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Effect of sodium oleate as a buffer on the synthesis of superparamagnetic magnetite colloids

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ABSTRACT

In this study, superparamagnetic monodisperse magnetite colloids, around 5 nm in size, were prepared by dissolving iron chlorides, sodium hydroxide (NaOH) and sodium oleate (NaOL), in toluene/ethanol/water mixtures and refluxing for 4 h. The concentrations of NaOH and NaOL were varied to systematically investigate the effect on the surface properties, size, dispersion, and magnetic properties of magnetite nanoparticles (MNPs). The samples were characterized via XRD, FTIR, TGA, TEM, SAED, DLS, and VSM. The results indicated that the surface coatings of MNPs could be manipulated from oleate to hydroxyl groups via increasing the molar ratio of NaOH/Fe(II) more than 8. The amount of NaOH had no obvious influence on the size and the saturation magnetization of MNPs. Therefore NaOH was not a necessary reactant for forming magnetite crystals. On the contrary, NaOL was shown to be the most important component for synthesizing stable magnetite colloids. The NaOL acted as both a key reactant to buffer the pH environment and a surfactant to keep the MNPs stable in nonpolar solvent media.

1. Introduction

Magnetite nanoparticles (MNPs) in different carrier solutions called magnetic colloids (ferrofluids) have attracted more and more scientific and technological interest since the 1960s. Because of their unique properties in the magnetic field, extensive applications have been developed for more than three decades, such as magnetic sealing [1,2], heat transfer [3], damping [4], optics [5,6], as well as biomedical engineering [7,8]. Most applications require that MNPs are monodisperse and nonagglomerated in solvents for homogeneous physical and chemical properties, which has motivated much research in the preparation and processing of stable ferrofluids. Owing to van der Waals forces and magnetic forces, MNPs used for magnetic colloids are often covered with surfactants to prevent agglomeration.

Oleic acid (OA) or sodium oleate (NaOL), as an amphiphilic surfactant, has much higher affinity to MNP surfaces compared to other surfactants [9,10]. It can form a waterproof shell around the MNP core so that these nanocrystals are well dispersed in nonpolar organic solvents such as hexane and toluene. Therefore, several preparation methods for grafting MNPs with oleate have been developed. One conventional way is the chemical coprecipitation method. Excess base (e.g., NaOH) is introduced to form magnetite precipitates in Fe^{2+} and Fe^{3+} aqueous salt solutions. Then unadorned particles are mixed with OA or NaOL directly for surface modification and transferred into the oil phase finally [11,12]. The temperature of this reaction is relatively low, but nanoparticles obtained were polydisperse with irregular shapes. Another common approach is the thermal decomposition method. Sun et al. [13] first used $Fe(acac)_3$, OA, and oleic amine to prepare superparamagnetic monodisperse MNPs. Park et al. [14] also prepared uniform-sized Fe_3O_4 nanocrystals by refluxing iron–oleate complexes in different solvents. With this method, magnetite colloids are quite stable in nonpolar solvents, but the reactants often contain toxic organometallic compounds and the reaction temperature is too high to control.

To overcome the above-noted disadvantages, a novel method of preparing stable magnetite colloids has been proposed by our group [15,16], which requires iron salts, NaOH and NaOL, as reactants and surfactant. But as synthesized, the properties of MNPs mostly depend on the reacting conditions, especially the pH value of the solvent and the nature of the stabilization agent. In order to control the products properties precisely, the reaction mechanism should be indicated definitely.

In this research, our aim is to explore the formation process of MNPs and the function of NaOL and NaOH in the reaction. So we changed the reacting dose of NaOH and NaOL to manipulate the concentration of hydroxyl ions (OH^-) in solvent. Then we systematically studied the properties of MNPs in terms of chemical composition, surface property, particle morphology and size, hydrophobicity and hydrophilicity, magnetic behavior, and so on.

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2. Materials and methods

2.1. Materials

Sodium oleate ($C_{18}H_{33}O_2Na$, CP) was purchased from Sinopharm Chemical Reagent Co., Ltd. Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%), Iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 99%), and oleic acid ($C_{18}H_{34}O_2$, 90%) were obtained from Sigma–Aldrich. Sodium hydroxide (NaOH, 96%) was provided by Chengdu Kelong Co. Other solvents were all analytically pure. All chemicals were used as received without further purification. Milli-Q water was used throughout the experiments.

2.2. Synthesis of magnetite colloids

Magnetite colloids were synthesized as the reference published by our group with some improvement [15]. Briefly, 16 mmol $C_{18}H_{33}O_2Na$, 4 mmol $FeCl_3 \cdot 6H_2O$, 2 mmol $FeCl_2 \cdot 4H_2O$, and a certain amount of NaOH were dissolved in the mixture of 9 ml water (deoxygenated water by Ar gas bubbling for 30 min), 12 ml ethanol, and 21 ml toluene one by one under Ar atmosphere and refluxed at 74 °C for 4 h. The black mixture was cooled to room temperature by removing the heat source. Then the suspension was precipitated with ethanol and the sediment was isolated from the solvent by magnetic decantation. The precipitates were dispersed in *n*-hexane and centrifugated for 10 min at 8000 rpm to remove all the undispersed residues. After that, the black *n*-hexane dispersion was precipitated with ethanol again and the solvent was removed through magnetic separation. Finally, MNPs were redispersed in *n*-hexane to form stable colloids.

