

Full Paper

Electrochemical Synthesis of Magnetite Nanoparticles and their Doping with Cu²⁺ Cations and Surface Coating with Polyethylenimine

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Abstract- In this paper, an electrochemical method was developed for fabrication of copper ions doped iron oxide particles and their surface coating with a bio-compatible layer. Using this method, polyethylenimine-coated Cu²⁺ doped super-paramagnetic magnetite nanoparticles were prepared on the cathode surface through base electro-generation strategy. The prepared PEI/Cu-IOs powder was analyzed by XRD, FE-SEM, EDS and VSM technique. The crystalline magnetite phase of the prepared PEI/Cu-IOs powder was verified by XRD data. FE-SEM observations and EDS data revealed the particle morphology and presence of Cu²⁺ ions content in the prepared sample, respectively. The FT-IR analysis proved the PEI layer on the surface of the fabricated Cu-IOs nanoparticles. The super-paramagnetic performance of the prepared powder was concluded through the measured negligible remanence (i.e. $M_r=0.36$ emu/g) and low intrinsic coercivity (i.e. $H_{ci}=8.54$ G). These results certificated the eligibility of prepared nanoparticles for various biomedical applications.

Keywords- Electrochemical synthesis, Iron oxide, Nanoparticles, Biomedical applications

1. INTRODUCTION

Nanocrystalline nano-particles with iron oxide cores have great potential for application in bio-medicine [1-3], because of their bio-degradability [4,5], bio-compatibility [6-9], proper magnetism [10,11], facile preparation [12-15], and easy surface modification [16-18].

Among pure natural phases of iron oxide, the most popular magnetic nanoparticles (MNPs) are magnetite and maghemite. These two phases exhibit various physico-chemical characters as results of different Fe oxidation states, and ability of contaminant removal [19,20]. Magnetite (Fe_3O_4) phase of iron oxide has been the most extensively investigated for use in many fields [21]. Furthermore, superparamagnetic spherical NPs of Fe_3O_4 (with sizes less than 100 nm) are favorable nanomaterials to be used as drug delivery, hyperthermia, cancer therapy, tissue repair, detoxification of biological fluids, cell separation, immunoassay, and magnetic resonance imaging (MRI) contrast enhancement [22-29]. The nano-size of MNPs render them to show a high surface area-to-volume ratio, which leads to large surface energies. Hence, passivation of the magnetic cores of IONs should be designed and done to receive suitable *in vivo* performance. Up now, various coats including PEG [30-33], PVP [34-36], amino acids [37-39], saccharides [40], dextran [41], chitosan [42], and PVA [43,44] have been used to graft the iron oxide core of SPIONs.

The common synthesis methods applied to prepare iron oxides (IOs) include chemical coprecipitation, hydrothermal, sol-gel, polyol, and electrochemical methods [45-50]. The fabricated IOs are typically grafted with biocompatible materials to improve their water dispersibility, colloidal stability, and prevent their precipitation and agglomeration in biological media [51]. Up now, various grafting methods have been applied to coat surface of IOs, including *in situ* coating, post-synthesis adsorption or post-synthesis grafting [52].

Covalent grafting was reported to enhance the colloidal stability compared with adsorption coating [53]. In the chemical preparation routs of IOs, if *in situ* grafting be simultaneously applied, several removing and washing steps of byproducts and applied chemicals should be performed to minimize the chemical hazard of the prepared IOs NPs [54]. However, an *in situ* electrochemical coating of IOs have been recently developed to produce Fe_3O_4 NPs surface grafted with various biocompatible materials without needing the mentioned steps [55]. Furthermore, it was reported that electrochemical strategy could be a simple and fast rout for preparation of nanostructured oxides and hydroxides [56-65]. In this work, we report facile electrochemical method for fabrication of IOs and *in situ* doping with copper cations and also their surface grafting with polyethylenimine (PEI). The prepared polyethylenimine grafted, and Cu^{2+} doped super-paramagnetic iron oxide (PEI/Cu-IOs) NPs are characterized with FT-IR, FE-SEM, VSM and XRD analyses, and verified their suitability for biomedical uses.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of samples

