**Effect of Surfactant Concentration on Size and Morphology of Electrooxidated Fe₃O₄ Nanoparticles**

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**Abstract:** Electrostatic surfaced Fe₃O₄ nanoparticles without agglomeration were successfully synthesized using electrooxidation of iron by chronoamperometry technique in the presence of tetramethylammoniumchlorid surfactant from an organic medium. The effect of surfactant concentrations and ultrasonic waves on structural properties of the particles was spontaneously studied using XRD, FT-IR, TEM and UV-Visible. XRD results, clearly approved the formation of spinel phase of Fe₃O₄ and no other iron oxide phase. Based on FT-IR spectrometer results, it is suggested that the surfaces of the Fe₃O₄ nanoparticles were covered with amine surfactant through electrostatic interaction. Through, TEM images the particles size and their distributions were found to be well controllable with surfactant concentration and ultrasonic waves. According to these images, the increase in surfactant concentration led to the reduction of the particles size and also led to particles shape from cubic, tetragonal, hexagonal and triangular to quasi-spherical. Additionally, TEM images show that Fe₃O₄ nanoparticles grow in a solution with higher surfactant concentration and also under ultrasonic waves are narrowly distributed. Namely, the use of ultrasonication with higher surfactant concentration led to the formation of fine particles. Electron diffraction patterns of the particles consist of many spots and rings, indicating their polycrystalline structures. UV-Visible spectroscopy results show the peak width of UV-Visible spectrum for sonoelectrooxidated nanoparticles was less than those prepared without ultrasonication indicating size uniformity of the particles.

**Keywords:** Fe₃O₄ nanoparticles; Ultrasonication; Structural properties; Surfactant effect; UV-Visible spectroscopy

**Introduction**

Magnetite (Fe₃O₄) nanoparticles occupy a singular position in the field of magnetic materials, owning to their special physiochemical properties. For instance, they exhibit many interesting phenomena such as charge ordering, mixed valence, and metal insulator transition known as the Verwey transition. For its exceptional biocompatibility, magnetite including other forms of iron oxide nanoparticles has been highlighted for biomedical applications, with ultrasmall superparamagnetic iron oxides mostly interesting for rapid elimination of nanoparticles and perfusion imaging.

Fe₃O₄ nanoparticles can be obtained by several methods [1]. New optimized method of synthesis is necessary to allow for the control of the shape and size distribution of nanoparticles. Electrooxidation method synthesis has recently begun to fabricate some of oxidized nanoparticles. In this study, a novel synthesis technique based on ultrasonic waves and electrooxidation, named the sonoelectrooxidation is developed and size-controlled Fe₃O₄ nanoparticles are prepared using this method. In fact, the particles are grown using both electrooxidation and sonoelectrooxidation methods in an organic medium and the effects of surfactant concentration on the particles shape and size are investigated.

**Experimental**

Two Iron plates, (1cm x1cm) and (1cmx4cm), were purchased from Alfa Aesar (purity 99.97%), and used as anode and cathode, respectively. The electrodes were cleaned and mounted by a distance of 1cm apart from each other. The electrolyte was aqueous solution of (CH₃)₃NCl (Merck) salt with various concentrations. (CH₃)₃NCl acts as a supporting electrolyte and stabilizer, so it covers the surface of Fe₃O₄ particles and controls the particles size during the synthesis process. In order to investigate the effect of surfactant on particles properties, several samples were synthesized with various surfactant concentrations (i.e. 0.02M, 0.03M, 0.04M, 0.05M, 0.06M and 0.08M) meanwhile, other growth conditions were kept the same. Electrolyte temperature was controlled with the help of a thermostatic water bath at 60°C. In order to produce Fe₃O₄ a sufficient potential was applied between the electrodes using a potentiostat/galvanostat (SAMA 500). After a few hundred of seconds the solution became black and the particles started to precipitate. In order to prepare more uniform nanoparticles with controlled size, an ultrasonic bath was used. The products were then washed with distilled water and dried at constant temperature. The phase formation and nanostructure of the obtained samples were analyzed using XRD model PW 1840 with Cu Kα radiation and also particles size and shape were analyzed by TEM model LEO 906E. The absorption wavelength of the samples was studied using an UV-Visible spectrophotometer model PERKIN ELMER LX185256.

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Results and Discussion

Fig. 1 shows XRD pattern of a typical electrooxidated powder prepared under V=7V from a solution with 0.04M surfactant. The figure shows the formation of Fe$_3$O$_4$ phase using (reference code: JCPDS 88-0315).

![Figure 1. XRD pattern of Fe$_3$O$_4$ nanoparticles grown under V=7V from a bath with 0.04M surfactant concentration.](image)

FT-IR analysis was performed to detect the presence of surfactants adsorbed by the nanoparticles surface. Fig. 2 shows the IR spectrum of a typical sample. The spectrum shows 3495 cm$^{-1}$ band belongs to the O-H vibrations of water and broad bands at 1073 cm$^{-1}$ (marked with arrows in the spectrum) representing vibrations of C-N bond, coming from the amine surfactant. Finally, between the 850 cm$^{-1}$ and 400 cm$^{-1}$ a strong bond due to the stretching vibration mode of Fe-O bonds in Fe$_3$O$_4$ can be observed.

