

**Photocatalytic degradations of malachite green on
magnetically separable $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles synthesized
by a hydrothermal process**

Abstract: A series of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0-1.0$) ferrite nanoparticles were synthesized by a hydrothermal process. The nanoparticles had a nano-scale average particle sizes of $\sim 15-90$ nm and a narrow band gap of $\sim 1.75-1.91$ eV, decreasing as increasing Co content. The nanoparticles showed an excellent sunlight-excited photocatalytic activity to malachite green in a water. Moreover, a small amount of H_2O_2 addition resulted in an obviously enhanced photodegradation of the dye in a water, indicating a Fenton-like reaction. The photodegradation and Fenton-like photodegradation rates increased as the increase of Co content. Quasi-kinetic rate constant k values were in the range of $\sim 2.23-7.2 \times 10^{-2} \text{ min}^{-1}$ and increased to $\sim 1.3-6.0 \times 10^{-1} \text{ min}^{-1}$ as the addition of H_2O_2 . The measurement of oxidation-reduction potential of the nanoparticles in the photodegradation condition indicated a reductive characteristics enhanced with the increase of Co content. Furthermore, the nanoparticles possessed high saturation magnetizations of $\sim 50.7-64.2 \text{ emu} \cdot \text{g}^{-1}$ and low coercivity $\sim 0.4-1.7 \text{ kOe}$, and so were well magnetic separable in finally degraded dye aqueous solution.

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

23

24 **1. Introduction**

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

34 Spinel ferrites have narrow band gap energy (~2.0 eV), so their nanoparticles may be
35 potential photocatalysts for the decontamination of environment because of their
36 superiority in full utilization of natural sunlight. Moreover, this type of ferrites are
37 ferromagnetic and so have magnetic separable performance from aqueous solution.
38 Previous researches have shown the excellent photocatalytic activity of some ferrite
39 nanoparticles [1, 2]. Recent studies further indicate that the composites of different
40 ferrites [2] and ferrite with other photocatalysts [3, 4] have more efficiency than single
41 ones.

42 In recent years, advanced oxidation processes (AOPs) by using UV/H₂O₂ has
43 become a way to degrade organic compounds in dilute solutions. In general, it is
44 believed that the UV/H₂O₂ processes result in the formation of OH radicals in the

45 solution, which accelerate the oxidation degradation of the organic compounds in the
46 water. The using H_2O_2 has a main disadvantage of its high cost, whereas the low
47 oxidation rate is the major draw back of semiconductors such as TiO_2 . The combined
48 use of H_2O_2 and semiconductors is a way of solving this problem. Many studies have
49 been devoted to the examination of organic compound photodegradation in the
50 presence of H_2O_2 and TiO_2 [5,6]. This process is usually called as Fenton-like process
51 because it is similar with the advanced oxidation process based on the homogeneous
52 Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) or Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) [7,8]. Up to today, various
53 Fenton and Fenton-like processes have been researched for the degradation of organic
54 pollution. For example, activated carbon fibers [9], impure bismuth ferrite [10],
55 copper slag (90% Fe_2SiO_4) [11], ferrioxalate complexes [12], iron/ordered
56 mesoporous carbon catalyst [13], iron oxide nanotube layer [14], Cu^{2+} [15], et al.
57 were used as a Fenton-type photocatalyst or assisted Fenton-type photocatalysts.
58 However, the photocatalytic and Fenton-like photocatalytic activities of
59 $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ferrite nanoparticles have not been found for dye removal from
60 wastewater in previous literature.

61 To date, many methods have been developed to fabricate spinel ferrite nanoparticles,
62 such as aerosol route [16], co-precipitation method [17, 18], usual ceramic technique
63 [19], hydrolysis method [20], microwave-hydrothermal method [21], and
64 hydrothermal method [22]. The hydrothermal process is widely used for the spinel
65 ferrite synthesis because of its simple process, low cost, low synthesis temperature,
66 and small particle size of synthesized nanoparticles [22].

