

Full Paper

One-step Electrochemical Preparation of Oleic Acid Capped Superparamagnetic Iron Oxide Nanoparticles in Ethanol Medium and its Characterization

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Abstract- In this paper, oleic acid capped iron oxide nanoparticles (OA-IONPs) is prepared through a simple and efficient electrochemical synthetic route. OA-IONPs were synthesized from the Fe(III) nitrate (0.005 M) and 10 cc oleic acid dissolved in ethanol (96%) solution with applying 5 mA cm⁻². The prepared IONPs were characterized by different techniques of XRD, FE-SEM, TEM, FT-IR, TGA, DLS and VSM. The OA layer on the surfaces of IONPs was confirmed by FT-IR, DLS and DSC-TGA analyses. The magnetic analysis by VSM revealed that the prepared OA-IONPs exhibit negligible *Mr* and *Ce* values at the condition of $H \rightarrow 0$, implicating their superparamagnetic nature.

Keywords- Nanoparticles, Cathodic Electrodeposition, *In situ* capping, Oleic acid

1. INTRODUCTION

Iron oxide nanoparticles (IONPs) with superparamagnetic nature are interested for use in hyperthermia, drug delivery, cancer therapy, magnetic resonance imaging (MRI) contrast agent, immunoassay and cell separation [1-4]. IONPs could exhibit an unprecedented size-dependent superparamagnetism property due to their small size and high surface area to volume ratio [5]. For obtaining the highest level of magnetization, the nano-size particles (10-

20 nm) should be fabricated [6]. For fabrication of 10-20 nm IONPs, their agglomeration is a major challenge, which could be resolved through surface capping strategy [7]. In this regard, different coating agents have been introduced to surface capping of IONPs. Therefore, the major requirements of optimum particle size (<100 nm), high magnetization level, biocompatible surface layer and a narrow distribution of particle size should be fulfilled in all biomedical applications of IONPs [7]. The IONPs capped surface layer should be also formed from nontoxic and biocompatible materials, which get the IONPs to be more bio-distributable, easier cellular absorption and optimum blood circulation [8-11]. Recently, due to great potential uses of IONPs in biomedical subjects, extensive investigations have been done on the IONPs preparation and surface modification. As one of the most common surface capping agents, polysaccharides including agarose, oleic acid, alginate, heparin, carrageenan, chitosan, pullulan, hyaluronic acid, starch have been applied for the modification of IONPs [12-15]. Oleic acid (OA) is a branched polymer of glucose molecules in which the units of α -linked *D*-glucopyranosyl are repeated to form the linear backbone. OA polymer could attached onto the surface of IONPs in the alkaline media, which formed IONPs enmeshed cores *through* non-covalent interactions between its COO^- groups and Fe atoms [16-18]. Then, the hydroxyl groups of OA can be easily cross-linked and functionalized using primary amines to connect to several of target compounds like as peptides and ligands [16-22].

Up now, many works have been reported on the chemical synthesis of IONPs, which most commons are hydrothermal, sol-gel, solvothermal, precipitation, and thermal decomposition [24-27]. It was reported that major challenge in these methods is the preparation of mono-dispersed IONPs since the particle size and their distribution controlling are ungovernable. Furthermore, mixed phases of iron oxide nanoparticles e.g. magnetite along with hematite and/or maghemite are synthesized when using chemical methods [24-27]. As an alternative, electrochemical synthesis seems that to refine these problems in the fabrication of nanoparticles of pure magnetite phase of iron oxide. It was reported that cathodic deposition presents a facile and controllable route for the fabrication of metal oxides/hydroxides NPs [28-36]. Furthermore, Karimzadeh et al. introduced an electrochemical platform based on the cathodic electrosynthesis for the preparation of naked and surface capped IONPs [37-40]. Very recently, metal-ion doped IONPs have been also fabricated through one-pot cathodic electrodeposition [41-45]. The results of these reports have proved that cathodic deposition is facile and controllable procedure in the fabrication of mono-dispersed iron oxide NPs and has no problems mentioned for the chemical methods. However, cathodic deposition of surface capped IONPs from ethanol media has been rarely studied and there is only on report in this area [46]. In this work, oleic acid capped IONPs (OA-IONPs) are cathodically deposited from ethanol media for the first time. The provided results through XRD, FT-IR, TGA, DLS, VSM and TEM supported that the electrodeposited OA-IONPs have proper size, crystal structure, spherical shape and magnetic properties.