Note that, the Fe$_3$O$_4$ surfaces are readily covered with Cl$^-$ ions and (CH$_3$)$_4$N$^+$ in an aqueous environment. According to Harris et al. [2], the surface characteristics were the dominant factors for the particle stabilization and control of particle size and morphology. The surface charge of metal oxides was pH dependent, and the point of zero charge (PZC) was expressed as the pH conditions in solution where the surface charge was zero. The PZC of Fe$_3$O$_4$ particles reported in the literature ranged from 6.3 to 7.2 [3]. Thus, the surface of Fe$_3$O$_4$ nanoparticles are positively charged at acidic conditions and negatively charged at alkaline conditions.

Optical absorbance spectra of electrooxidated and sonoelctrooxidated Fe$_3$O$_4$ nanoparticles were determined using UV-Visible spectrophotometer in wavelength range of 300-550nm. Fig. 3 shows the absorbance curve in term of wavelength ($\lambda$).

![Figure 3. UV-Visible spectra of Fe$_3$O$_4$ nanoparticles prepared by, electrooxidation (up) and sonoelctrooxidation (down) with various surfactant concentrations.](image)

Obviously the wavelength at the highest absorbance, $\lambda_{max}$, decreased from 390.251nm to 358.036nm with increasing the surfactant concentrations from 0.02M to 0.08M for electrooxidated Fe$_3$O$_4$ nanoparticles. Additionally, this parameter decreased from 374.231nm to 339.125nm with increasing the surfactant concentrations from 0.02M to 0.08M for sonoelctrooxidated Fe$_3$O$_4$ nanoparticles. In all cases the peak width decreases with increasing the surfactant concentrations. In fact, in comparison with electrooxidation method, the $\lambda_{max}$ and peak width were strongly influenced by use of ultrasonic waves. The optical data were analyzed to estimate the transition energy of electron around Fe$_3$O$_4$ nuclei using photon energy (h$\nu$). Fig 4. shows the dependence of $\lambda_{max}$ and transition energy on surfactant concentrations for Fe$_3$O$_4$ nanoparticles synthesized with various surfactant concentrations using both electrooxidation and sonoelctrooxidation methods, respectively.
Subsequently, TEM was utilized to investigate the shape and size dependence of Fe$_3$O$_4$ nanoparticles as a function of surfactant concentration and ultrasonication (Fig 5). Through TEM studies, it was demonstrated that the shape and size of Fe$_3$O$_4$ nanoparticles were strongly influenced by surfactant concentration and applied synthesis method. For example, quasi-spherical, cubic, tetragonal, hexagonal and triangular form of sonoelectrooxidated Fe$_3$O$_4$ nanoparticles with approximately 5-45nm were synthesized with 0.02M surfactant (Fig 5a). However, as the concentration increased up to 0.08M spherical shaped sonoelectrooxidated Fe$_3$O$_4$ nanoparticles with approximately 8-20nm was only observed (Fig 5b). Based on TEM images in Fig. 5c it appears the electrooxidated Fe$_3$O$_4$ nanoparticles agglomerated during the synthesis process and their size become bigger. Furthermore with lower surfactant concentration, the particles size distribution would become so wide. The change in morphology and size with the increase in surfactant concentration and by use of ultrasonication occurs because the coating agent and vibration do not allow the particles to stick to each other, so the particles become small and so uniform. In addition, the ED patterns of these particles are shown in the insets of Fig 5. Spotty of patterns were obtained from polycrystalline samples, while broad ring patterns were obtained from the samples consisting of fine particles.

**Conclusion**

Two methods of synthesis of Fe$_3$O$_4$ nanoparticles coated with (CH$_3$)$_4$NCl surfactant, based on electrochemical oxidation and ultrasonication were investigated with a control on their size. FT-IR spectra showed the existence of stabilizer agent on the surface of nanoparticles. According to TEM observation, it was clarified that the surfactant concentration used in the synthesis and ultrasonication played important role in determining the morphology and the size of particles. It can be observed that the particles size decreased from 5-45nm range to 8-20nm range and their distribution gradually improved with increasing surfactant concentration from 0.02M to 0.08M and by use of ultrasonic bath. The peak width of UV-Visible spectra for sonoelectrooxidated nanoparticles was less than those prepared by electrooxidation without ultrasonic and $\lambda_{max}$ decreased from 390.251nm to 358.036nm (from 374.231nm to 339.125nm) with increasing the surfactant concentrations from 0.02M to 0.08M for electrooxidated (sonoelectrooxideted) nanoparticles. This means ultrasonic waves could help us to produce uniform particles in size and also distribution.

**References**