All precursors including $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ and polyethylenimine (PEI, Mw~25,000) were purchased from Sigma-Aldrich and used as received. The cathodic deposition through base electro-generation on the cathode surface [66,67] was applied in the production of the iron oxide NPs. The base electro-generation was achieved by water molecule reduction on the cathode side. The anode electrode was chosen to be graphite plate with size of 10 cm*5 cm. The stainless steel plate with size of 5 cm*5 cm was also used as the cathode electrode. Direct current of 50 mA was applied in the electro-deposition runs for 25 min. The product was black film on the cathode surface. For production of PEI grafted copper cations doped Fe_3O_4 , bath composition was comprised of 1.2 g iron(III) nitrate, 0.5 g iron(II) chloride, 0.1 g copper chloride and 0.1 PEI dissolved in the distilled H_2O . At the end of each deposition run, the steel plate was pulled out from the deposition bath and washed with ethanol (96%) for several times. Then, the deposit was removed from the steel surface and dried at temperature of 80 °C for 4h. The prepared powder was final product and named PEI/Cu-IOs.

2.2. Characterization of samples

The morphology of PEI/Cu-IOs sample was observed with a field-emission scanning electron microscope (FE-SEM, model Mira 3-XMU), and the elemental data was collected through Energy Dispersive Spectroscopy (EDS) on this system. XRD experiment of the crystalline phase of the fabricated Cu-IOs powder was carried out by an X-ray diffractometer (PW-1800, Philips) with $\text{CuK}\alpha$ ($\lambda=0.15406$ nm) radiation. The analysis parameters were; 40 kV and 30 mA, 2 theta range 10 to 80 degree (in steps of 0.05 degree per second). The PEI surface coat of the fabricated PEI/Cu-IOs was recognized using Fourier transform infrared spectroscopy (FTIR, Bruker Vector 220). Dried PEI/Cu-IOs powder were mixed and pressed with KBr to provide pellets for FTIR analysis. Magnetization curves were provided at room temperature using vibrating sample magnetometer (VSM, Lake Shore Cryotronics 7407) analysis.

3. RESULTS AND DISCUSSION

Surface morphology (i.e. FE-SEM images) for the fabricated PEI coated Cu-IOs sample are provided in Fig. 1. In the FE-SEM observations (Figs. 1a,b), particle-like morphology is observed for the PEI/Cu-IOs sample. In fact, the prepared sample is composed of nearly spherical particles. The particle sizes in the range of 18-35nm have been measured in the FE-SEM observation for the PEI coated Cu-IOs sample.

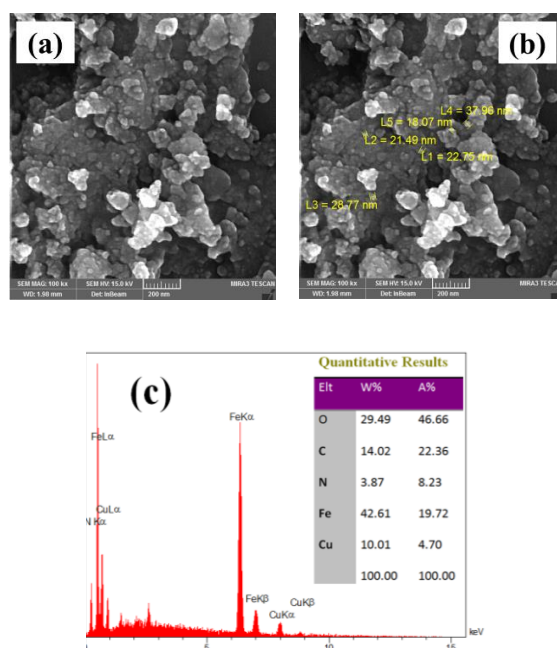


Fig. 1. (a,b) FE-SEM images and (c) EDS data of the prepared PEI coated Cu-IOs sample