2. MATERIALS AND METHODS

2.1. Materials

Ferric nitrate tetra hydrate ($\text{Fe}(\text{NO}_3)_3$, 99.9%), and oleic acid (cis-9-Octadecenoic acid, $\geq 99\%$) were purchased from the Sigma Aldrich Company. All materials were used without any further purification.

2.2. Preparation of naked SPIONs

Iron oxide nanoparticles (IONPs) capped with oleic acid were fabricated through one-step cathodic deposition method reported in Refs. [45,46]. In a similar electrochemical set up, a two-electrode electrochemical cell containing 96% ethanol solution was electro-synthesis set up (Fig. 1). The stainless-steel sheet (316 L) and graphite plates was selected to be cathode and anode electrodes, respectively (as shown in Fig. 1). Before performing cathodic deposition process, the electropolishing of steel electrodes were performed according to the reported procedure in Refs. [47]. 2.5 g $\text{Fe}(\text{NO}_3)_3$ dissolved in ethanol (96%) was used as the electrolyte and 10 cc L^{-1} oleic acid as capping agent was then added. The deposition of OA-IONPs was performed using a power supply system at the conditions of $i=10 \text{ mA cm}^{-2}$, $t=30 \text{ min}$ and $T=25 \text{ }^\circ\text{C}$. After deposition onto cathode, the following steps were performed (Fig. 1); (i) the deposited black film was scraped from the steel, (ii) the obtained wet powder was dispersed in ethanol and centrifuged at 6000 rpm for 20 min to removal of free ions and OA molecules, (iii) the deposit was then separated from ethanol solution by a magnet, dried at $60 \text{ }^\circ\text{C}$ for 1h, and (iv) the resulting black dry powder was labeled OA-IONPs, and used in characterization evaluations.

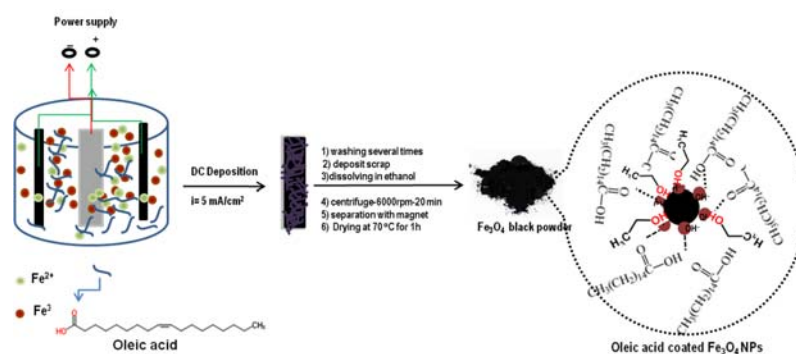


Fig. 1. Schematic showing the electro-synthesis of the oleic acid capped IONPs

2.2. Characterization of nanoparticles

The size and morphology of the prepared OA-IONPs was observed using FE-SEM (Model Mira 3-XMU) and TEM (Model Phillips EM 208) microscopes. The XRD patterns of

the prepared NPs were taken using X-ray diffraction of powder (XRD, Phillips Model X'PERT MPD with Co K α radiation ($\lambda=1.789$ Å)). Also, hydrodynamic diameter of the prepared oleic acid capped NPs was determined by dynamic light scattering (DLS, 4700 Malvern Instruments, UK). FT-IR spectra were obtained using a Bruker Vector 22 Fourier transformed infrared spectroscope. DCS-TG analysis was carried out in N₂ atmosphere between room temperature and 600 °C at a heating rate of 5 °C min⁻¹ using a thermoanalyzer (STA-1500). A vibrational sample magnetometer (VSM, model: Meghnatis Daghigh Kavir, Iran) were used to provide the hysteresis profile for the prepared IONPs (i.e. OA-IONPs). The VSM measurements were carried out in the applied fields of -18000 to 18000 Oe in room temperature.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The representative XRD pattern of the oleic acid capped IONPs is given in Fig. 2. The observed diffraction peaks are fully matched with (111), (220), (311), (400), (442), (511) and (440) planes of Fe₃O₄ (JCPDS 01-088-0315, $a=0.83980$ nm). The average crystallite size (D) was calculated using the diffraction line-width of XRD patterns, based on Scherrer's equation ($D=0.9\lambda/\beta \cos(\theta)$), where, β is the full width at half maximum (FWHM) of the (311) peak. The calculations revealed that the OA-capped particles have average crystallite size of 7.1 nm. It is worthwhile noting that electrochemical preparation of OA-IONPs in ethanol media through cathodic electrosynthesis has not been reported until now.

