

Communication

# Recyclable Magnetic Cu/CuFe<sub>2</sub>O<sub>4</sub> Nanocomposites for the Rapid Degradation of 4-NP

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Abstract: Magnetic Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites were prepared by the one-pot thermal decomposition of acetylacetone compounds. Adjusting the molar ratios of Fe to Cu was used to control the content of Cu in the synthetic process. XRD, TEM, XPS and UV-Vis were employed to reveal detailed structural and catalytic activities of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites. Magnetic measurements demonstrated that Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites possessed a considerable magnetic saturation. Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites showed superb efficiency in the degradation of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). 4-NP could be reduced by Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites within 40 s in the attendance of NaBH<sub>4</sub>. Cu nanocrystals played an indispensable rose in the enhancement of catalytic performance. The synergistic effect of Cu and CuFe<sub>2</sub>O<sub>4</sub> nanocrystals achieved the high-efficiency catalytic reduction for 4-NP. After six recycling experiments, the efficiency of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites was almost stable. Our work advances a straightforward strategy to synthesize efficient and recoverable Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites, which has promising utilizations in the purifying of nitrophenolic contamination.

Keywords: Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites; 4-nitrophenol; magnetic materials; catalytic reduction

## 1. Introduction

Nitrophenolic compounds are the most important organic chemical intermediates and have been widely employed as the main raw materials for manufacturing pharmaceuticals, pesticides and dyes [1–3]. There are three kinds of isomers: namely, o-nitrophenol, m-nitrophenol and p-nitrophenol (synonym: 4-nitrophenol (4-NP)) [4]. Among the three isomeric nitrophenols, 4-NP has the highest toxicity and the most stable structure, which makes it a fearful hazard to both the ecotope and the human body's health [5–8]. Considerable research efforts have been devoted to the removal and harmless disposal of 4-NP. For example, Liu et al. prepared a novel ethylenediamine rosin-based resin as adsorbent material to remove 4-NP from aqueous solutions [9]. Tan et al. synthesized magnetic imprinted porous foams and achieved the selective identification and physical removal of 4-NP from the aqueous environment [10]. Considering that physical adsorption does not fundamentally solve the problem of phenolic pollution, the degradation of 4-NP to the relatively environmentally friendly 4-aminophenol (4-AP) has attracted much more attention [11,12]. Many methods have been implemented for the conversion of 4-NP to 4-AP, including the photocatalytic method [13], Fenton [14] and electrochemical methods [15,16]. Unfortunately, the catalytic efficiency of these approaches is frequently very low. More seriously, byproducts with higher toxicity might be created in these protocols



of elimination of 4-NP. Recently, chemical degradation of 4-NP with the help of the reducing agent NaBH<sub>4</sub> has attracted widespread attention due to high catalytic efficiency [17,18].

The spinel-type ferrites (MFe<sub>2</sub>O<sub>4</sub>), where M represents the divalent metal cation, were mainly applied to the fields of magnetic resonance image (MRI) and drug delivery in the earlier study due to their unique magnetic properties [18–20]. Interestingly, the recent studies revealed that  $MFe_2O_4$ has high catalytic performance. For instance,  $MFe_2O_4$  (M = Zn, Co, Mn) nanoparticles were prepared via the sol-gel-hydrothermal method and achieved elimination of nitrophenol [21]. Several research studies have proved that the copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) possesses the highest catalytic performance among all the metal ferrites due to high efficiency of inter-valence electron motion between Cu<sup>+</sup>-Cu<sup>2+</sup> and  $Fe^{2+}-Fe^{3+}$  ion pairs in the octahedral sites [22–24]. In order to further enhance the catalytic performance of CuFe<sub>2</sub>O<sub>4</sub>, noble metal/ferrite nanocomposites are considered to be the most promising nanocatalysts, owing to the synergistic effects of the bi-catalyst [25–27]. However, the high costs and the scarce resources of noble metals limit their practical application. The cheap, easily available and environmentally friendly transition metal Cu nanocrystals are desirable alternatives to noble metals. Li et al. utilized the solvothermal method to synthesize Cu/CuFe2O4 nanocomposite as a pivotal catalyst to obliterate detrimental stain blue in a Fenton-like reaction and confirmed that the synergetic effect between Cu<sup>0</sup> and CuFe<sub>2</sub>O<sub>4</sub> facilitated catalytic degradation for dyestuff [28]. Koley et al. announced that the biomass-derived furfural was catalyzed to 2-methylfuran by a  $Cu/CuFe_2O_4@C$  composite [29]. However, there are comparatively few studies devoted to the catalytic degradation of 4-NP with Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites as catalysts.

