

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

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7 **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

8 by a hydrothermal process. The nanoparticles had a nano-scale average particle sizes

9 of 14.8–29.4 nm and a narrow band gap of 1.75–1.91 eV, decreasing as increasing

10 Co content. The nanoparticles showed an excellent sunlight-excited photocatalytic

11 activity to malachite green in water. Moreover, a small amount of H_2O_2 addition

12 resulted in an obviously enhanced photodegradation of the dye in a water, indicating a

13 Fenton-like reaction. The photodegradation and Fenton-like photodegradation rates

14 increased as the increase of Co content. Complete Co substitution for Ni cation

15 resulted in an optimal effect. Quasi-kinetic rate constant k values were in the range of

16 $2.23-7.2 \times 10^{-2} \text{ min}^{-1}$ and increased to $1.3-6.0 \times 10^{-1} \text{ min}^{-1}$ as the addition of H_2O_2 .

17 The measurement of oxidation-reduction potential of the nanoparticles in the

18 photodegradation condition indicated a reductive characteristics enhanced with the

19 increase of Co content. Furthermore, the nanoparticles possessed high saturation

20 magnetizations of 50.7–64.2 $\text{emu} \cdot \text{g}^{-1}$ and low coercivity of 0.4–1.7 kOe, which ensured that

21 well magnetic separable in finally degraded dye aqueous solution.

22 **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 ^{narrower} ~~shorter~~ band gap semiconductor than pure TiO₂ ^{should be of} ~~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 ^{after the} ~~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 ^{could} ~~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} ~~ferromagnetic~~ and ^{thus} ~~so have~~ magnetic separable ~~performance~~ from aqueous solution.

Previous ^{studies} ~~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 ^{higher} ~~more~~ efficiency than single ones. Different metal cations have different physical chemical behavior. Thus, it is necessary to investigate the effect of Co substitution for Ni ~~cation~~ ^{on the} photocatalytic activity of ~~the~~ nickel ferrite nanoparticles.

45 In recent years, advanced oxidation processes (AOPs) by using UV/H₂O₂ ^{have} ~~are~~
46 become a way to degrade organic compounds in dilute solutions. In general, it is
47 believed that the UV/H₂O₂ processes result in the formation of OH radicals in ~~the~~
48 solution, which accelerate the oxidation degradation of the organic compounds in ~~the~~
49 water. The ^{use of} ~~using~~ H₂O₂ has a main disadvantage of ~~its~~ high cost, whereas the low
50 oxidation rate is the major draw back of semiconductors, such as TiO₂. The combined
51 use of H₂O₂ and semiconductors is a way of solving this problem. Many studies have
52 been devoted to the examination of organic compound photodegradation in the
53 presence of H₂O₂ and TiO₂ [5,6]. This process is usually called ~~as~~ Fenton-like process,
54 because it is similar ^{to} ~~with~~ the advanced oxidation process based on the homogeneous
55 Fenton reagent (Fe²⁺/H₂O₂) or Fenton-like (Fe³⁺/H₂O₂) [7,8]. Up to ^{now} ~~today~~, various
56 Fenton and Fenton-like processes have been ^{used} ~~researched~~ for the degradation of organic
57 pollution. For example, activated carbon fibers [9], impure bismuth ferrite [10],
58 copper slag (90% Fe₂SiO₄) [11], ferrioxalate complexes [12], iron/ordered
59 mesoporous carbon catalyst [13], iron oxide nanotube layer [14], Cu²⁺ [15], et al.
60 ^{have been} ~~were~~ used as a Fenton-type photocatalyst or assisted Fenton-type photocatalysts.
61 However, the photocatalytic and Fenton-like photocatalytic activities of
62 Ni_{1-x}Co_xFe₂O₄ ferrite nanoparticles have not been ^{reported as} ~~found for~~ dye removal from waste
63 water in ~~previous literature~~. ^{Synthesize}
64 To date, many methods have been developed to ^{synthesize} ~~fabricate~~ spinel ferrite nanoparticles,
65 such as aerosol route [16], co-precipitation method [17, 18], ^{used} ~~usual~~ ceramic technique
66 [19], hydrolysis method [20], microwave-hydrothermal method [21], and

hydrothermal method [22]. The hydrothermal process ^{has been} ~~is~~ widely used ^{to synthesize} ~~for the~~ spinel ferrite ^S ~~synthesis~~ because of its simple process, low cost, low synthesis temperature, and small particle size of ~~synthesized nanoparticles~~ [22].