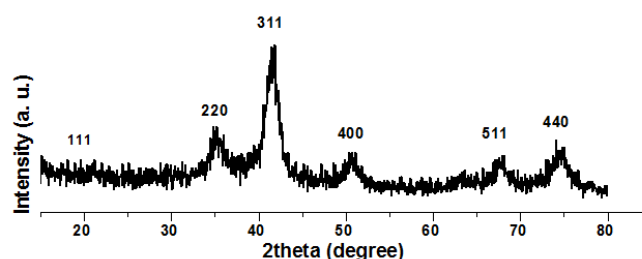


Fig. 2. XRD pattern of the electro-synthesized OA-capped IONPs

3.2. Morphological evaluation

Morphologies of the electro-synthesized IONPs were observed by FE-SEM and TEM microscopes. The FE-SEM image of the oleic acid capped IONPs is illustrated in Fig. 3a. It is clearly observed that the synthesized IONPs have particle morphology with nano-size diameters. For our sample, agglomerated packages composed of several nano-particles are

obvious in FE-SEM image (Fig. 3a). The observed packages have sizes up to 100 nm. The diameters of 15-20 nm were measured for OA-IONPs in Fig. 3a.

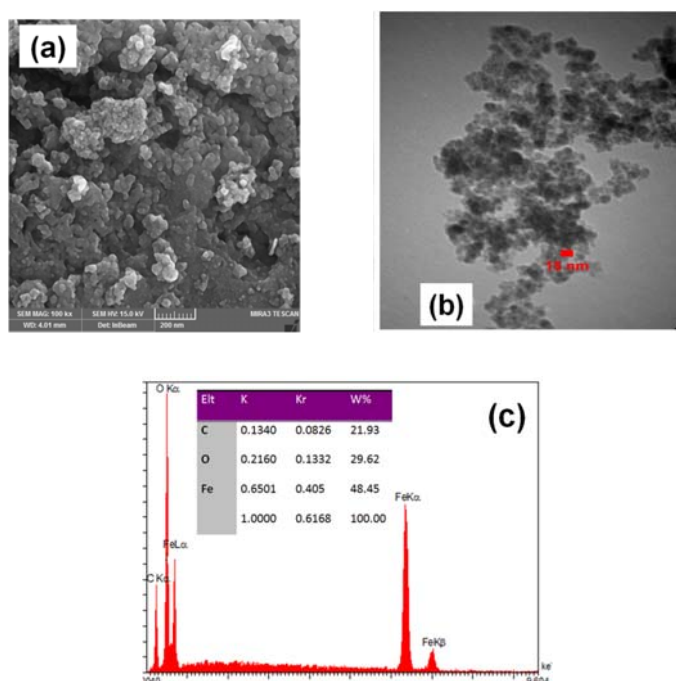


Fig. 3. (a) FE-SEM and (b) TEM images and (c) EDS data of the prepared oleic acid capped IONPs

TEM image disclosed that IONPs have fine particle morphology at nano-scale. As seen in the TEM images (Fig. 3b), the prepared IONPs have proper dispersion. This observation indicated that the *in situ* oleic acid capping on Fe₃O₄ NPs surface during CE preparation prevents them to stick with each other. Significantly, the aggregated form of IONs prevents them to exhibit the behavior of single particles and the advantages of the nanometer size. From TEM image in Fig. 3b and using *Size Measurement* software, the mean diameter of oleic acid capped IONPs were determined to be ~12 nm. Energy-dispersive X-ray (EDX) was used to determine the elemental content of both sample, as shown in Fig. 3c. It was observed that the sample is composed of 48.45%wt Fe, 21.93%wt C and 29.62%wt O elements. The high carbon and oxygen content in OA-IONPs composition clearly confirmed the oleic capped layer on the iron oxide NPs. Furthermore, the carbon content may come from the ethoxy (-C₂H₅O) presence on the surface of electro-synthesized SPIONs, as proved by Aghazadeh et al. in Ref. [46].

