \), \( C_6H_5COCH_2H_2NH(CH_3)_2^+ \), and \( CH_2NCH_2C_6H_5C_6H_4NHCH_2^+ \) respectively (Scheme 3). The dye solution still contains some organic residue species after 35 min of irradiation. Thus, the irradiation time was increased to 45 min and near 100% dye degradation was observed in the presence of Co3O4 NPs; the mass spectrum shows a small peak at \( m/z \) 400 due to the presence of some unknown impurities [Figure 12f]. The superior photocatalytic activity of the NPs was evidenced by comparing the near 100% degradation to the reported 42% MG degradation.50 The photocatalytic degradation of the dye molecules is analyzed in terms of total organic carbon (TOC), and the results are depicted in [Figure S12].

**Scavenging Effect.** A scavenging study was carried out to confirm whether an active species was involved in the photocatalytic degradation of MG using KB, KI, ST, and BQ. The outcome of the MG assessment is presented in Figure 13 and Figure S13; their optical images are given in Figures S14 and S15. It has been well established that photogenerated holes (h'), hydroxyl radicals (OH), and superoxide species \( (O_2^-) \) plays a key role in the photodegradation process.38 It can be seen that, in different dyes, different scavenging materials played a role individually along with their photocatalytic pathway. However, KI played the key role of an excellent scavenger compared to its counterparts. The degradation of the four industrially toxic dyes was very significant when KI was used as the \( O_2^- \) scavenger, which directly proved that the presence of \( O_2^- \) species in the abovementioned photocatalytic reaction. The difference in the roles of the superoxide and OH radicals is very minute in their corresponding photocatalytic reaction [Figure 13 and Figure S13]. The photocatalytic patterns of the four dyes were entirely different when KB and ST were used as the scavenging agent. In the photocatalytic reaction mechanism, the photogenerated holes (h') were primarily the responsible species for the degradation of the aforementioned toxic dyes. Finally, the three species, hydroxyl (OH), superoxide \( (O_2^-) \), and photogenerated holes (h'), played important roles in the degradation of the corresponding dyes. The strong contribution of OH, h', and \( O_2^- \) in the reaction medium further supports the involvement of the photogenerated holes and electrons.5

**CONCLUSIONS**

The present work provides a simple synthetic method for tailoring the morphology, texture, and other physicochemical properties of Co3O4 NPs. Remarkably, SDS plays a key role in the formation of exclusively mesoporous, octahedron-shaped Co3O4 NPs with a narrow size distribution. Among spinel-type photocatalysts, the present mesoporous Co3O4 NPs show excellent photocatalytic performances under visible light irradiation toward degradation of MR, EBT, BPB, and MG dyes due to the presence of mesoporosity, scaffold morphology, surface area, and tuned band gap energy. The kinetics mechanism and radical confirmations were investigated using the scavenger assay. Moreover, the complete photochemical degradation of MG under visible light irradiation at different times was investigated by the LC−MS study.

**EXPERIMENTAL SECTION**

**Materials and General Methods.** Analytical-grade cobalt chloride hexahydrate \((CoCl_2 \cdot 6H_2O)\), monosodium succinate \((C_6H_5O_2Na)_2\), sodium dodecyl sulfate \((NaCl_2H_2SO_4)\) hydrate hydrate \((NaCl_2H_2SO_4)_2\), methyl red \((MR)\), Eriochrome Black-T \((EBT)\), bromophenol blue \((BPB)\), and malachite green \((MG)\) as organic dyes; potassium iodide \((KI)\), potassium bromate \((KB)\), sodium thiosulfate \((ST)\), benzoquinone \((BQ)\) as
Fabrication of Co₃O₄ NPs. Co₃O₄ NPs were fabricated using a sol–gel method³⁵ (Scheme 1). In a typical procedure, 100 mL (0.1 M) of aqueous solution of COCl₂·6H₂O was placed in a clean round-bottom flask and stirred at 50 °C for 15 min, and 50 mL of C₆H₅O₄Na (0.26 M) was then added slowly into the hot solution and continuously stirred for another 20 min. Afterward, 10 mL of NaC₂₃H₂₅SO₄ (0.017 M) was added dropwise, and 1.5 mL of (5 M) N₂H₄ was added dropwise in order to hydrolyze and reduce the corresponding material. One hour after the addition of N₂H₄, a pinkish-white color gel appeared, and it was collected through centrifugation, washed with an ethanol/acetone mixture, dried at 60 °C in a preheated vacuum oven, and finally calcined at 500 °C for 3 h in a muffle furnace. The synthesized Co₃O₄ NPs were examined by various analytical techniques to determine their structural, compositional, and morphological features. The detailed characterizations of Co₃O₄ NPs are given in Supplementary Information S1.