In this work, pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals and Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites were prepared via the one-pot thermal decomposition method. The effect of the addition of an amount of precursor Cu(acac)<sub>2</sub> on structures, morphologies and catalytic properties of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites was investigated. Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites exhibited an ultrahigh synergistic catalysis for 4-NP degradation. A possible reaction model was proposed. Furthermore, the reusability of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites was studied.

## 2. Results

Figure 1 presents a schematic diagram of the preparation process of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites. The molar ratios of Fe/Cu in initial solution are set as 2:1.5, 2:1.4, 2:1.3 and 2:1.2, which are named as FC-1.5, FC-1.4, FC-1.3 and FC-1.2, respectively. Figure 2 exhibits the XRD patterns of the Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites with different molar ratios of Fe to Cu. For comparison, the XRD diffraction pattern of pure CuFe<sub>2</sub>O<sub>4</sub> is shown in Figure S1. The diffraction patterns for FC-1.5 have six peaks at 30.1°, 35.5°, 43.1°, 57.1°, 62.7° and 74.2°, corresponding to (220), (311), (400), (511), (440) and (533) of cubic spinel structural CuFe<sub>2</sub>O<sub>4</sub> (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 77-0010), respectively [30]. In addition, the diffraction peaks marked with green pentagrams can be attributed to characteristic crystal planes of Cu (JCPDS card no. 04-0836) [31]. Notably, although the diffraction peaks of CuFe<sub>2</sub>O<sub>4</sub> and Cu at around 43° and 74° overlap, the peak at 50.4° is the characteristic of metallic Cu, which demonstrates the coexistence of CuFe<sub>2</sub>O<sub>4</sub> and Cu. A possible explanation is that partial Cu<sup>2+</sup> ions are reduced to Cu in the preparatory course of CuFe<sub>2</sub>O<sub>4</sub> nanocomposites owing to the strong reducing ability of oleylamine [32]. With the increase of the molar ratios of Fe to Cu, no evident shift of diffraction peak position is observed, but the peak intensity of Cu decreases gradually, implying the decrease of Cu content.

TEM, high-angle annular dark-field (HAADF-STEM) and the corresponding energy-dispersive X-ray (EDS) elemental mapping images were used to characterize morphology and element distribution of FC-1.2 and FC-1.5, as shown in Figure 3. For both samples, agglomeration of nanoparticles is observed due to the magnetic interaction between CuFe<sub>2</sub>O<sub>4</sub>. The elements Fe, Cu and O are equably interspersed on the surfaces of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites based on the corresponding EDS elemental mapping pictures of FC-1.2 (Figure 3c) and FC-1.5 (Figure 3d). Since the atomic number of the elements determines the contrast of HAADF-STEM, it can be concluded that the bright dots in HAADF-STEM

correspond to the Cu nanocrystals with higher atomic number. Moreover, with the increase of Cu contents, the amount of Cu nanocrystals increases, which is consistent with the above XRD results.

In order to definitely verify the coexistence of  $CuFe_2O_4$  and Cu, elemental valence states and the elementary composition of  $Cu/CuFe_2O_4$  nanocomposites prepared by the thermal decomposition method were evaluated with XPS measurement. As seen from Figure S2, XPS survey scans of FC-1.2 and FC-1.5 show C, O, Fe and Cu peaks, among which C element is possibly assigned to the remaining carbon during the reaction [33–35]. Figure 4 presents the high resolution XPS spectra about Cu 2p and Fe 2p. Based on Gauss fitting, Cu 2p XPS spectra of FC-1.2 and FC-1.5 can be split into five peaks, which come from Cu 2p  $_{3/2}$ , Cu 2p  $_{1/2}$  and satellite peaks of Cu<sup>2+</sup> (Figure 4a). The doublet peaks located at 954.7 eV and 934.6 eV are assigned to Cu 2p  $_{1/2}$  and Cu 2p  $_{3/2}$  of Cu<sup>2+</sup> from CuFe<sub>2</sub>O<sub>4</sub> [36]. The coexistence of Cu<sup>2+</sup> and Cu<sup>0</sup> in Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites is proven by the peaks at 952.7 eV and 932.8 eV, which are ascribed to Cu<sup>0</sup> species. The Fe 2p spectra can also be separated into five individual peaks in Figure 4b. Peaks at 726.1 eV and 713.5 eV with a shakeup satellite at 719.5 eV can testify to the existence of Fe<sup>3+</sup>. The existence of Fe<sup>2+</sup> is confirmed by the peaks at 723.9 eV and 710.9 eV [37]. In addition, the ratios of XPS peak area of Cu<sup>2+</sup>/Cu<sup>0</sup> were calculated for the two samples, and the mass percentage of Cu<sup>0</sup> for FC-1.2 and FC-1.5 is 33.3% and 53.6%, respectively, implying that the molar ratios of Fe to Cu can affect the content of Cu<sup>0</sup> in the Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites.