The reacting dose of NaOH and NaOL was varied as in Tables 1 and 2 without other alteration.

2.3. Characteration of MNPs

Powder X-ray diffraction (XRD, X′ Pert Pro MPD, Philips, Netherlands) was employed to study the crystal structure of samples with angles ranging from 20° to 90°. Fourier transform infrared (FTIR, PE spectrometer) spectra were recorded with wavenumber range 400–4000 cm^{-1}. The step length was 4 cm^{-1}. Thermogravimetric analysis (TGA) measurements were performed with simultaneous thermal analysis (STA 449 C Jupiter, NETZSCH). The mass loss of the dried sample was monitored under N_2 at temperatures from 25 to 800 °C at a heating rate of 10 K/min. Hydrodynamic diameters and size distributions of MNPs were measured by dynamic light scattering (DLS, Malvern Nano-ZS, $l = 632.8$ nm). Samples were dispersed in *n*-hexane or Milli-Q water in a glass cuvette and tested at 25 °C. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements (JEM-2010, Japan electronic) were carried out with samples prepared by evaporating dilute suspensions on carbon-coated copper grids in air under ambient conditions. The particle size and size distribution were calculated from TEM images for all prepared samples using an image analysis program by measuring the diameters of at least 100 particles. The magnetization of the dried sample was measured by a vibrating sample magnetometer (VSM, Model BHV-525, Riken Japanese Electronics Company) with field from 0 to 15,000 Oe at 300 K.

Table 1
The reacting dose of NaOH (NaOL was 16 mmol).

	Sample					
	N0	N3	N6	N7	N8	N9
Molar ratio of NaOH/Fe(II)	0/1	3/1	6/1	7/1	8/1	9/1
Amount of NaOH (mmol)	0	6	12	14	16	18

Table 2
Reacting dose of NaOL.[a]

	Sample				
	S0	S5	N0	S12	S15
Molar ratio of NaOL/Fe(II)	0	5/1	8/1	12/1	15/1
Amount of NaOL (mmol)	0	10	16	24	30

[a] Samples were synthesized without NaOH except Sample S0. For S0, OA and NaOH were used instead of NaOL. Briefly, 16 mmol OA, 4 mmol $FeCl_3 \cdot 6H_2O$, 2 mmol $FeCl_2 \cdot 4H_2O$, and 16 mmol NaOH (molar ratio 8/2/1/8) were dissolved in a mixture of water/ethanol/toluene and refluxed at 74 °C for 4 h. The other procedures of producing MNPs were the same as shown above.

3. Results and discussion

3.1. Chemical composition, structure, and surface properties of MNPs

XRD patterns in Fig. 1 revealed the nanocrystal nature of MNPs synthesized with different amounts of NaOH and NaOL. The diffraction grams of all samples showed characteristic peaks close to the literature values of standard Fe_3O_4 powder diffraction data: 30.09° (2 2 0), 35.44° (3 1 1), 43.08° (4 0 0), 53.44° (4 2 2), 56.97° (5 1 1), and 62.55° (4 4 0) [17]. So the particles were magnetite crystals with spinel structures [13]. However, due to the coating outside, only the most intense reflections (3 1 1 and 4 4 0) were obvious. Significant broadening of the peaks caused by small crystalline size effects of the samples was consistent with the TEM and DLS results [18].

To understand the surface chemical composition of MNPs and the adsorption behavior of oleate, FTIR measurements were carried out on pure NaOL as well as MNPs prepared with different amounts of NaOH and NaOL (Fig. 2). An overview of the most important IR vibrations of different samples is also shown in Table S1 of the Supporting Information.

Fig. 2B is the spectrum of Sample N0 prepared without NaOH. The IR bands at 609 and 450 cm^{-1} were characteristic of the Fe–O vibrations related to the ferrite core [19]. N0 also showed strong C–H stretching of alkyl chains at 2923 and 2852 cm^{-1} corresponding to the bands at 2922 and 2852 cm^{-1} of NaOL in spectrum A. The presence of oleate on the surface of MNPs was further confirmed by alkene stretchings at 3009 and 1623 cm^{-1}, and two carboxylate stretchings at 1525 and 1430 cm^{-1} [20]. There are four

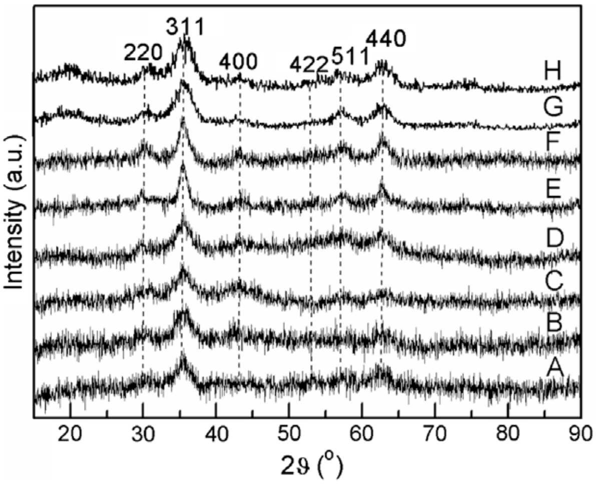

Fig. 1. XRD patterns of MNPs: (A) N0; (B) N3; (C) N6; (D) N7; (E) N8; (F) N9; (G) S12 and (H) S15.