

1 **Photocatalytic degradations of malachite green on**
2 **magnetically separable Ni_{1-x}Co_xFe₂O₄ nanoparticles synthesized**
3 **by a hydrothermal process**

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8 **Abstract:** A series of Ni_{1-x}Co_xFe₂O₄ (x=0–1.0) ferrite nanoparticles were synthesized
9 by a hydrothermal process. The nanoparticles had a nano-scale average particle sizes
10 of ~14.8–29.4 nm and a narrow band gap of ~1.75–1.91 eV, decreasing as increasing
11 Co content. The nanoparticles showed an excellent sunlight-excited photocatalytic
12 activity to malachite green in a water. Moreover, a small amount of H₂O₂ addition
13 resulted in an obviously enhanced photodegradation of the dye in a water, indicating a
14 Fenton-like reaction. The photodegradation and Fenton-like photodegradation rates
15 increased as the increase of Co content. Complete Co substitution for Ni cation
16 resulted in an optimal effect. Quasi-kinetic rate constant *k* values were in the range of
17 ~2.23–7.2×10⁻² min⁻¹ and increased to ~1.3–6.0×10⁻¹ min⁻¹ as the addition of H₂O₂.
18 The measurement of oxidation-reduction potential of the nanoparticles in the
19 photodegradation condition indicated a reductive characteristics enhanced with the
20 increase of Co content. Furthermore, the nanoparticles possessed high saturation
21 magnetizations of ~50.7–64.2 emu·g⁻¹ and low coercivity ~0.4–1.7 kOe, and so were
22 well magnetic separable in finally degraded dye aqueous solution.

Keywords: Nanostructure; semiconductors; dye photodegradation; Fenton-like reaction; magnetic separation

1. Introduction

Photocatalysis play an important role in dealing with today's challenging demand for decontamination of environment. For this purpose, nano-TiO₂ material as a photocatalyst has been widely studied because of its excellent chemical stability and photocatalytic activity. To fully utilize sunlight and enhance the photocatalytic activity of the nano-photocatalyst, developing photocatalyst with shorter band gap semiconductor than pure TiO₂ are usually interesting. In some cases, such as waste water treatment, the photocatalyst nanoparticles are also required to be separated from the photodegraded aqueous solution as photodegradation process is completed. Magnetic separation is generally believed to be an effective technique.

Spinel ferrites have narrow band gap energy (~ 2.0 eV), so their nanoparticles may be potential photocatalysts for the decontamination of environment because of their superiority in full utilization of natural sunlight. Moreover, this type of ferrites are ferromagnetic and so have magnetic separable performance from aqueous solution. Previous researches have shown the excellent photocatalytic activity of some ferrite nanoparticles [1, 2]. Recent studies further indicate that the composites of different ferrites [2] and ferrite with other photocatalysts [3, 4] have more efficiency than single ones. Different metal cations have different physuical chemical behavior. Thus, it is necessary to investigate the effect of Co substitution for Ni cation on the

45 photocatalytic activity of the nickel ferrite nanoparticles.

46 In recent years, advanced oxidation processes (AOPs) by using UV/H₂O₂ has
47 become a way to degrade organic compounds in dilute solutions. In general, it is
48 believed that the UV/H₂O₂ processes result in the formation of OH radicals in the
49 solution, which accelerate the oxidation degradation of the organic compounds in the
50 water. The using H₂O₂ has a main disadvantage of its high cost, whereas the low
51 oxidation rate is the major draw back of semiconductors such as TiO₂. The combined
52 use of H₂O₂ and semiconductors is a way of solving this problem. Many studies have
53 been devoted to the examination of organic compound photodegradation in the
54 presence of H₂O₂ and TiO₂ [5,6]. This process is usually called as Fenton-like process
55 because it is similar with the advanced oxidation process based on the homogeneous
56 Fenton reagent (Fe²⁺/H₂O₂) or Fenton-like (Fe³⁺/H₂O₂) [7,8]. Up to today, various
57 Fenton and Fenton-like processes have been researched for the degradation of organic
58 pollution. For example, activated carbon fibers [9], impure bismuth ferrite [10],
59 copper slag (90% Fe₂SiO₄) [11], ferrioxalate complexes [12], iron/ordered
60 mesoporous carbon catalyst [13], iron oxide nanotube layer [14], Cu²⁺ [15], et al.
61 were used as a Fenton-type photocatalyst or assisted Fenton-type photocatalysts.
62 However, the photocatalytic and Fenton-like photocatalytic activities of
63 Ni_{1-x}Co_xFe₂O₄ ferrite nanoparticles have not been found for dye removal from waste
64 water in previous literature.