3.3. FT-IR analysis

The FT-IR spectrum of the oleic acid capped IONPs sample is presented in Fig. 4. The main IR bands correspond to the magnetite phase of iron oxide are seen below 600 cm^{-1} , which are (i) 455 cm^{-1} resulting from the ν_1 band of the Fe—O bond [15,38], and (ii) a broad band around 581 cm^{-1} originating from the ν_2 stretching vibrations of Fe-O bond [38,39]. There are several IR bands related to the chemical bonds of OA in this spectrum, including asymmetric vibration of $-\text{CH}_2-$ chain at 2989 cm^{-1} , symmetric vibration of CH_2- chain at 2854 cm^{-1} [17,48], C-O bending at 1032 cm^{-1} , C-C stretching at 1163 cm^{-1} , CH_3 rock at 1371 cm^{-1} [49,50], $-\text{CH}_2$ stretching at 1240 cm^{-1} [51,52], C-O stretching at 1104 cm^{-1} and C-H bending at 826 cm^{-1} [17,53]. Furthermore, the peak at 1687 cm^{-1} is attributed to the vibration of the double covalent bond in $-\text{CH}=\text{CH}-$ [17,19,22,48], and the peaks at 1534 cm^{-1} and 1412 cm^{-1} are due to the symmetric and asymmetric vibrations of the double covalent bond in $-\text{COO}^-$ [17,18,55,56]. These two bands at 1412 cm^{-1} and 1534 cm^{-1} can be assigned to the oleate ion immobilized on the IONPs surface [18,56]. According to Refs [18,55,56], the interaction between the $-\text{COO}^-$ head and the Fe atom can be categorized as four types: (i) monodentate, (ii) bridging (bidentate), (iii) chelating (bidentate), and (iv) ionic interaction [18,56]. The wavenumber separation, $\Delta\nu$, between the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ IR bands has been applied to specify this interaction type, where the largest $\Delta\nu$ ($200\text{--}320\text{ cm}^{-1}$) is ascribed to the monodentate interaction and the smallest $\Delta\nu$ ($<110\text{ cm}^{-1}$) indicates the chelating bidentate. The medium range $\Delta\nu$ ($140\text{--}190\text{ cm}^{-1}$) is also for the bridging bidentate. For our sample, the $\Delta\nu=122\text{ cm}^{-1}$, which reveals existence of a bidentate chelating between two oxygen atoms of the COO^- and Fe atoms [18]. From the above data, the OA capping layer on the IONPs surface was confirmed.

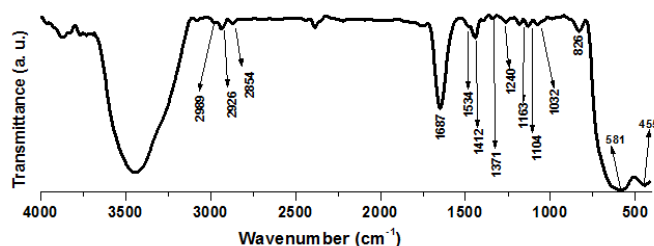


Fig. 4. IR spectra of the OA-capped IONPs

3.4. Thermogravimetric analysis

Thermogravimetric profile of the oleic acid-capped NPs was recorded at the temperature range of $25\text{--}600\text{ }^{\circ}\text{C}$, and the results are presented as DSC and TGA diagrams in Fig. 5. The prepared OA-IONPs exhibited a 2.5% weight loss at the temperatures up to $150\text{ }^{\circ}\text{C}$. It was found that the surface of Fe_3O_4 nanoparticles is covered with OH groups during their

deposition from the ethanol solutions [37,55]. Hence, the observed weight loss is connected to the removal of the hydroxyl groups linked to the surface of IONPs [22-24,37]. After this stage, there is a sharp endothermic peak on the DSC diagram at about 245 °C, and TG exhibits a sharp weight loss of 25%. This sharp peak at about 245 °C is corresponded to the boiling or decomposition point of oleic acid, and hence the related 25% weight loss is due to the removal of the capped oleic acid from the surface of IONPs [17-22].

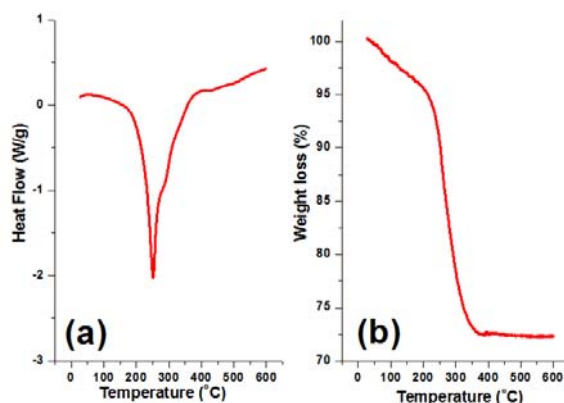


Fig. 5. Thermogravimetric analysis of the prepared oleic acid capped SPIONs

3.5. Dynamic light scattering (DLS)

The hydrodynamic diameter of the prepared IONPs was measured by using the DLS analyzer. Fig. 6 indicates the distributions of hydrodynamic diameter of OA-IONPs sample. It was observed that this sample has the average hydrodynamic diameter of ~105 nm. Since the iron oxide core has particle size of 15 nm, as confirmed by FE-SEM and TEM observations, hence this increased size completely reveals the presence of OA capped layer onto the surface of electrosynthesized IONPs.

