

Effect of Non-ionic Igepal CO-520 in Sonochemical Synthesis of Monodisperse Fe₃O₄ Nanoparticles

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We have investigated a surfactant-assisted sonochemical approach to produce monodisperse Fe₃O₄ nanoparticles (NPs). The non-ionic surfactant Igepal CO-520 (Poly(oxyethylene)(5) nonylphenyl ether) has been used for the preparation of NPs and the effects on the NP size, size distribution, and magnetic properties have been studied. The Fe₃O₄ NPs were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM). The results reveal that the NPs prepared by a Igepal CO-520-assisted sonochemical method exhibit a narrow range of size distributions and a high monodispersity compared to the NPs from the conventional sonochemical method. The analysis of NPs prepared in the presence of the surfactant suggested that it could be used not only as a protector to prevent the oxidation of Fe (II), but also as a controller to vary the size of the NPs.

Keywords : sonochemistry, magnetic nanoparticles, magnetite, Igepal CO-520

1. Introduction

Superparamagnetic monodisperse iron oxide nanoparticles (NPs) have received great attention for their possible biomedical applications, such as magnetically controlled transport of drugs, magnetic resonance molecular imaging contrast agent etc [1-6]. A variety of methods for synthesizing magnetic nanoparticles have been developed, including dry and wet methods. Dry methods include gas condensation, the flame aerosol process, mechanochemical synthesis, and arc-discharge, all of which are used to synthesize various kinds of magnetic NPs [1-4]. Wet chemical methods such as co-precipitation, thermal decomposition, microemulsion, hydrothermal synthesis, and the sol-gel method are also widely used to synthesize a variety of nanosized particles [5-16]. In the case of Fe₃O₄ NPs, several methods have been reported for synthesizing NPs which also provide efficient synthetic routes for shape-controlled and monodisperse mag-

netite NPs [17, 18]. Among these methods, the sonochemical method offers rapid chemical reactions through the process of acoustic cavitations to produce superparamagnetic monodisperse magnetite NPs rather than polydisperse NPs [19, 20]. However, the development of a novel preparation method is still required to synthesize smaller and more uniformly sized NPs for their possible practical applications. It is well known that surfactants with a differently charged head group generally can affect the growth of NP properties, such as shape, structure etc. For example, the experiments on Fe NPs have shown that the non-ionic surfactant tetraethylene glycol dodecyl ether (C₁₂E₄) induces fcc γ -Fe, while cationic didodecyl dimethylammonium bromide (DDAB) induces α -Fe NPs [21, 22]. In addition, recently, we have reported a mono (ethylene glycol) (MEG)-assisted sonochemical method for monodisperse magnetite NP synthesis and have found that a surfactant-assisted synthesis could possibly solve an oxidation and toxicity problem in the sonochemical method [23]. In this study, we have investigated a new facile synthetic route for the preparation of superparamagnetic monodisperse Fe₃O₄ NPs via the sonochemical method in

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the presence of the non-ionic surfactant Igepal CO-520 (Poly(oxyethylene)(5) nonylphenyl ether) acting as a modifier of the reaction environment.

2. Experimental

The NPs were prepared by the sonochemical coprecipitation of ferric and ferrous ions with ammonium hydroxide under an ambient temperature. All chemicals used in this experiment were either HPLC grade or American Chemical Society analytical grade reagents, and they were used without further purification. A prepared mixture of 7.033 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich) and 2.587 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (90%, Aldrich) in 50 ml $\text{C}_2\text{H}_5\text{OH}$ was rapidly injected via a fine plastic tube to the reaction vessel, which contained 100 ml ethanol and 20 ml ammonia solution (28-30%). In order to modify the reaction environment, the non-ionic Igepal CO-520 solution with volumes of 1, 2, and 4 ml was added to the reaction solution, respectively (referred to as the sample A, B, and C). Then the mixture was sonicated for 30 minutes. The ultrasonic processor (Vibra Cell-VCF 1500, Sonics and Materials) with a maximum power of 1,500 W generating capacity was used during the reaction. A schematic diagram of the sonochemical experiment setup is shown in Fig. 1. The sonoreactor was equipped with a titanium horn with 5 cm^2 of irradiating surface area and a piezoelectric transducer supplied by a 20 kHz generator. Finally, the obtained NPs were washed by repeated cycles of centrifugation and dispersion in distilled water and ethanol and then dried in a vacuum oven.