65 To date, many methods have been developed to fabricate spinel ferrite nanoparticles,
66 such as aerosol route [16], co-precipitation method [17, 18], usual ceramic technique

[19], hydrolysis method [20], microwave-hydrothermal method [21], and hydrothermal method [22]. The hydrothermal process is widely used for the spinel ferrite synthesis because of its simple process, low cost, low synthesis temperature, and small particle size of synthesized nanoparticles [22].

In the current study, we focus on the hydrothermal synthesis of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles and examining the effects of Co content on the microstructure, photocatalytic activity for malachite green removal from aqueous solution, and magnetic property of the synthesized nanoparticles.

75

76 **2. Experimental**

Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Shenyang Hua Bai Tai Chemical Co. Ltd., China), cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Hebei Kingway Chemical Co. Ltd., China), and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Beijing Baishunchem. Co. Ltd., China) were used as starting materials. The starting materials used were all analytical agent without further processing. The starting materials were first weighed according to the compositions of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$, and 1.0) and dissolved in 15 mL deionic water for each composition. Such solutions have a Fe^{3+} concentration of 0.02 mol L^{-1} . The solutions were then transferred into autoclaves (volume: 25 mL). Subsequently, NaOH with fourfold gram equivalent of all metal cations was dissolved in deionic water (5 mL for each composition) and added dropwise into the metal cation aqueous solutions with constant magnetic stirring. Such excess NaOH addition can assure full precipitation of all cations to their hydroxides. After sealing, hydrothermal reaction was carried out in a hydrothermal oven at 180°C for 24 h. Heating rate was about

90 30 °C·min⁻¹. After naturally cooling in the oven, the products were finally washed
91 repeatedly with distilled water, and then dried at 100 °C for 24 h.

92 The crystalline structural phase of the synthesized Ni_{1-x}Co_xFe₂O₄ nanoparticles was
93 identified at room temperature using X-Ray diffractometer (XRD, CuK_{α1},
94 λ=0.15406nm, Model No: D/Max--2200PC, Rigaku, Japan). The morphology of the
95 nanoparticles was analyzed using scanning electron microscope (SEM, Model No:
96 JXM-6700F, Japan). Fourier transform infrared spectra of the nanoparticles were
97 measured with Fourier transform infrared spectrometer (FTIR, Model no: VERTEX
98 70, Bruke, German). KBr was used as matrix to disperse the ferrite nanoparticles for
99 compressing disk sample. The absorbance spectra of the nanoparticles were
100 determined with an ultraviolet-visible spectrophotometer (Model No: 722, Hengping,
101 China). The magnetic property was measured with a vibrating sample magnetometer
102 (VSM, Model No: Versa Lab, Quantun Design, USA)

103 To study the photocatalytic and photo-Fenton like degradations of malachite green in
104 a water on the nanoparticles. The malachite green aqueous solution with a
105 concentration of 1×10⁻⁶ M was first prepared. In each experiment, 50 mL malachite
106 green aqueous solution and 25 mg one of the ferrite nanoparticles were added into a
107 glass beaker with constant stirring for 1-2 min. The photocatalysis experiment was
108 carried out under the irradiation of sunlight. The intensity of sunlight reaching the
109 surface of the solutions was measured with a solar power meter (Model no: SM206,
110 China) and is ~250 W·m⁻². After leaving to steady state in dark for 10 min and
111 afterward each irradiation interval, ~3 mL solutions were took out and filtrated out the

suspended tiny particles and subsequently measured for their absorbance on a spectrophotometer (Model No: 722N, Hengping, China). The solutions after the test were returned to the beakers to maintain the normal volume of the solutions under test. Similar experiment was carried out in the condition of adding 0.5 mL H_2O_2 into each of the 50 mL dye aqueous solution.

