**Synthesis of Magnetite Nanoparticles by Electrochemical Method Using Pulsed-Direct Current**

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**Extended Abstract**

Magnetite (Fe₃O₄) is one of the most important magnetic materials and is widely used in industry. In recent years, monodispersed magnetite nanoparticles have attracted increasing attention due to their good biocompatibility, strong superparamagnetic properties, low toxicity and easy preparation process [1]. Magnetite nanoparticles find many applications in the biomedical industry, such as targeted drug delivery, hyperthermia treatment, cell separation, magnetic resonance imaging, immunoassays and the separation of biochemical products [2]. They are also useful for environmental processes, such as the treatment of water and wastewater [3].

Recently, we have successfully prepared nearly monodispersed magnetite nanoparticles with a mean size ranging from 10 to 30 nm using a surfactant-free electrochemical method with a sacrificial iron anode and plain water as the electrolyte using continuous direct current (CDC) [4]. The nanoparticles exhibit ferromagnetic properties with a relatively high saturation magnetization, although some impurities in the form of FeOOH, a nonmagnetic material, were retained. These impurities could be eliminated by electro-oxidizing in sodium silicate solution (100–200 ppm) to obtain high purity silica-coated magnetite nanoparticles having superparamagnetic properties [5].

In this paper, we report on the preparation of high purity magnetite nanoparticles by a surfactant-free electrochemical method with a sacrificial iron anode and plain water as the electrolyte using pulsed-direct current (PDC). The experiments were conducted in an electrochemical cell made of acrylic. Pure iron to be electro-oxidized was prepared by electroplating an iron plate of size (45 × 12) mm in FeSO₄ solution. The electro-oxidation was carried out in demineralized water. The electroplated iron plate was connected with the positive terminal of the DC power supply (the anode) and an unplated iron plate counter electrode was connected to the negative terminal (the cathode). Both electrodes were set paralelly with an interelectrode spacing of about 2 cm. The voltage between electrode was oscilated in a pulse-mode by a function generator for ~20 h. The particles produced were filtered and dried for characterization.

Although for both methods, i.e., CDC and PDC, a black precipitate was obtained, the purity of the powders is very different. As shown in Fig. 1, the characteristic peaks of the XRD pattern for the sample obtained by CDC correspond not only to magnetite (JCPDS 19-0629) but also to FeOOH (JCPDS 44-1415). FeOOH is an intermediate product in the formation of Fe₃O₄ during synthesis by CDC [6]. PDC appears to perturb the diffusion OH⁻ ion required for basic condition in anode region to favor the formation of FeOOH, and hence there is no FeOOH remaining once Fe₃O₄ particles are formed.

The size of the particles, as measured indirectly by measuring their specific surface area by Brunauer-Emmet-Teller (BET) method (Nova 1200, Quantachrome), is in the range between 7 to 23 nm depending on the operating condition including pH, duty cycle, frequency and amplitude of the pulse-wave. In this study, the pH was varied from 7 to 10, duty cycle from 50 to 80%, frequency from 5 to 8 Hz and amplitude from 5 to 10 V. It seems that increasing the four parameters tends to increase the particle size. In addition, the crystallinity of the magnetite nanoparticles also increases with an increase in the parameters.
The magnetic properties of the magnetite nanoparticles were examined by vibrating sample magnetometer (Type 1.2H VSM, Oxford). Fig. 2 shows the magnetization curve at room temperature for magnetite nanoparticles prepared at various conditions. The results suggest that the magnetite nanoparticles possess ferromagnetic properties as indicated by a hysteresis loop, which is typically observed for ferromagnetic materials of sizes larger than 10 nm. The saturation magnetization of the nanoparticles is ranging from 18 to 55 emu g$^{-1}$ depending on operating condition, i.e., particle size.

Analysis using thermal gravimetry/differential thermal analysis (TG/DTA) from room temperature up to 500°C shows that there are two stages of mass reduction of the samples. The first stage occurs at temperature < 100°C indicating the desorption of H$_2$O bound physically at magnetite surface. The second stage occurs at 200–300°C that probably comes from the transformation of magnetite to maghemite. The transformation is supported by the presence of exothermic peak in the DTA curve at this temperature range.

In conclusion, magnetite nanoparticles with high purity can be synthesized by electro-oxidation of iron in plain water using PDC. The nanoparticles have a mean size ranging from 7 to 23 nm and exhibit ferromagnetic properties with relatively high saturation magnetization. They are stable at a temperature below 200°C. Heating further results in the conversion of magnetite into maghemite.

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