Figure 1. Schematic diagram for preparation of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites.



Figure 2. XRD patterns of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites (FC-1.2, FC-1.3, FC-1.4 and FC-1.5).





**Figure 3.** TEM images of FC-1.2 (**a**) and FC-1.5 (**b**). High-angle annular dark-field (HAADF-STEM) pictures and the corresponding energy-dispersive X-ray (EDS) elemental mapping images (Cu, Fe and O) of FC-1.2 (**c**) and FC-1.5 (**d**).



Figure 4. High resolution XPS scans of Cu 2p (a) and Fe 2p (b) for FC-1.5 and FC-1.2.

A superconducting quantum interference device (SQUID) with an external magnetic field of -20,000 to 20,000 Oe was employed to study magnetic properties of the Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites under room temperature conditions. Figure 5 reveals the magnetization versus magnetic field loops of the Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites. All the samples exhibit ferromagnetic behaviors at room temperature conditions. The saturation magnetization (Ms) values of FC-1.5, FC-1.4, FC-1.3 and FC-1.2 are 20.2 emu g<sup>-1</sup>, 30.3 emu g<sup>-1</sup>, 42.5 emu g<sup>-1</sup> and 47.5 emu g<sup>-1</sup>, respectively. The decrease of Ms along with an increase of Cu content is possibly attributed to the counteraction between the magnetic CuFe<sub>2</sub>O<sub>4</sub> and the non-magnetic Cu nanocrystals, which indicates indirectly the presence of Cu in Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites [38]. The inset of Figure 5 demonstrates that FC-1.5 with the minimum value of Ms can easily be separated from the aqueous solution by an extra magnetic field, suggesting that all samples can be circulated in practical application.



**Figure 5.** Magnetization versus magnetic field loops of the Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites at different molar ratios (FC-1.2, FC-1.3, FC-1.4 and FC-1.5). Inset is the photograph of FC-1.5 in aqueous circumstance before and after external magnet force separation.

The reduction reaction of 4-NP in the attendance of excess NaBH<sub>4</sub> was chosen as a typical example system to evaluate reactive performance of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites. The catalytic process of 4-NP was detected by a UV-Vis absorption spectrophotometer. The extent of the reduction can be identified by observing the variation of absorption peak of 4-NP located in 400 nm. As seen from Figure 6a, when the NaBH<sub>4</sub> solution is instilled into the reaction system, the characteristic peak of 4-NP in 300 nm moves to 400 nm accompanied by an integral color change of the mixture from faint yellow to luminous yellow, which can be ascribed to the appearance of 4-nitrophenolate ions attributed to the addition of NaBH<sub>4</sub>. The 4-NP solution is steady and the peak at 400 nm remains nearly immobile about 10 h. As presented in Figure 6b, once the FC-1.5 participates in the system, the intensity of absorption bands in 400 nm significantly decreases and disappears within 40 s. In the meantime, a brand new peak appears and increases at 300 nm owing to the appearance of 4-AP [39]. Photographs of the degradation of the 4-NP solution catalyzed by FC-1.5 within 40 s are shown in Figure S3. As can be observed from Figure 6c, the catalytic activity of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites for 4-NP decreases with the decrease of Cu content, indicating that Cu nanocrystals play a significant role in Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites for reduction in the degradation of 4-NP. As seen from Figure S4, the reaction rate constant of FC-1.5 is 0.07 s<sup>-1</sup>, which is higher than that of other samples, obtained via the equation  $\ln (C_t/C_0) = -kt$ .  $C_t$  is used to represent the concentration of 4-NP at reaction time t and  $C_0$  represents delivery of the original concentration of 4-NP before the reaction starts. The rate constant (*k*) is calculated by the above equation. It is clear that the efficiency of  $Cu/CuFe_2O_4$  nanocomposites is superior to that of the pure CuFe<sub>2</sub>O<sub>4</sub> (Figure S5) [40]. In addition, to assess the reusability of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites, FC-1.5 was separated by using the magnet and rinsed with deionized water after the reaction was finished. The catalytic reactivity of FC-1.5 decreases slightly after six cycles, as presented in Figure 6d. The slight decrease of efficiency could be on account of loss of Cu nanocrystals in the circulation process.