In first hour of the above processes, the oxidation-reduction potential (ORP) of the malachite green aqueous solutions with and without the photocatalysts was determined on an oxidation-reduction potential tester (ORP-286, China). The ORP of the nanoparticle surfaces in the condition of dye photodegradation were estimated by calculating the differences between the measured ORP of the dye aqueous solutions with and without the nanoparticles. The absorbance and ORP of the dye aqueous solutions were all their average value of two repeated measurement values

3. Results and discussion

3.1. XRD analysis

Figure 1a shows the XRD patterns of the synthesized nanoparticles. All diffraction peaks match with the reported powder diffraction data of spinel ferrites including Fe_3O_4 (JCPDS: 88-0315), CoFe_2O_4 (JCPDS: 22-1086), and NiFe_2O_4 (JCPDS: 74-2081 and 10-0325). This indicates that the nanoparticles are composed of single phase $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ without any other impurities. The intensity of the XRD peaks first slightly decreases when Co content (x) increase from 0 to 0.8 and then increases with further cobalt substitution, drawing out variation trend in crystallinity of the

134 nanoparticles. This decrease trend of the crystallinity with cobalt substitution was also
 135 reported for the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles synthesized by solvothermal route [23].
 136 This could be mainly due to smaller radius difference (0.72–0.64 Å) between Ni^{2+}
 137 and Fe^{3+} ions than (0.74–0.64 Å) between Co^{2+} and Fe^{3+} ions. The smaller radius
 138 difference leads to smaller inhibition of Ni^{2+} substitution for Fe^{3+} to the spinel crystal
 139 growth than Co^{2+} substitution. Moreover, the position of strong peak (311) shifts to
 140 lower 2θ with cobalt substitution (Fig. 1b). This can be ascribed to the decrease in the
 141 interplanar crystal spacing (d) based on Bragg's equation, for which smaller ionic
 142 radius of Ni^{2+} (0.72 Å) than the Co^{2+} (0.74 Å) may be main reason. The lattice
 143 parameter of the nanoparticles with cubic crystal structure can be calculated by
 144 following equation using XRD analysis data:

$$145 \quad \frac{a^2}{d^2} = h^2 + k^2 + l^2 \quad (1)$$

146 Calculated a values equal 0.8236 nm, 0.8263 nm, 0.8298 nm, 0.8321 nm, 0.8339 nm
 147 and 0.8377 nm for the Co content $x=0, 0.2, 0.4, 0.6, 0.8,$ and $1.0,$ respectively (Fig.
 148 1c). This indicates the expansion of the lattice with the cobalt substitution, agreeing
 149 with the position shift of (311)-peak. Similar lattice parameter variation was also
 150 reported in previous literature [16, 24]. This lattice expansion may be caused by larger
 151 cation radius of Co^{2+} than Ni^{2+} and the decrease in crystallinity. Moreover, the lattice
 152 parameter a of CoFe_2O_4 equals to 0.8391 nm (JCPDS: 22-1086) that is larger than
 153 0.83379 nm (JCPDS: 74-2081) and 0.83390 nm (JCPDS: 10-0325) of the NiFe_2O_4 .
 154 This clearly indicates that Co^{2+} enters the ferrite lattices by replacing the Ni^{2+}
 155 according to Vegard's law. Furthermore, the lattice parameter of the all ferrites is

156 smaller than the value given in the JCPDS card, especially as the Co content
157 approaches zero. This could be ascribed to the high-pressure effect in the condition of
158 hydrothermal synthesis. Similarly, the lattice parameter of the NiFe_2O_4 nanoparticle is
159 smaller when they were synthesized by hydrothermal process than by sol-gel method
160 [25]. The average crystal sizes of the nanoparticles are determined from XRD data
161 analysis with Debye–Scherrer’s formula [26]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

163 where λ is the X-ray wavelength, β the full width at half maximum (FWHM) of the
164 considered peak and θ is the Bragg angle. The determined results are 23.4, 29.4, 23.6,
165 19.4, 16.5, and 14.8 nm for the $x=0, 0.2, 0.4, 0.6, 0.8, 1.0$, respectively. They first
166 increase with the increase of cobalt content (x) from 0 to 0.2 and then decrease with
167 further cobalt substitution (Fig. 1c).

168 **3.2. SEM analysis**

169 Figure 2 shows the typical SEM micrographs of the nanoparticles. Most of the
170 nanoparticles show spherical particle morphology with somewhat agglomerated (Fig.
171 2c–2f), while the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0.8$ and 1.0) nanoparticles have approximately
172 cubical particle morphology (Fig. 2a and 2b). This could be mainly due to same
173 reason of the difference in crystallinities of the nanoparticles. From the SEM
174 micrographs, the average particle sizes are also increased as the increase of x from
175 0 to 0.8 and then decreases with further cobalt substitution. The sizes of the
176 nanoparticles with $x=0.8$ and 1.0 are obviously larger than the results of XRD analysis,
177 which could show that these nanoparticles are polycrystalline.