Visible Light-Induced Photocatalytic Activity. The photocatalytic activity of the Co₃O₄ NPs was studied for the degradation of MR, EBT, BPB, and MG under visible light irradiation. The photocatalytic reactor was equipped with a cylindrical (400 W) tungsten lamp as a visible light source. Co₃O₄ NPs (100 mg) were dispersed in 100 mL of 20 ppm aqueous dye solution (pH = 6.5) at 25 ± 2 °C. Prior to light illumination, the suspension was stirred in the dark for 60 min for adsorption–desorption equilibrium. Afterwards the 100 mL suspension was exposed to visible light in the photocatalytic reactor. The solution (5 mL) was removed from the reactor at 5 min intervals and centrifuged to eradicate the corresponding photocatalyst; then, its absorption was measured using a UV–vis absorption spectrophotometer (UV-1800, Shimadzu, Japan), and the dye degradation percentage was calculated from the concentration of the initial dye (20 ppm) (C₀) and the dye concentration at time t of the visible light exposure (Cₜ) as follows:

\[
\text{degradation (\%) = } \left( \frac{C₀ - Cₜ}{C₀} \right) \times 100
\]

The apparent zero-order rate constant (k, mol m⁻³ h⁻¹) of the degradation reaction catalyzed by the Co₃O₄ photocatalyst is determined by plotting Cₜ/C₀ versus irradiation time (t) using the following equation:

\[
Cₜ = C₀ - kt
\]

Detection of Trapping Species. For the holes and radicals, the trapping test was carried out by adding 0.1 mmol of scavengers (KI, KB, ST, and BQ) to the corresponding nanostructured octahedral Co₃O₄ NPs, and the holes (h⁺), hydroxyl radicals (OH), and superoxide radical anions (O₂⁻) were detected in the corresponding photocatalytic dye degradation.

Associated Content

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03998. Section S1: Characterization of Co₃O₄ NPs; Figure S1: different reaction steps and their corresponding UV–vis absorption spectra; Figure S2: SEM images of before-
calcined Co₃O₄ NPs; Figure S3: EDS spectrum of calcined Co₃O₄ NPs; Figure S4: XRD profile of the mixed phase CoO–Co₃O₄; Figure S5: FT-IR spectra; Figure S6: Mott–Schottky plot; Figure S7: UV–vis absorption spectra; Figure S8: changes in UV–vis absorption pattern; Figure S9: photos of the corresponding dye degradation; Figure S10: photocatalytic degradation of the industrial effluent; Figure S11: XRD pattern of reused Co₃O₄; Figure S12: TOC removal after 240 min; Figure S13: scavenging test; Figure S14: photos of the scavenging test for EBT and BPB; Scheme S1: thermal degradation mechanism; and Table S1: thermal data (PDF)

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Author Contributions

This work was collaboratively done by all authors whose names are stated in the paper. The fabrication work was done by V.S., A.K.P., and R.G.C. The photocatalytic performances, diagrammatic scheme preparation, and writing work were executed by V.S., G.B., A.M., and R.M. In addition, the electronic result data interpretation was done by A.A.A., R.G.C., and H.D.J.

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REFERENCES


(2) Ravichandran, A. T.; Srinivas, J.; Karthick, R.; Manikandan, A.; Baykal, A. Facile combustion synthesis, structural, morphological, optical and antibacterial studies of Bi1−xAlxFeO3 (0.0 ≤ x ≤ 0.15) nanoparticles. Ceram. Int. 2018, 44, 13247–13252.


(18) Kavivaram, K.; Manikandan, E.; Kennedy, J.; Maaza, M. A comparative study on the morphological features of highly ordered Mg3Ag0Ag2O nanocube arrays prepared via a hydrothermal method. RSC Adv. 2015, 5, 82421–82428.