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

71

72 **2. Experimental**

73 Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Shenyang Hua Bai Tai Chemical Co. Ltd, China),
74 cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Hebei Kingway Chemical Industry Co. Ltd. China), and
75 iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Beijing Baishunchem. Co. Ltd., China) were used as
76 starting materials. The starting materials used were all analytical agent without further
77 processing. The starting materials were first weighed according to the compositions of
78 $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$, and 1.0) and dissolved in 15 ml deionized water
79 for each composition. Such solutions have a Fe^{3+} concentration of 0.02 mol l^{-1} . The
80 solutions were then transferred into autoclaves (volume: 25 ml). Subsequently, NaOH
81 with fourfold gram equivalent of all metal cations was dissolved in deionized water (5
82 ml for each composition) and added dropwise into the metal cation aqueous solutions
83 with constant magnetic stirring. Such excess NaOH addition can assure full
84 precipitation of all cations to their hydroxides. After sealing, hydrothermal reaction
85 was carried out in a hydrothermal oven at 180°C for 24 h. Heating rate was about
86 $30^\circ\text{C} \cdot \text{min}^{-1}$. After naturally cooling in the oven, the products were finally washed
87 repeatedly with distilled water, and then dried at 100°C for 24 h.

88 The crystalline structural phase of the synthesized $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles was
89 identified at room temperature using X-Ray diffractometer (XRD, $\text{CuK}_{\alpha 1}$,

90 $\lambda=0.15406\text{nm}$, Model No: D/Max--2200PC, Rigaku, Japan). The morphology of the
91 nanoparticles was analyzed using scanning electron microscope (SEM, Model No:
92 JXM-6700F, Japan). Fourier transform infrared spectra of the nanoparticles were
93 measured with Fourier transform infrared spectrometer (FTIR, Model no: VERTEX
94 70, Bruke, German). KBr was used as matrix to disperse the ferrite nanoparticles for
95 compressing disk sample. The absorbance spectra of the nanoparticles were
96 determined with an ultraviolet-visible spectrophotometer (Model No: 722, Hengping,
97 China). The magnetic property was measured with a vibrating sample magnetometer
98 (VSM, Model No: Versa Lab, Quantun Design, USA)

99 To study the photocatalytic and photo-Fenton like degradation of malachite
100 green in a water on the nanoparticles. The malachite green aqueous solution with a
101 concentration of $1\times 10^{-6}\text{M}$ was first prepared. In each experiment, 50 ml malachite
102 green aqueous solution and 25 mg one of the ferrite nanoparticles were added into a
103 glass beaker with constant stirring for 1-2 min. The photocatalysis experiment was
104 carried out under the irradiation of sunlight. The intensity of sunlight reaching the
105 surface of the solutions was measured with a solar power meter (Model no: SM206,
106 China) and is $\sim 250\text{ W}\cdot\text{m}^{-2}$. After leaving to steady state in dark for 10 min and
107 afterward each irradiation interval, $\sim 3\text{ ml}$ solutions were took out and filtrated out the
108 suspended tiny particles and subsequently measured for their absorbance on a
109 spectrophotometer (Model No: 722N, Hengping, China). The solutions after the test
110 were returned to the beakers to maintain the normal volume of the solutions under test.
111 Similar experiment was carried out in the condition of adding $0.5\text{ ml H}_2\text{O}_2$ into the

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 increases when nickel content (x) increase from 0 to 0.2 and then decreases with further cobalt substitution, drawing out variation trend in crystallinity of the nanoparticles. This decrease trend of the crystallinity with cobalt substitution was also reported for the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles synthesized by solvothermal route [23]. This could be mainly due to smaller radius difference (0.72–0.64 Å) between Ni^{2+} and Fe^{3+} ions than (0.74–0.64 Å) between Co^{2+} and Fe^{3+} ions. The

134 smaller radius difference leads to smaller inhibition of Ni^{2+} substitution for Fe^{3+} to
135 the spinel crystal growth than Co^{2+} substitution. Moreover, the position of strong peak
136 (311) shifts to lower 2θ with cobalt substitution (Fig. 1b). This can be ascribed to the
137 decrease in the interplanar crystal spacing (d) based on Bragg's equation, for which
138 smaller ionic radius of Ni^{2+} (0.72 Å) than the Co^{2+} (0.74 Å) may be main reason. The
139 lattice parameter of the nanoparticles with cubic crystal structure can be calculated by
140 following equation using XRD analysis data:

$$141 \quad \frac{a^2}{d^2} = h^2 + k^2 + l^2 \quad (1)$$

142 Calculated a values equal 0.8236 nm, 0.8263 nm, 0.8298 nm, 0.8321 nm, 0.8339 nm
143 and 0.8377 nm for the Co content $x=0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 , respectively (Fig.
144 1c). This indicates the expansion of the lattice with the cobalt substitution, agreeing
145 with the position shift of (311)-peak. Similar lattice parameter variation was also
146 reported in previous literature [16 24]. This lattice expansion may be caused by larger
147 cation radius of Co^{2+} than Ni^{2+} and the decrease in crystallinity. Moreover, the lattice
148 parameter a of CoFe_2O_4 equals to 0.8391 nm (JCPDS: 22-1086) that is larger than
149 0.83379 nm (JCPDS: 74-2081) and 0.83390 nm (JCPDS: 10-0325) of the NiFe_2O_4 .
150 This clearly indicates that Co^{2+} enters the ferrite lattices by replacing the Ni^{2+}
151 according to Vegard's law. Furthermore, the lattice parameter of the all ferrites is
152 smaller than the value given in the JCPDS card, especially as the Co content
153 approaches zero. This could be ascribed to the high-pressure effect in the condition of
154 hydrothermal synthesis. Similarly, the lattice parameter of the NiFe_2O_4 nanoparticle is
155 smaller when they were synthesized by hydrothermal process than by sol-gel method

[25]. The average particle sizes of the nanoparticles determined from XRD data analysis are in a range of ~ 13.8 – 26.2 nm. They also first increase with the increase of cobalt content (x) from 0 to 0.2 and then decrease with further cobalt substitution (Fig. 1c).

3.2. SEM analysis

Figure 2 shows the typical SEM micrographs of the nanoparticles. Most of the nanoparticles show spherical particle morphology with somewhat agglomerated (Fig. 2ac–2df), while the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x=0.8$ and 1.0) nanoparticles have approximately cubical particle morphology (Fig. 2e and 2f). This could be mainly due to same reason of the difference in crystallinities of the nanoparticles. From the SEM micrographs, the average particle sizes are in the range of ~ 15 – 90 nm that increases as the increase of x from 0 to 0.8 and then decreases with further cobalt substitution. The sizes of the nanoparticles with $x=0.8$ and 1.0 are obviously larger than the results of XRD analysis, 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 ~ 3416 cm^{-1} is attributed to the stretching vibration of surface hydroxyls absorbed on surface and O–H groups in absorbed water [26]. The peak centered at 1620 cm^{-1} is assigned to the H–O–H bending vibration in water molecular [27] or the OH deformation vibration due to surface hydroxyls [28, 29]. 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 [30] due to the adsorbed CO_2 . The

178 two peaks at $\sim 483\text{ cm}^{-1}$ and $\sim 616\text{ cm}^{-1}$ are assigned as the vibrations of ferrite groups
179 [31], corresponding to the octahedral and tetrahedral sites of positive ions in the
180 ferrite, respectively [27, 32]. The difference in absorption positions of the octahedral
181 and tetrahedral complexes of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ crystals is due to the different distances
182 between $\text{Fe}^{3+}-\text{O}^{2-}$ in the octahedral and tetrahedral sites. This confirms the formation
183 of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ structure.

184 **3.4. Optical absorption analysis**

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

190 **3.5. Photocatalytic degradation of the dye in a water on the nanoparticles**

191 Figure 5 shows the concentration variations of the malachite green aqueous solutions
192 on the nanoparticles with the irradiation time of sunlight. The degradation rate
193 increases as the increase of Co content. This increase of degradation rate could be
194 ascribed to the decreases of band gap and average particle size and the increase of
195 light absorbance of nanoparticles as the increase of Co content. In addition, the ORP
196 values are negative and decrease as the increase of Co content (Fig. 6). This indicates
197 that the nanoparticles surface are dominantly reductive in the photocatalysis condition
198 and this characteristics enhances as the increase of Co content.

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

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

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

In which, *C*₀ is initial concentration, *k* is quasi-kinetic rate constant, *T* is reaction temperature, and *A* is a constant. Fig. 8 shows the plots of ln(*C*/*C*₀) versus *t*. The plots are approximately linear. The *k* values can be estimated directly from the linear regression analyses of the plots. The estimated *k* values are in the range of

222 $\sim 2.23\text{--}7.2 \times 10^{-2} \text{ min}^{-1}$ and increase about one magnitude to $\sim 1.3\text{--}6.0 \times 10^{-1} \text{ min}^{-1}$ as
223 H_2O_2 is used. The k values increase as the increase of Co content in both cases with
224 and without H_2O_2 .