3.3. FTIR analysis

Figure 3 shows the FTIR spectra of the nanoparticles. The peak centered at $\sim 3416\text{ cm}^{-1}$ is attributed to the stretching vibration of surface hydroxyls absorbed on surface and O–H groups in absorbed water [27]. The peak centered at 1620 cm^{-1} is assigned to the H–O–H bending vibration in water molecular [28] or the OH deformation vibration due to surface hydroxyls [29, 30]. These imply good nanoparticle surface hydrophilicity that may be favorable for the photocatalytic activity. The weak peak at 1124 cm^{-1} could be assigned to the C–O stretching [31] due to the adsorbed CO_2 . The two peaks at $\sim 483\text{ cm}^{-1}$ and $\sim 616\text{ cm}^{-1}$ are assigned as the vibrations of ferrite groups [32], corresponding to the octahedral and tetrahedral sites of positive ions in the ferrite, respectively [28, 33]. The difference in absorption positions of the octahedral and tetrahedral complexes of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ crystals is due to the different distances between $\text{Fe}^{3+}\text{--O}^{2-}$ in the octahedral and tetrahedral sites. This confirms the formation of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ structure.

3.4. Optical absorption analysis

Figure 4 shows the absorbance spectra of the ferrite nanoparticles. The absorbances in UV-visible region are large and increases as the increase of Co content. The estimated absorption edge increases from $\sim 648\text{ nm}$ to $\sim 710\text{ nm}$ as the increase of Co content. Accordingly, the band gap energies of the nanoparticles decrease from $\sim 1.91\text{ eV}$ to $\sim 1.75\text{ eV}$ as the increase of Co content (Inserted figure in Fig. 4).

3.5. Photocatalytic degradation of the dye in a water on the nanoparticles

Figure 5 shows the concentration variations of the malachite green aqueous solutions

on the nanoparticles with the irradiation time of sunlight. The degradation rate increases as the increase of Co content. This increase of degradation rate could be ascribed to the decreases of band gap and average particle size and the increase of light absorbance of nanoparticles as the increase of Co content. In addition, the ORP values are negative and decrease as the increase of Co content (Fig. 6). This indicates that the nanoparticles surface are dominantly reductive in the photocatalysis condition and this characteristics enhances as the increase of Co content.

3.6. Fenton-like photodegradation of the dye in a water on the nanoparticles

Figure 7 shows the concentration variations of the malachite green aqueous solution with H₂O₂ on the nanoparticles with the irradiation time of sunlight. The degradation is obviously faster than that without H₂O₂, which indicates a significant photo-Fenton-like reaction. Similarly, The degradation rate increases as the increase of Co content. This increase could also be mainly ascribed to the decreases of band gap and average particle size and the increase of light absorbance as the increase of Co content. The photo-generated electron-hole pairs in the nanoparticles could play similar role of the Fe²⁺ and Fe³⁺ in Fenton reaction. The concentration increase of photo-generated electrons and holes as the increase of Co content leads to the enhanced photo-Fenton-like reaction. The ORP values in this process are larger than that in the case without H₂O₂. The ORP also show a nonlinear variation with Co contents, that is, first increased from negative to positive and then decreased to negative as the increase of Co content (Fig. 6). The difference and variation of ORP could be related to the surface characteristics of the nanoparticles, the acidic-alkaline

222 behavior of the dye, oxidation of H₂O₂, and Fenton-like reaction.

223 Kinetic relation between the concentration (*C*) of the malachite green aqueous
224 solution and the photocatalytic reaction time (*t*) can be generally given by:

$$225 \quad \frac{C_0}{C} = A \exp\left(\frac{kt}{T}\right)$$

226 In which, *C*₀ is initial concentration, *k* is quasi-kinetic rate constant, *T* is reaction
227 temperature, and *A* is a constant. Fig. 8 shows the plots of ln(*C*/*C*₀) versus *t*. The plots
228 are approximately linear. The *k* values can be estimated directly from the linear
229 regression analyses of the plots. The estimated *k* values are in the range of
230 ~2.23–7.2×10⁻² min⁻¹ and increase about one magnitude to ~1.3–6.0×10⁻¹ min⁻¹ as
231 H₂O₂ is used. The *k* values increase as the increase of Co content in both cases with
232 and without H₂O₂.