**Figure 6.** (a) UV-Vis absorptions of 4-NP before and after adding NaBH<sub>4</sub> solution. (b) UV-Vis absorption spectral line for the degradation of 4-NP by FC-1.5 in the attendance of NaBH<sub>4</sub>. (c) Time taken for as-prepared samples to catalyze 4-NP. (d) The recyclability of FC-1.5 for the catalytic of 4-NP.

According to the above experimental data, a possible catalytic process for degradation of 4-NP by Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites is proposed, as shown in Scheme 1. Based on the thermodynamics principle, a catalytic reaction of 4-NP in attendance of NaBH<sub>4</sub> is feasible; however, it is impractical from the perspective of the kinetics because of the differences in reduction potential between borate to borohydride and 4-NP to 4-AP [41–43]. Therefore, the introduction of suitable nanocatalysts is vital in realizing the degradation of 4-NP. In the reaction system,  $BH_4^-$  ions generated by the ionization of NaBH<sub>4</sub> act as electron donors and hydrogen suppliers [44–46]. When Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites are added to the mixture, 4-NP and the BH<sub>4</sub><sup>-</sup> ions in aqueous medium are absorbed on the surfaces of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites. Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites serve as intermediates to transfer electrons from donor BH<sub>4</sub><sup>-</sup> to receptor 4-NP, which can surmount the kinetic barrier of the reaction and lead to the formation of 4-AP [47]. It is noted that Cu<sup>2+</sup> can be expediently converted to Cu<sup>+</sup> in the presence of BH<sub>4</sub><sup>-</sup> anion. The changes of valence state between Cu<sup>+</sup>-Cu<sup>2+</sup> and Fe<sup>2+</sup>-Fe<sup>3+</sup> ion pairs in CuFe<sub>2</sub>O<sub>4</sub> can enhance catalytic activity, which is the distinct advantage over CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> [48]. Notably, Cu nanocrystals play key roles in the enhancement of catalytic degradation of 4-NP. On one hand, Cu nanocrystals can directly transfer electrons from BH<sub>4</sub><sup>-</sup> ions to 4-NP. On the other hand, Cu nanocrystals can participate in and boost the electron transfers of neighboring CuFe<sub>2</sub>O<sub>4</sub> nanocrystals between  $Cu^+-Cu^{2+}$  and  $Fe^{2+}-Fe^{3+}$  ion pairs [49–51].



**Scheme 1.** Possible process of the degradation of 4-NP to 4-AP by Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites in the attendance of NaBH<sub>4</sub>.

#### 3. Materials and Methods

The chemicals in this work are exhibited in Supplementary Materials and all the chemicals are not in need of further purification. Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites were fabricated by the one-pot thermal decomposition process. The following was dissolved in a mixed solution of oleylamine and benzyl ether: 0.262 g of Cu(acac)<sub>2</sub> and 0.762 g of Fe(acac)<sub>3</sub>. After the mixed solution was vigorously stirred for 2 h, the solution was transferred to a three-necked flask. The mixture was heated to 110 °C for 1.5 h with sustained stirring under the protection of argon to remove water. Then, the mixture was heated to 300 °C and refluxed for 1 h. After the mixed solution was cooled down naturally, the applied magnetic field could collect the samples from the reaction media. Ethanol and deionized water were used to rinse the product several times to achieve pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals. In addition, the molar ratios of Fe<sup>2+</sup>/Cu<sup>2+</sup> in the initial solution were adjusted to 2:1.5, 2:1.4 2:1.3 and 2:1.2 and the same synthetic procedure as the pure CuFe<sub>2</sub>O<sub>4</sub> was carried out, which were named FC-1.5, FC-1.4, FC-1.3 and FC-1.2, respectively. Figure 1 presents a schematic diagram of the acquirement process of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites.