225 **3.7. Magnetic property of the nanoparticles**

226 Figure 9a show the room temperature hysteresis loops of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$
227 nanoparticles. The nanoparticles are all ferromagnetic. With increasing applied field,
228 the magnetization of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles increases, and nearly reaches
229 saturation state under highest applied magnetic fields of 30 KOe. Maximum value of
230 magnetization at applied field of 30 KOe (saturation magnetization M_s) is in the
231 ranges of $\sim 50.7\text{--}64.2 \text{ emu} \cdot \text{g}^{-1}$, and first increases and then decrease with the increase
232 of Co content (Fig. 9b). The coercivity (H_c) is in the range of $\sim 0.4\text{--}1.7 \text{ kOe}$ (Fig. 9b).
233 The ferrite nanoparticles with Co content $x=0.8$ show maximal M_s and M_r . This can
234 be mainly ascribed to the maximal cation distribution of Fe^{3+} and Co^{2+} at the
235 octahedral site (B-site) at Co content $x=0.8$ since the magnetic moments of Zn^{2+} , Co^{2+}
236 and Fe^{3+} are 0 μB , 3 μB and 5 μB , respectively. Other reasons may be the difference
237 in particle size, easy magnetization axis, and shape anisotropy. Such large M_s low
238 H_c can provide an excellent magnetically separable performance for the ferrite
239 nanoparticles in the final degraded dye aqueous solution.

240

241 **4. Conclusions**

242 The effect of the Co content on the microstructure, photocatalytic activity and

243 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.
244 The room temperature X-ray diffraction confirmed the formation of single-phase
245 Co-Ni ferrites. High photocatalytic activity of the nanoparticles was observed in the
246 sunlight-excited photodegradation of malachite green in a water. Significantly, a small
247 amount of H_2O_2 addition into the dye aqueous solution resulted in remarkably
248 enhanced photodegradation, indicating an Fenton-like reaction. Since the increases of
249 light absorbance and the decreases of band gap and average particle size with the
250 increase of Co content, the photodegradation and Fenton-like photodegradation rates
251 increased as the increase of Co content. Quasi-kinetic rate constant k values are in the
252 range of $\sim 2.23-7.2 \times 10^{-2} \text{ min}^{-1}$ and increase about one magnitude to $\sim 1.3-6.0 \times 10^{-1}$
253 min^{-1} as H_2O_2 is used. The measurement of oxidation-reduction potential reveals the
254 dominant reductive photocatalytic characteristics of the nanoparticle surface in the
255 photodegradation condition without H_2O_2 . This reductive characteristics linearly
256 increased as the increase of Co content. Whereas the oxidation-reduction potential as
257 using H_2O_2 was larger than that without H_2O_2 and showed nonlinear variation with
258 the Co content. The synthesized ferrite nanoparticles also show high saturation
259 magnetizations and low coercivities, which can provide a excellence magnetically
260 separable performance for the nanoparticles in the final photodegraded dye solution.