233 3.7. Magnetic property of the nanoparticles

234 Figure 9a show the room temperature hysteresis loops of the Ni_{1-x}Co_xFe₂O₄
235 nanoparticles. The nanoparticles are all ferromagnetic. With increasing applied field,
236 the magnetization of the Ni_{1-x}Co_xFe₂O₄ nanoparticles increases, and nearly reaches
237 saturation state under highest applied magnetic fields of 30 KOe. Maximum value of
238 magnetization at applied field of 30 KOe (saturation magnetization *M*_s) is in the
239 ranges of ~50.7–64.2 emu·g⁻¹, and first increases and then decrease with the increase
240 of Co content (Fig. 9b). The coercivity (*H*_c) is in the range of ~0.4–1.7 kOe (Fig. 9b).
241 The ferrite nanoparticles with Co content *x*=0.8 show maximal *M*_s and *M*_r. This can
242 be mainly ascribed to the maximal cation distribution of Fe³⁺ and Co²⁺ at the
243 octahedral site (B-site) at Co content *x*=0.8 since the magnetic moments of Zn²⁺, Co²⁺

244 and Fe^{3+} are 0 μB , 3 μB and 5 μB , respectively. Other reasons may be the difference
245 in particle size, easy magnetization axis, and shape anisotropy. Such large M_s low
246 H_c can provide an excellent magnetically separable performance for the ferrite
247 nanoparticles in the final degraded dye aqueous solution.

248

249 **4. Conclusions**

250 The effect of the Co content on the microstructure, photocatalytic activity and
251 magnetic property of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0.1-1.0$) ferrite nanoparticles was studied.
252 The room temperature X-ray diffraction confirmed the formation of single-phase
253 Co-Ni ferrites. High photocatalytic activity of the nanoparticles was observed in the
254 sunlight-excited photodegradation of malachite green in a water. Significantly, a small
255 amount of H_2O_2 addition into the dye aqueous solution resulted in remarkably
256 enhanced photodegradation, indicating an Fenton-like reaction. Since the increases of
257 light absorbance and the decreases of band gap and average particle size with the
258 increase of Co content, the photodegradation and Fenton-like photodegradation rates
259 increased as the increase of Co content. Quasi-kinetic rate constant k values were in
260 the range of $\sim 2.23-7.2 \times 10^{-2} \text{ min}^{-1}$ and increased about one magnitude to
261 $\sim 1.3-6.0 \times 10^{-1} \text{ min}^{-1}$ as H_2O_2 was used. The measurement of oxidation-reduction
262 potential reveals the dominant reductive photocatalytic characteristics of the
263 nanoparticle surface in the photodegradation condition without H_2O_2 . This reductive
264 characteristics linearly increased as the increase of Co content. Whereas the
265 oxidation-reduction potential as using H_2O_2 was larger than that without H_2O_2 and

266 showed nonlinear variation with the Co content. The synthesized ferrite nanoparticles
267 also show high saturation magnetizations and low coercivities, which can provide a
268 excellence magnetically separable performance for the nanoparticles in the final
269 photodegraded dye solution.