X-ray powder diffraction (XRD) analysis was conducted using a Rigaku D/MAX 2500 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Transmission electron microscopy (TEM) images were obtained by using a Hitachi H-800 transmission electron microscope operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, ThermoFisher Scientific, Waltham, MA, USA) was employed to observe element composition. The magnetic properties were conducted with a superconducting quantum interference device (SQUID, Quantum Design MPMS3 VSM-SQUID, Quantum Design, San Diego, CA, USA) magnetometer at room temperature. Change in 4-NP concentration was monitored with an ultraviolet-visible spectrophotometer (UV-Vis, UV-3600 plus, Shimadzu, Kyoto, Japan) in the range of 250–700 nm.

The degradation of 4-NP by pure  $CuFe_2O_4$  nanocrystals and  $Cu/CuFe_2O_4$  nanocomposites was performed in a standard quartz cuvette. The reaction of pure  $CuFe_2O_4$  nanocrystals and  $Cu/CuFe_2O_4$ nanocomposites was observed via the UV-Vis spectroscopy at room temperature. Typically, 2 mL of 4-NP and 1 mL of NaBH<sub>4</sub> were infused into a standard quartz cuvette with a 1 cm path length. After the color of the liquid turned from faint yellow to luminous yellow, 100 µL of the prepared pure  $CuFe_2O_4$  nanocrystals and  $Cu/CuFe_2O_4$  nanocomposites were added to catalyze the reaction, respectively. Sequential change regarding the reaction in real time was observed by UV-Vis absorption spectra every 10 s in a scanning range of 200–700 nm. Moreover, to assess the reusability of the  $Cu/CuFe_2O_4$  nanocomposites, the  $Cu/CuFe_2O_4$  nanocomposites were separated by using a magnet and then rinsed with ethanol and deionized water after the reaction was finished. The identical reduction process of 4-NP was carried out another five times.

## 4. Conclusions

In conclusion, pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals and Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites were synthesized successfully by the thermal decomposition route. The XRD and TEM results proved the formation of Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites and the amount of Cu in Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites increased with the increase of the additive amount of acetylacetonate. XPS results indicated that Cu occurred in both zero-valent and divalent states and Fe existed in both divalent and trivalent states. Magnetic measurements showed that Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites were ferromagnetic at room temperature and the Ms value decreased from 47.5 to 20.2 emu  $g^{-1}$  with increase of Cu content due to the counteraction between the magnetic  $CuFe_2O_4$  and non-magnetic Cu nanocrystals. In addition, Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites could efficiently catalyze degradation of 4-NP with the help of the NaBH<sub>4</sub> under the synergism of Cu and CuFe<sub>2</sub>O<sub>4</sub> nanocrystals. It was shown that Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites showed higher degradation efficiency compared to pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals. The rate constant (k) of FC-1.5 was 0.07, which was almost three times higher than that of pure  $CuFe_2O_4$  nanocrystals. Cu/CuFe<sub>2</sub>O<sub>4</sub> nanocomposites could also be swiftly collected and recycled six times without obvious decline of efficiency. Our research provides a complementary strategy in preparation for promising multifunctional nanocatalysts and extends knowledge into the catalysis mechanism for reduction of nitrophenolic compounds.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/12/1437/s1. Figure S1. XRD pattern of pure CuFe2O4 nanocrystals. Figure S2. XPS full survey spectra of FC-1.2 and FC-1.5. Figure S3. Photographs of the degradation of 4-NP solution catalyzed by FC-1.5 within 40 s in the attendance of NaBH4. Figure S4. (a)  $C/C_0$  versus reaction time during 4-NP reduction by FC-1.5, FC-1.4, FC-1.3, FC-1.2 (every 10 s). (b) Relationship of the ln[ $C/C_0$ ] and the reaction time during 4-NP reduction by pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals (every 20 s). (b) Relationship of the ln[ $C/C_0$ ] and the reaction time t for the reduction of 4-NP to 4-AP over pure CuFe<sub>2</sub>O<sub>4</sub> nanocrystals.

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