The crystal structure of the synthesized NPs was analy-

zed using an X-ray diffraction (XRD) system (Rigaku, D/MAX-RC, Cu K_α radiation and a Ni filter). Magnetization measurements were performed by using a LakeShore 7400 series vibrating sample magnetometer (VSM) at room temperature. The shape and size of the synthesized NPs were characterized using a typical transmission electron microscope (TEM, Technai F-20, operated at 200 kV) and carbon-coated 300 mesh TEM copper grid. The size distributions of the particles were measured from the enlarged TEM images.

3. Results and Discussion

To identify the crystallographic structure of the NPs, XRD measurements were performed. Fig. 2 shows the XRD patterns of samples A, B, and C (1, 2, and 4 ml of Igepal CO-520, respectively). The evident peaks of the XRD patterns of the samples A, B, and C in Fig. 2 are the peaks representing the magnetite phase (JCPDS No. 79-0418). It is noteworthy from the XRD results that there is no reflection characteristic of maghemite, which indicates that the Igepal CO-520 successfully prevented Fe (II) from oxidizing. The mean size of the NPs can also be roughly determined by using Debye-Scherrer equation from the reflection peak of (311) [24]:

$$D = \frac{K\lambda}{\beta \cos(\theta)}, \quad (1)$$

Here, “ D ” is the average particle size in the axis parallel to the (311) plane ($2\theta = 35.426^\circ$), “ λ ” is the X-ray wavelength (1.5406 Å), “ K ” is a geometric constant with a typical value of 0.89 for spherical particles, and β is the full width at half maximum (FWHM) in radians of the peak (311). The mean particle sizes roughly determined

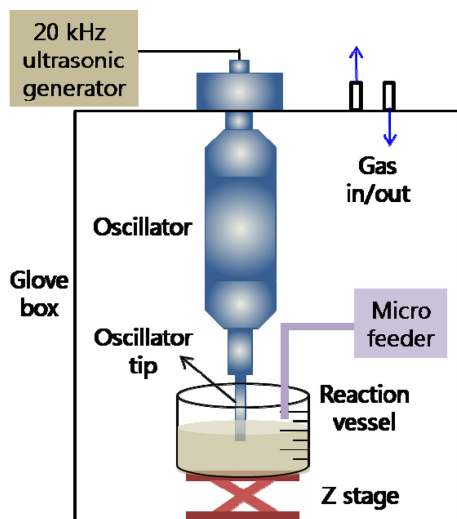


Fig. 1. Schematic representation of the sonochemistry experiment setup used for the synthesis of Fe_3O_4 NPs.

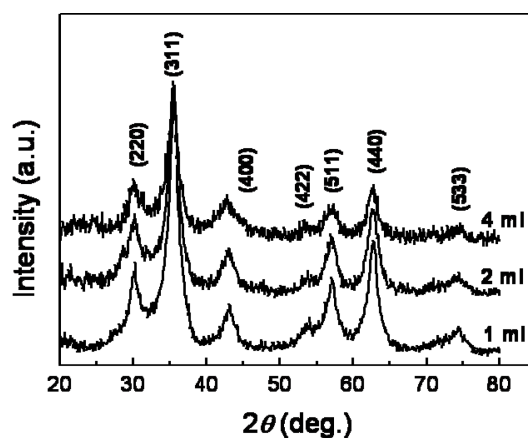


Fig. 2. XRD patterns of sample A (1 ml Igepal CO-520), sample B (2 ml Igepal CO-520), and sample C (4 ml Igepal CO-520).