270

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273 **References**

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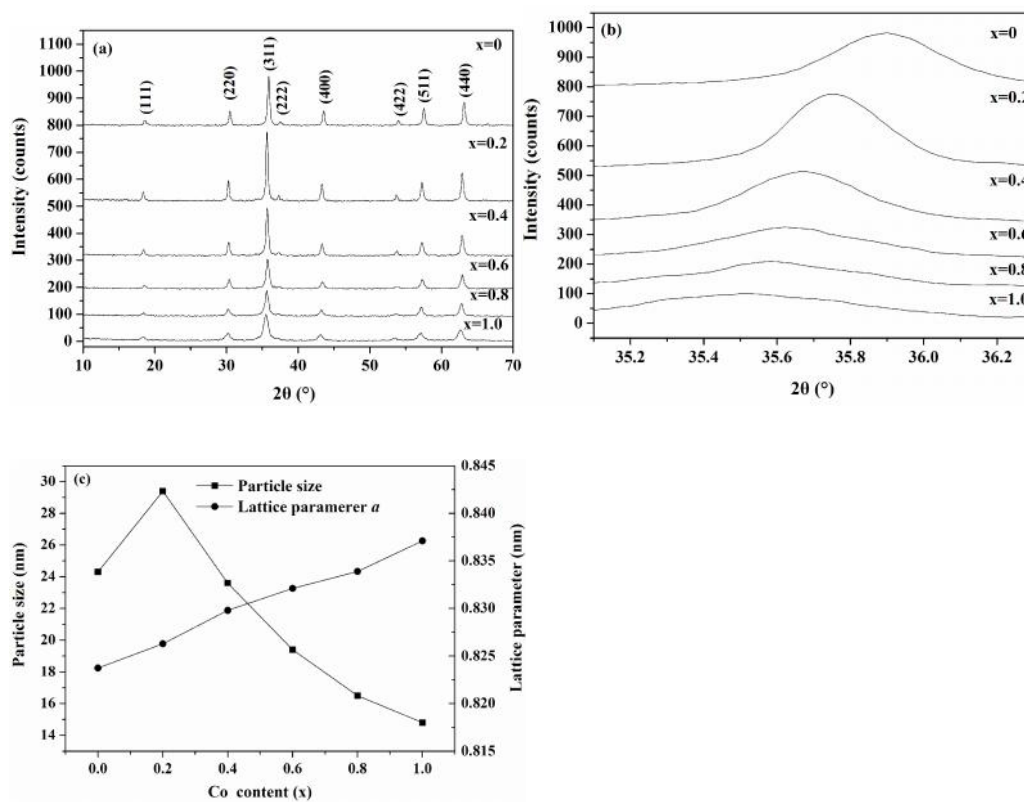
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394 **Figures:**



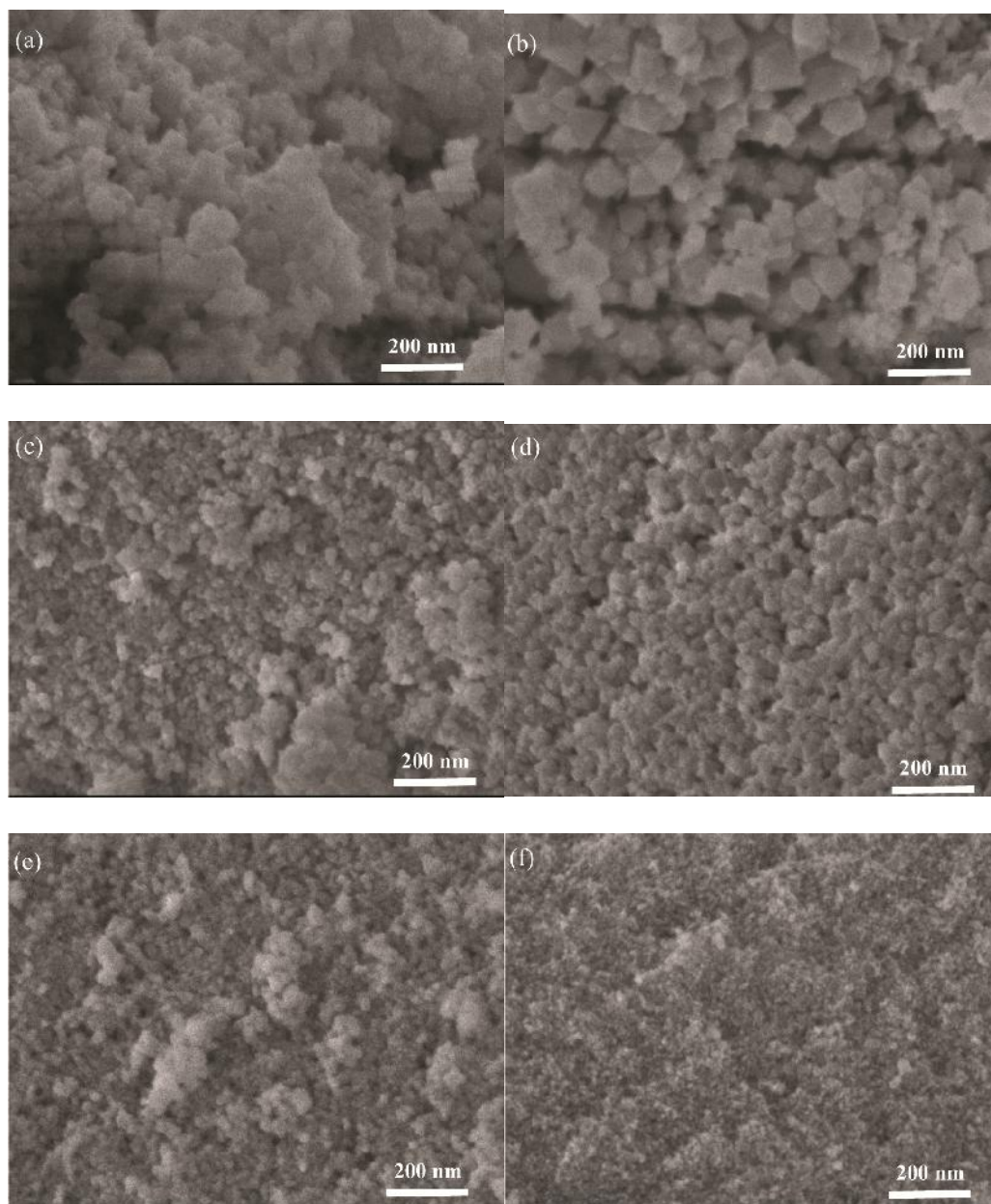
397 Figure 1. (a) XRD patterns and (b) Enlarged (311) peak in the XRD patterns (c)
 398 Average particle size and lattice parameter of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$
 399 nanoparticles.