In ^{this} ~~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.

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~~ ^{The} 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. ^{The use of} ~~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 $30^\circ\text{C} \cdot \text{min}^{-1}$. After naturally cooling in the oven, the products were finally washed

90 repeatedly with distilled water, and then dried at 100 °C for 24 h.

91 ~~The crystalline structural phase~~ ^{Phase composition} of the synthesized $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles was
92 identified ~~at room temperature~~ ^{by} using X-Ray diffractometer (XRD, $\text{CuK}_{\alpha 1}$,
93 $\lambda=0.15406\text{nm}$, Model No: D/Max--2200PC, Rigaku, Japan). ~~The morphology~~ ^M of the
94 nanoparticles was analyzed ^{by} using scanning electron microscope (SEM, Model No:
95 JXM-6700F, Japan). Fourier transform infrared spectra of the nanoparticles were
96 measured with Fourier transform infrared spectrometer (FTIR, Model no: VERTEX
97 70, Bruke, German). KBr was used as matrix to disperse the ferrite nanoparticles for
98 compressing disk sample. ~~The~~ ^A absorbance spectra of the nanoparticles were
99 determined with an ultraviolet-visible spectrophotometer (Model No: 722, Hengping,
100 China). ~~The~~ ^M magnetic property was measured with a vibrating sample magnetometer
101 (VSM, Model No: Versa Lab, Quantun Design, USA)

102 To study the photocatalytic and photo-Fenton like degradations of malachite green in
103 a water on the nanoparticles, ~~The~~ malachite green aqueous solution with a
104 concentration of $1 \times 10^{-6} \text{M}$ was first prepared. In each experiment, 50 mL malachite
105 green aqueous solution and 25 mg ~~one~~ of the ferrite nanoparticles were added into a
106 glass beaker with constant stirring for 1-2 min. The photocatalysis experiment was
107 carried out under the irradiation of sunlight. The intensity of sunlight reaching the
108 surface of the solutions ~~was~~ ^{was} measured with a solar power meter (Model no: SM206,
109 China) ~~and is~~ ^{at} $\sim 250 \text{W} \cdot \text{m}^{-2}$. After leaving to steady state in dark for 10 min and
110 ~~afterward~~ ^{at} each irradiation interval, $\sim 3 \text{mL}$ solutions were took out and filtrated out the
111 suspended tiny particles and subsequently measured ~~for~~ ^{to check} 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~~^{by} adding 0.5 mL H₂O₂ 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~~^{by using} an oxidation-reduction potential tester (ORP-286, China). The ORP^S 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 ~~the~~^{the} 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~~ Fe₃O₄ (JCPDS: 88-0315), CoFe₂O₄ (JCPDS: 22-1086), and NiFe₂O₄ (JCPDS: ~~74-2081 and 10-0325~~). This indicates that the nanoparticles are ~~composed of~~ single phase ~~Ni_{1-x}Co_xFe₂O₄~~ 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 tend in crystallinity of the nanoparticles. This decrease trend of the crystallinity with cobalt substitution was also

134 reported for the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles synthesized by ^{using} solvothermal route [23].

135 This could be mainly due to ^{smaller} ~~smaller~~ radius difference (0.72–0.64 Å) between Ni^{2+}

136 and Fe^{3+} ions ^{than} (0.74–0.64 Å) between Co^{2+} and Fe^{3+} ions. The smaller radius

137 difference leads to smaller inhibition of Ni^{2+} substitution for Fe^{3+} to the spinel crystal
138 growth than Co^{2+} substitution. Moreover, the position of strong ^{est} peak (311) shifts to

139 lower 2θ with ^{Co} ~~cobalt~~ substitution (Fig. 1b). This can be ascribed to the ⁱⁿ ~~de~~crease in the