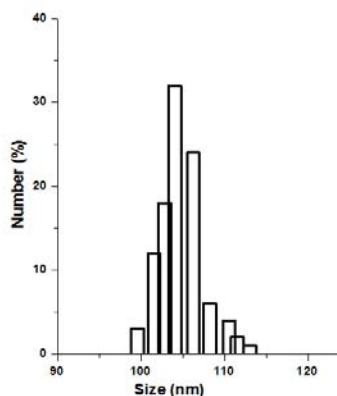


Fig. 6. Hydrodynamic size distribution profile of the electro-synthesized SPIONs

3.6. Magnetic evaluation

The magnetic behavior i.e. magnetizations (M) versus applied magnetic field (H) of oleic acid capped iron oxide NPs was specified by VSM. As evident from the VSM curve, the OA-IONPs exhibit superparamagnetic properties at room temperature (Fig. 7). The magnetic data extracted from the VSM curve have been listed in Table 1. Notably, the magnetic data of the pristine IONPs prepared in ethanol medium was also provided from Ref. [46]. The oleic acid capped IONPs shows the M_s value of 23.9 emu g^{-1} with $M_r=0.13 \text{ emu g}^{-1}$ and $C_e=3.76 \text{ G}$. These data indicated the suitable magnetic behavior of the electrodeposited OA-IONPs. From Table 1, the OA-IONPs displayed negligible M_r and C_e values as compared with pristine IONPs [46], revealing the improvement of the superparamagnetic nature of IONPs as a result of OA capping. These results proved that the fabricated OA-capped IONPs could be suitable candidate use in biomedical applications e.g. hyperthermia [57].

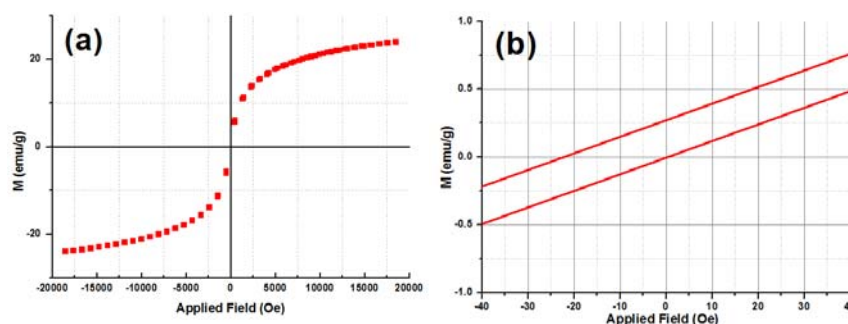


Fig. 7. Hysteresis loops for the oleic acid capped SPIONs

Table 1. Magnetic data for the electrosynthesized bare and oleic acid capped SPIONs

Sample name	M_s (emu/g)	Positive M_s (emu/g)	Negative M_s (emu/g)	Negative M_r (emu/g)	Positive M_r (emu/g)	Retentivity (emu/g)	Negative H_{ci} (G)	Positive H_{ci} (G)	Coercivity (G)
IONPs [46]	44.838	44.838	-44.838	-0.036	0.211	0.123	-8.22	1.384	4.81
OA-IONPs	23.97	23.97	-23.97	-0.004	0.271	0.137	-0.375	-22.19	3.766

4. CONCLUSION

The oleic acid-capped of iron oxide nanoparticles with magnetite phase were prepared in aqueous electrolyte solution *via* a one-step cathodic deposition route without using any surfactant or supporting electrolytes. Morphological observations through FE-SEM and TEM displayed that the prepared sample has well-dispersed nanoparticles with the size of 10 nm.

The presence of oleic acid on the surface of IONPs was specified through TG, DLS and FT-IR analyses. The prepared OA-IONPs have appropriate size and magnetic nature which are suitable for use in biomedical applications.

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