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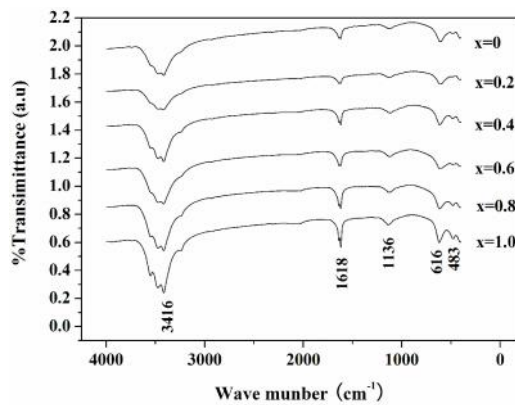
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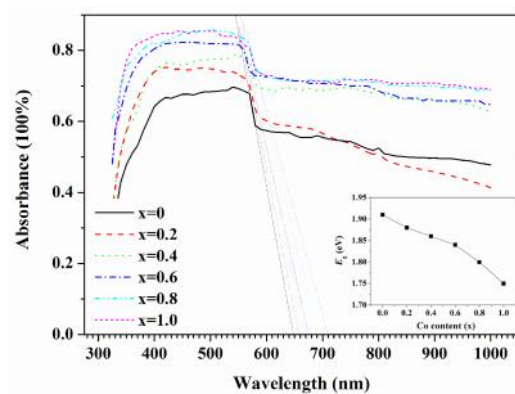
Figure 2. SEM micrographs of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with various Co content (a) $x=0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$.

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414 Figure 3. FTIR spectra of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles.



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416 Figure 4. Absorbance spectra of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles. Inserted figure is
417 the plots of band gap (E_g) vs. Co content (x).

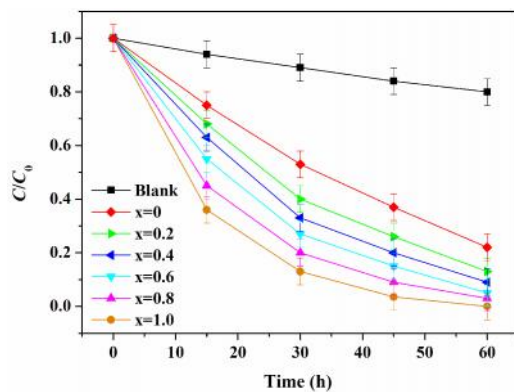
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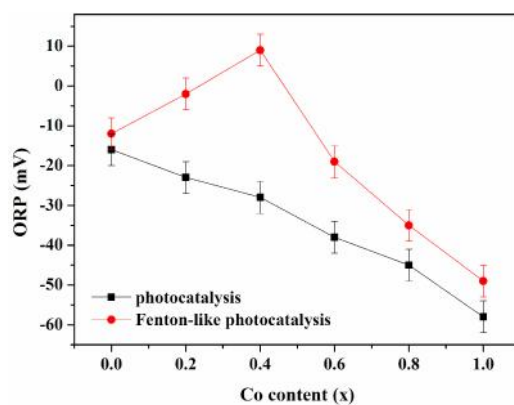
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424 Figure 5. Concentration variations of malachite green aqueous solutions on the
425 $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with the irradiation time of sunlight.