140 interplanar crystal spacing (d) based on Bragg's equation, ~~for which smaller ionic~~

141 ~~radius of Ni^{2+} (0.72 Å) than the Co^{2+} (0.74 Å) may be main reason.~~ The lattice

142 parameter of the nanoparticles with cubic crystal structure can be calculated by

143 following equation ^{with the} ~~using~~ XRD analysis data:

144
$$\frac{a^2}{d^2} = h^2 + k^2 + l^2 \quad (1)$$

145 Calculated a values ^{are} ~~equal~~ 0.8236 nm, 0.8263 nm, 0.8298 nm, 0.8321 nm, 0.8339 nm

146 and 0.8377 nm for the Co content $x=0, 0.2, 0.4, 0.6, 0.8$, and 1.0, respectively (Fig.

147 1c). This indicates the expansion of the lattice with the cobalt substitution, agreeing

148 with the ~~position~~ shift of (311)-peak. Similar lattice parameter variation was also

149 reported in ~~previous~~ literature [16, 24]. ~~This lattice expansion may be caused by larger~~

150 ~~cation radius of Co^{2+} than Ni^{2+} and the decrease in crystallinity.~~ Moreover, the lattice

151 parameter a of CoFe_2O_4 equals to 0.8391 nm (JCPDS: 22-1086) that is larger than

152 0.83379 nm (JCPDS: 74-2081) and 0.83390 nm (JCPDS: 10-0325) of the NiFe_2O_4 .

153 ~~This clearly indicates that Co^{2+} enters the ferrite lattices by replacing the Ni^{2+}~~

154 ~~according to Vegard's law.~~ Furthermore, the lattice parameter of the all ferrites is

155 smaller than the value given in the JCPDS card, especially as the Co content

approaches zero. This could be ascribed to the high-pressure effect in the condition of hydrothermal synthesis. Similarly, the lattice parameter of the NiFe_2O_4 nanoparticle is smaller when they were synthesized by hydrothermal process than ~~by~~^{using} sol-gel method [25]. The average crystal sizes of the nanoparticles are determined from XRD data ~~analysis~~ with Debye–Scherrer’s formula [26]:

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

where λ is the X-ray wavelength, β the full width at half maximum (FWHM) of the considered peak and θ is the Bragg angle. The determined results are 23.4, 29.4, 23.6, 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 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~~^{ion} morphology with some ~~that~~^{ion} agglomerated (Fig. 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 cubical ~~particle~~ morphology (Fig. 2a and 2b). 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 ~~also~~^{is increased} increased as the increase of x from 0 to 0.8 and then decrease^d 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~~^{means} 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 [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 ^{to} ~~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 ^{between} ~~of~~ the octahedral and tetrahedral complexes ^{we} 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 ^{single phase} of $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ^{structure} ~~structure~~.

191 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 ^{with increasing} ~~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 ~ 1.91 eV to ~ 1.75 eV as ~~the increase of Co content~~ (Inserted figure in Fig. 4).

197 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

200 increases ^{with increasing} ~~as the increase of~~ Co content. This increase of degradation rate could be
201 ascribed to the decreases of band gap and average particle size and the increase of
202 light absorbance of nanoparticles ~~as the increase of Co content~~. In addition, the ORP
203 values are negative and decrease ~~as the increase of Co content~~ (Fig. 6). This indicates
204 that the nanoparticles surface are dominantly reductive in the photocatalysis condition,
205 ~~and this characteristic~~ ^{is} ~~enhances as the increase of Co content.~~ ^{with increasing}

206 3.6. Fenton-like photodegradation ~~of the dye in a water on the nanoparticles~~

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

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

224
$$\frac{C_0}{C} = A \exp\left(\frac{kt}{T}\right)$$

225 ~~In which~~, C_0 is initial concentration, k is quasi-kinetic rate constant, T is reaction
 226 temperature, and A is a constant. Fig. 8 shows the plots of $\ln(C/C_0)$ versus t . The plots
 227 are approximately linear. The k values can be estimated directly ~~from the linear~~ ^{from}
 228 ~~regression analyses~~ of the plots. The estimated k values are in the range of
 229 ~~$2.23-7.2 \times 10^{-2} \text{ min}^{-1}$~~ ^{which is} ~~and increase about one magnitude~~ ^{and nearly one order of} to $\sim 1.3-6.0 \times 10^{-1} \text{ min}^{-1}$ as
 230 H_2O_2 is used. The k values increase ^{with increasing} ~~as the increase of~~ Co content in both cases with
 231 and without H_2O_2 .