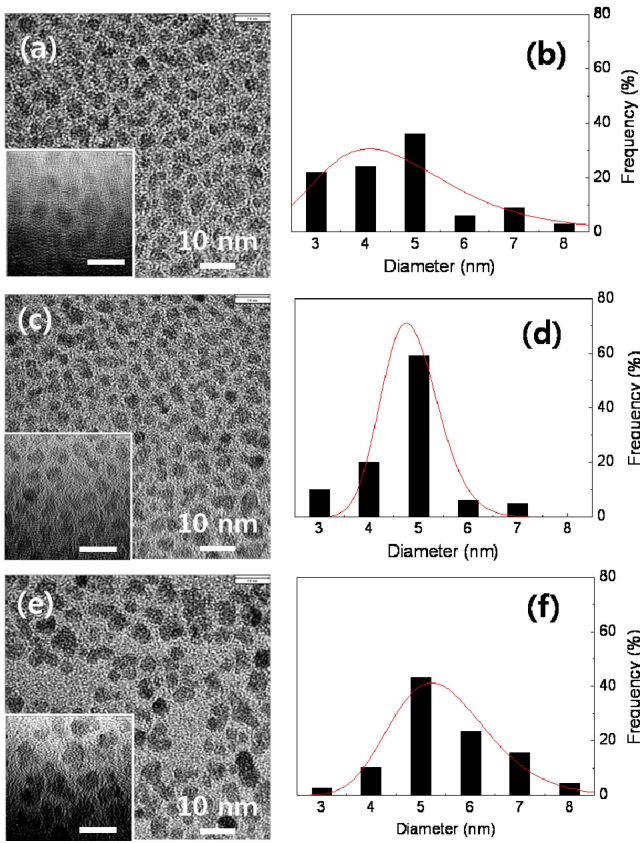


Fig. 3. TEM images and corresponding particle size distributions for sample A (a)-(b), sample B (c)-(d), and sample C (e)-(f). The insets show close-up images and all scale bars are 10 nm.

by the equation have been found to be 5.74 nm, 5.72 nm, and 5.65 nm for samples A, B, and C, respectively.

Then to determine the size, the size distribution, and morphology precisely, TEM measurements were carried out. The results are summarized in Fig. 3. Fig. 3(a)-(b), 3(c)-(d), and 3(e)-(f) show the TEM images of Fe₃O₄ NPs prepared with 1 ml, 2 ml, and 4 ml Igepal CO-520, respectively. In order to analyze the size distributions quantitatively, the size distributions were fitted using a log-normal function [25, 26]:

$$P(x) = \frac{1}{A\sigma_d\sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma_d^2}\left(\ln\frac{x}{x_0}\right)^2\right), \quad (2)$$

where σ_d is the standard deviation of the diameter and x_0 is the mean diameter. The particle sizes of sample A, sample B, and sample C were estimated to be about 4.50 ± 0.46 nm, 4.82 ± 0.11 nm, and 5.40 ± 0.14 nm, respectively. The results were almost coincident with the results obtained from the XRD analysis. However, the particle sizes from XRD measurements are slightly larger than the observed sizes from TEM due to the size distributions of

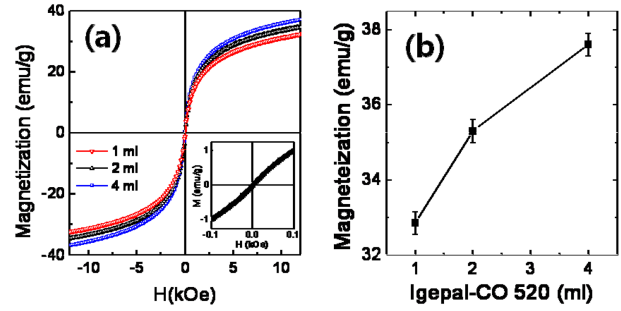


Fig. 4. (a) The magnetization curves of the Fe₃O₄ NPs measured at room temperature for sample A, sample B, and sample C. The inset is the magnetization curves in the small applied field range from -100 to +100 Oe. (b) Dependence of the magnetization with respect to the Igepal CO-520 concentration.

the NPs. It is indicated that the size of NPs is proportional to the Igepal CO-520 concentration. Based on the size distribution information, it is clear that the size of the Fe₃O₄ NPs in sample B (2 ml Igepal CO-520) is the most uniform among all the samples.