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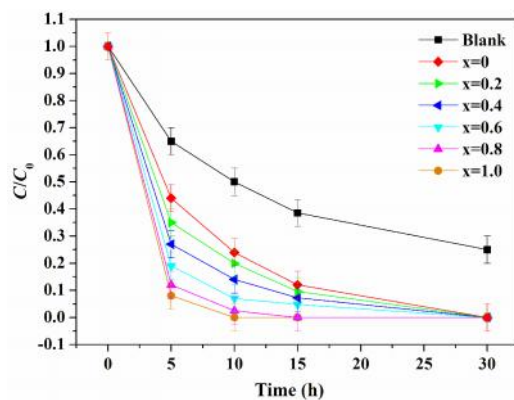
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428 Figure 6. ORP variations of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with Co content (x) in the
429 photocatalytic and photo-Fenton-like degradation systems.

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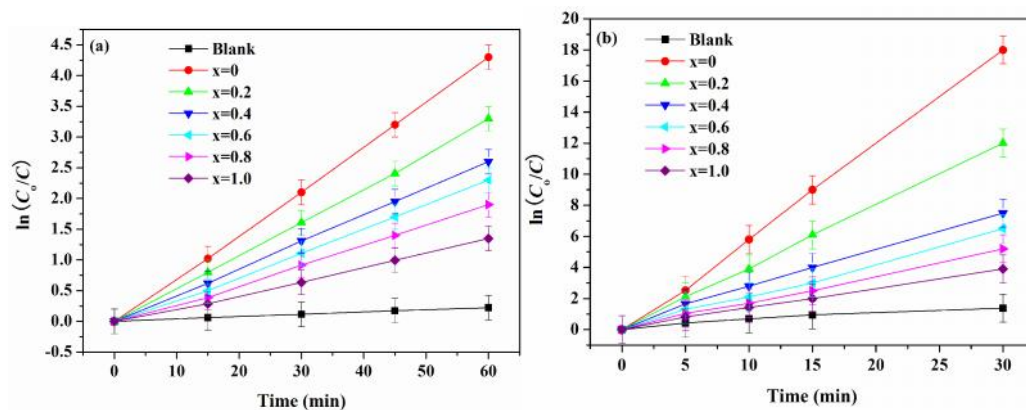
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434 Figure 7. Concentration variations of malachite green aqueous solutions containing
 435 H_2O_2 (concentration equal 10 ml/l) on the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with
 436 the irradiation time of sunlight.

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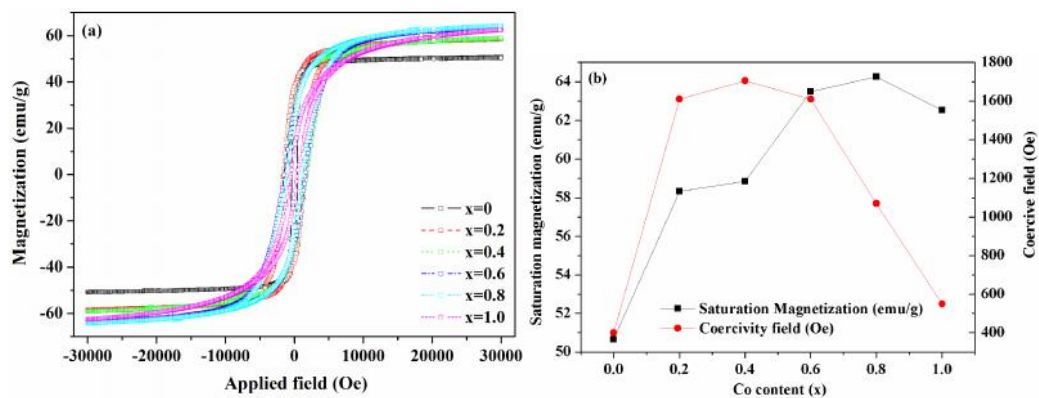
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439 Figure 8. The plots of $\ln(C/C_0)$ vs. the irradiation time of sunlight in case of (a) H_2O_2 -
 440 free and (b) using H_2O_2 .

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445 Figure 9. (a) Room temperature magnetic hysteresis loops of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$
 446 nanoparticles and (b) variations of saturation magnetization and coercivity
 447 with Co content.

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