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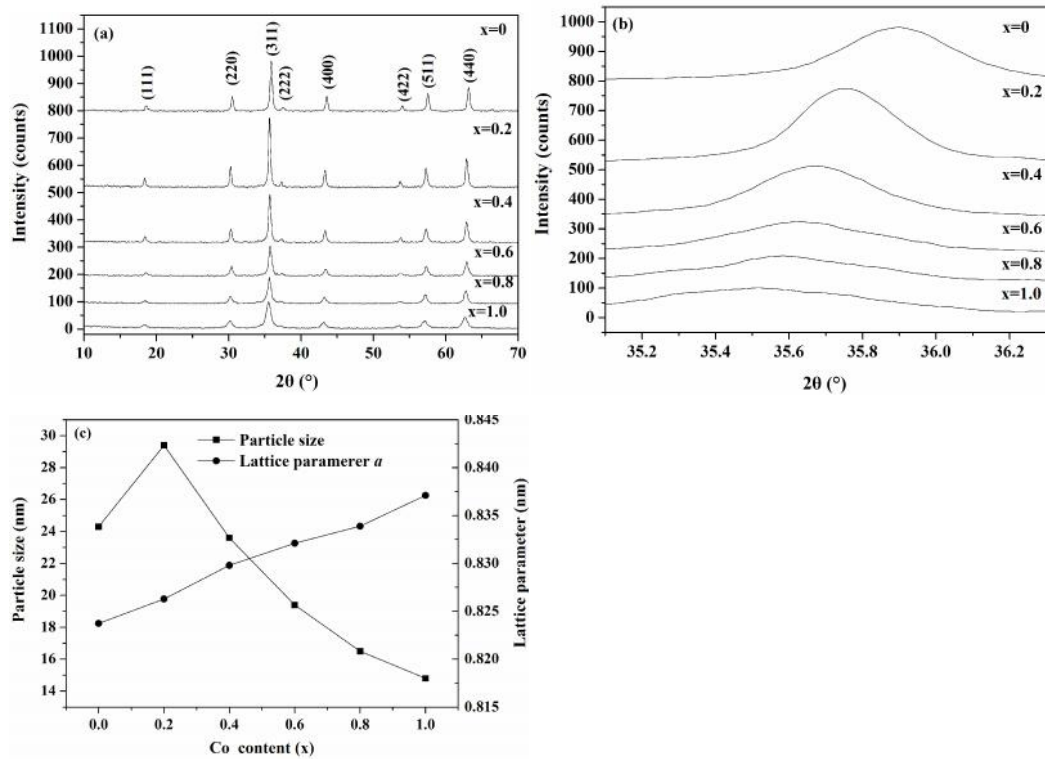
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372 **Figures:**



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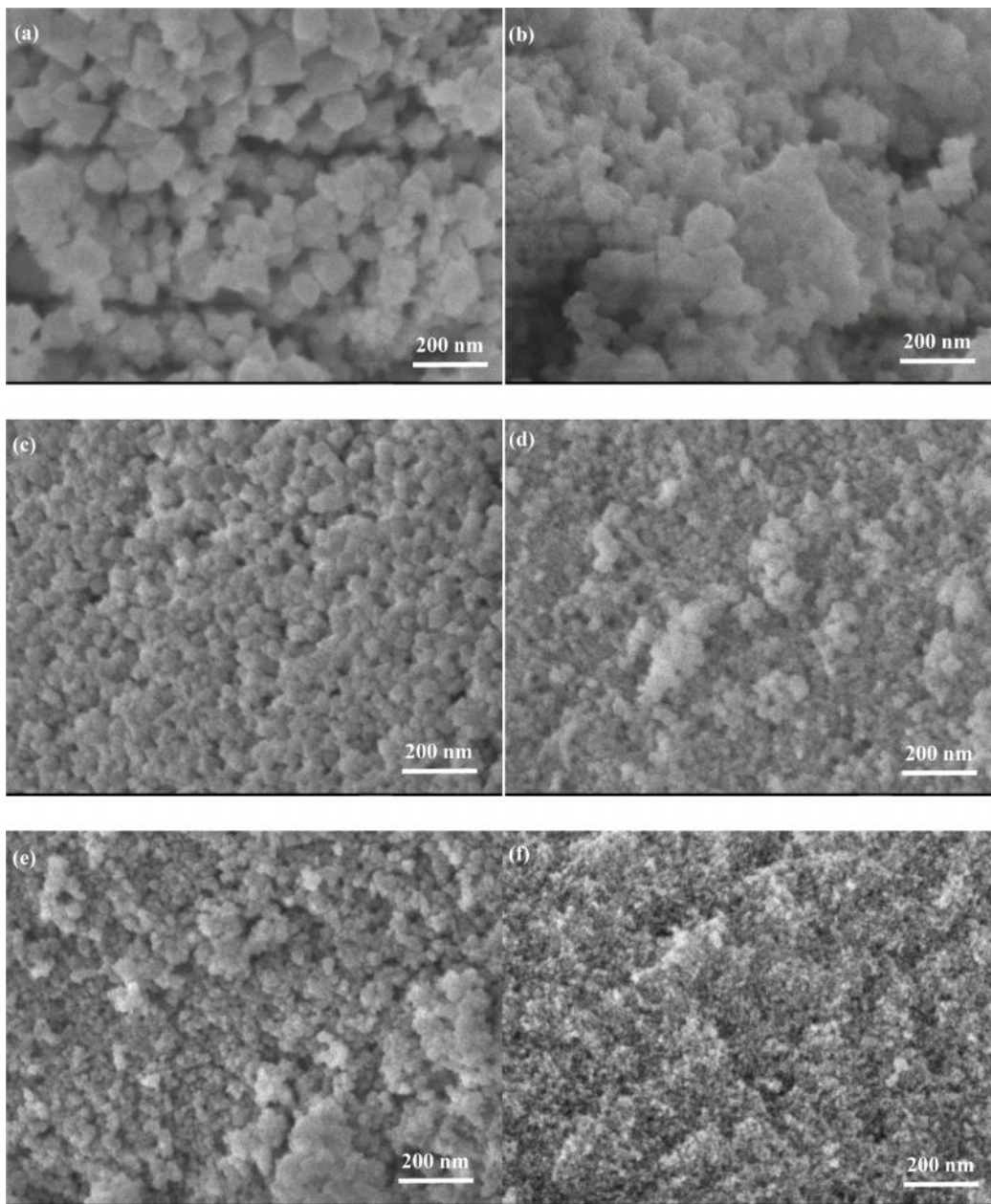
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375 Figure 1. (a) XRD patterns and (b) Enlarged (311) peak in the XRD patterns (c)