3.7. Magnetic property of the nanoparticles

233 Figure 9a show ~~the~~ room temperature hysteresis loops of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$
 234 nanoparticles. The nanoparticles are all ^{$\hat{i}$} ferromagnetic. With increasing applied field,
 235 the magnetization of the $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ nanoparticles increases, and ~~nearly~~ ^{k} reaches
 236 saturation state under highest applied magnetic fields of 30 ~~KOe~~ ^{k} . Maximum value of
 237 magnetization at applied field of 30 ~~KOe~~ ^{k} (saturation magnetization M_s) is in the
 238 ranges of ~~$45.7-64.2 \text{ emu} \cdot \text{g}^{-1}$~~ ^{$k$} ~~and first increases and then decrease with the increase~~
 239 ~~of Co content~~ (Fig. 9b). The coercivity (H_c) is in the range of ~~$0.4-1.7 \text{ kOe}$~~ (Fig. 9b).
 240 The ferrite nanoparticles with Co content $x=0.8$ show maximal M_s and M_r . This can
 241 be mainly ascribed to the maximal cation distribution of Fe^{3+} and Co^{2+} at the
 242 octahedral site (B-site) ~~at Co content $x=0.8$~~ ^{k} since the magnetic moments of Zn^{2+} , Co^{2+}
 243 and Fe^{3+} are $0 \mu_B$, $3 \mu_B$ and $5 \mu_B$, respectively. Other reasons ^{include} ~~may be~~ the difference

in particle size, easy magnetization axis, and shape anisotropy. ^{the and} Such large M_s low ^{tion} H_c can provide ~~an~~ excellent magnetic ~~ity~~ ^{tion} separable performance for the ferrite nanoparticles in the final degraded dye aqueous solution.

4. Conclusions

~~The effect of the Co content on the microstructure, photocatalytic activity and~~
^{Single phase} ~~magnetic property of the $Ni_{1-x}Co_xFe_2O_4$ ($x=0.1-1.0$) ferrite nanoparticles was studied.~~ ^{showed}
~~The room temperature X-ray diffraction confirmed the formation of single-phase~~
^h ~~Co-Ni ferrites. High photocatalytic activity of the nanoparticles was observed in the~~
^{the addition of} sunlight-excited photodegradation of malachite green in a water. Significantly, a small
amount of H_2O_2 ~~addition into the dye aqueous solution~~ ^{the presence of} resulted in remarkably
enhanced photodegradation, indicating ~~an~~ Fenton-like reaction. ^{Due to} ~~Since~~ the increases ^{of $\ln$}
light absorbance and the decreases ⁱⁿ of band gap and average particle size, ~~with the~~
~~increase of Co content~~ ^{with increasing}, 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 $2.23-7.2 \times 10^{-2} \text{ min}^{-1}$ and increased about one magnitude to
 $\sim 1.3-6.0 \times 10^{-1} \text{ min}^{-1}$ as H_2O_2 was used. ~~The measurement of oxidation-reduction~~
~~potential reveals the dominant reductive photocatalytic characteristics of the~~
~~nanoparticle surface in the photodegradation condition without H_2O_2 . This reductive~~
~~characteristics linearly increased as the increase of Co content. Whereas the~~
~~oxidation-reduction potential as using H_2O_2 was larger than that without H_2O_2 and~~
~~showed nonlinear variation with the Co content. The synthesized ferrite nanoparticles~~

266 also show ^{ed} high saturation magnetizations and low coercivities, which ~~can~~ ^d provide ⁿ
267 excellence magnetically ^{tion} separable performance for the nanoparticles in ~~the final~~
268 ~~photodegraded dye solution.~~

269

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