The magnetic properties of the NPs from samples A, B, and C were characterized via a VSM at room temperature in an external magnetic field ranging from -12 kOe to +12 kOe. Fig. 4 shows the magnetization curves for samples A, B, and C. The inset shows the magnetization curves in the small applied field range from -100 to +100 Oe to confirm the coercivity of the NPs. As can be seen in Fig. 4(a), all the NPs exhibit a superparamagnetic nature and the magnetization value at the maximum applied field increases from 32.86 emu/g (sample A) to 37.61 emu/g (sample C) as the concentration of the surfactant increases. In Fig. 4(b) we summarize the effect of the concentration of Igepal CO-520 on the magnetization and size of the NPs. According to the XRD results of Fig. 2, sample A, where 1 ml of surfactants was used, shows the largest peaks and it is thought that sample A has a well-ordered

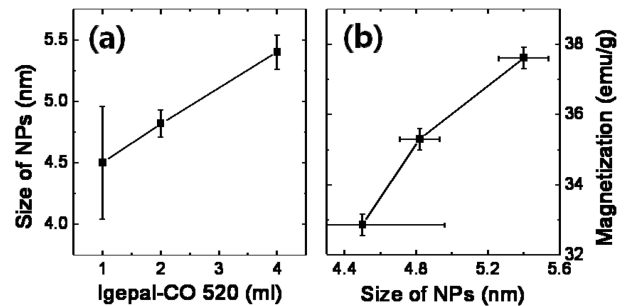


Fig. 5. (a) Effect of the concentration of Igepal CO-520 on the size of the NPs. (b) Dependence of the magnetization with respect to the size of the NPs.

structure, as compared to the others. However, sample A shows the smallest magnetization at the maximum magnetic field, as shown in Fig. 4(b).

In Fig. 5, in order to elucidate the surfactant concentration-dependent magnetization, we plot the dependence of the size of NPs against the Igepal concentration and we also plot the magnetization against the size of the NPs. It is clear from Fig. 5(a) and 5(b) that the size of NPs increased as the concentration of Igepal CO-520 increased and, consequently, the magnetization of the NPs increased as the size of the NPs increased. In general, the size dependent magnetization of the NPs could be ascribed to the crystallinity of the NPs, a nonmagnetic surface layer mainly originated from the residual surfactant layer on the NPs, and a spin disordered surface magnetic layer [23, 27]. However the linear increase of magnetization values on the surfactant concentration shown in Fig. 5(a) implies that the effect of the nonmagnetic surfactant layer on the magnetization and the crystallinity variations of the NPs could be neglected in this case. Therefore, it is likely that a surface layer with a higher magnetic disorder than the core leads to an increase of the magnetization as the concentration and size of the NPs increases [27].

4. Conclusion

A sonochemical synthesis of monodisperse magnetite (Fe_3O_4) NPs in the presence of the non-ionic surfactant Igepal CO-520 at an ambient temperature has been investigated. It is revealed from TEM and VSM measurements that the NPs prepared by this method have size distributions in a narrow range and the superparamagnetic properties with very low coercivity less than 0.3 Oe. It is also noteworthy from the XRD results that there is an evident characteristic of a magnetite phase with no reflection characteristics from the maghemite. This simple and fast synthetic route for the preparation of monodisperse Fe_3O_4 NPs by a sonochemical method in the presence of the non-ionic surfactant Igepal CO-520 could be applied to the synthesis of other magnetic NPs.

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