376 Average particle size and lattice parameter of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$

377 nanoparticles

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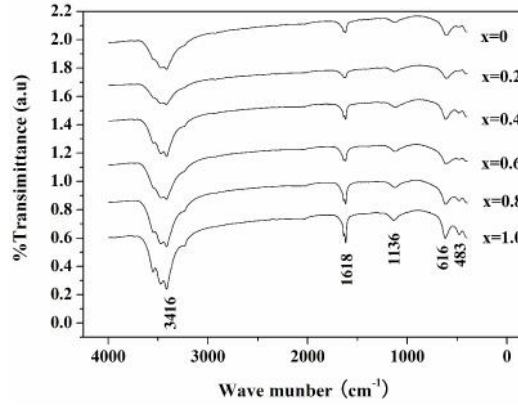
380 Figure 2. SEM micrographs of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with various Co

381 content x =(a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0

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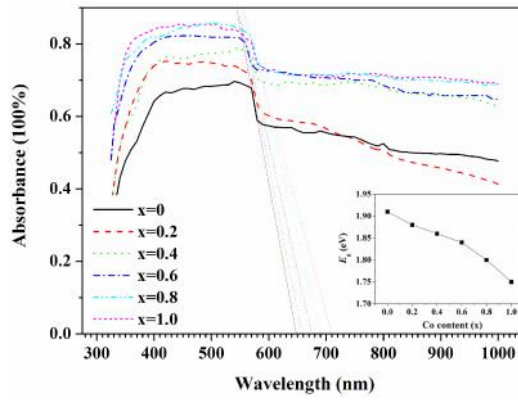
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386 Figure 3. FTIR spectra of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles

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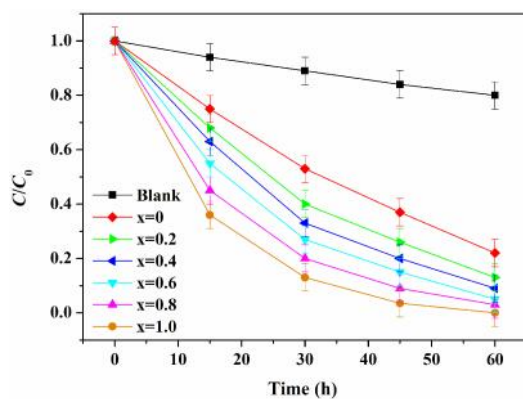


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391 Figure 4. Absorbance spectra of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles. Inserted figure is

392 the plots of band gap (E_g) vs. Co content (x)

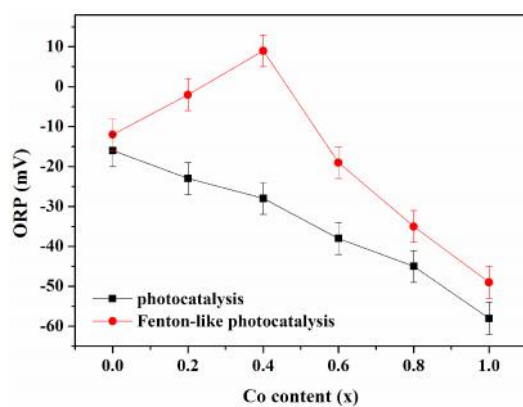
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395 Figure 5. Concentration variations of malachite green aqueous solutions on the

396 $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with the irradiation time of sunlight



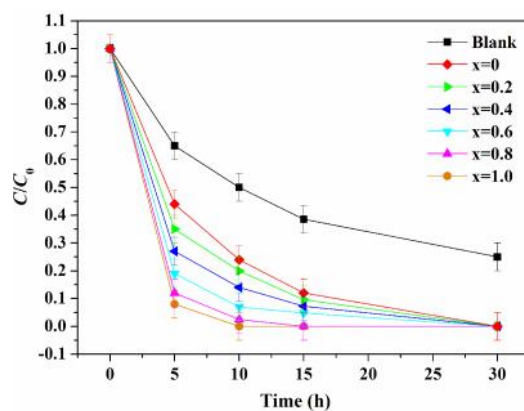
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398 Figure 6. ORP variations of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with Co content (x)

399 in the photocatalytic and photo-Fenton-like degradation systems

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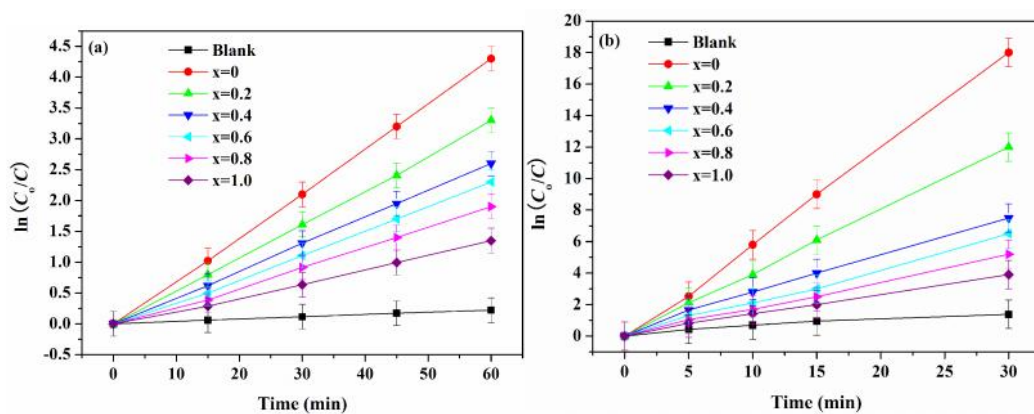
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403 Figure 7. Concentration variations of malachite green aqueous solutions containing
 404 H_2O_2 (concentration equal 10 ml/l) on the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles with
 405 the irradiation time of sunlight

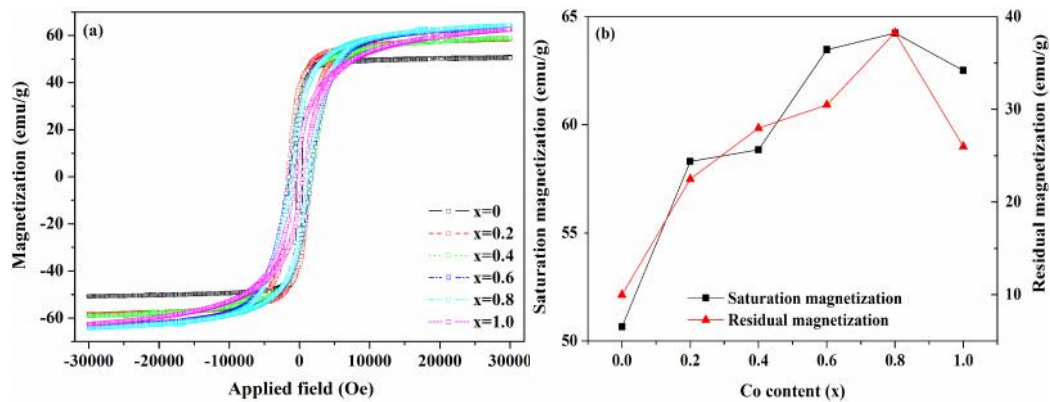
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408 Figure 8. The plots of $-\ln(C/C_0)$ vs. the irradiation time of sunlight in case of (a) H_2O_2
 409 free and (b) using H_2O_2

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