The elemental analysis graph and the related data are presented in Fig. 1c. For the fabricated PEI/Cu-IOs sample, the elements of carbon, oxygen, iron, copper and nitrogen are detected in its chemical composition. The carbon content in chemical composition of PEI/Cu-IOs sample was obtained to be 14.02% wt, which come from the polyethylenimine coat on the surface of the electrodeposited iron oxide nanoparticles. The nitrogen weight percentage in the prepared sample was found to be 3.87% wt, indicating the PEI (with chemical formula of $(C_2H_5N)_n$) presence on the surface of Cu-IOs nano-particles. Furthermore, the copper ions value on the composition of PEI/Cu-IOs sample was 10.01% wt. The Cu^{2+} presence in chemical formula of the prepared sample was proved the doping of the iron oxide deposit with copper ions during their electro-synthesis process. Finally, observation of iron (42.61% wt) and oxygen (29.49% wt) elements in the composition of PEI/Cu-IOs are also indicated the magnetite crystal nature of the fabricated product.

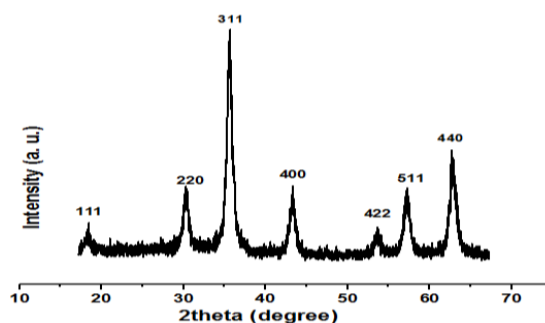


Fig. 2. XRD pattern of the prepared PEI coated Cu-IOs sample

The XRD pattern of the fabricated Cu-IOs is also provided in Fig. 2. In this pattern, the diffraction peaks of (111), (220), (311), (400), (422), (511) and (440) are seen at the 2theta of 19.24°, 31.12°, 36.87°, 43.66°, 54.15°, 57.45° and 62.41°, respectively. These peaks are related to the magnetite phase of iron oxide with JCPDS File no. 01-085-1436 [68]. No extra diffractions due to any impurity are observed in XRD pattern of PEI/Cu-IOs. An average grain size of 12.3 nm was calculated through the Debye- Scherrer relation.

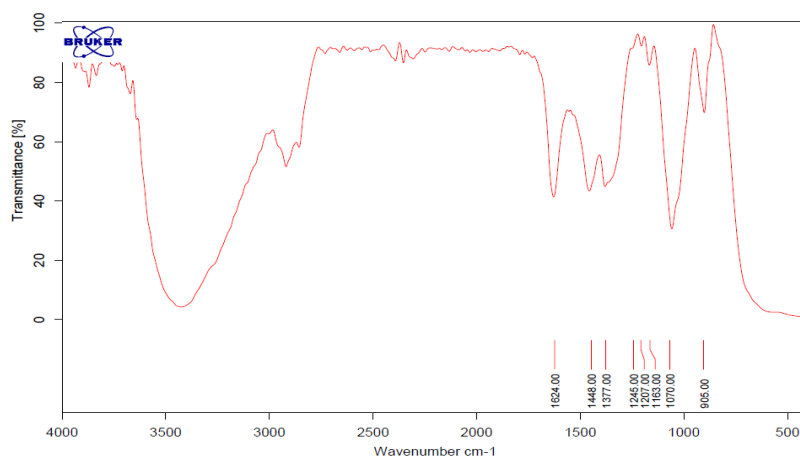


Fig. 3. IR spectrum of the deposited PEI-coated Cu- IOs sample

The FT-IR spectrum of the PEI/Cu-IOs powder is shown in Figure 3. Notably, this analysis is very useful technique to prove the presence of polyethylenimine polymer on the composition of the fabricated Cu-IOs powder [69]. In Fig. 3a, the IR bands located below 700 cm^{-1} are connected to the vibrations of metal-oxygen bonds (i.e. Fe-O-Fe and Cu-O-Fe) [70,71]. Also, several IR bands are observed at wavenumbers of 905 cm^{-1} , 1070 cm^{-1} , 1163 cm^{-1} , 1207 cm^{-1} , 1245 cm^{-1} , 1377 cm^{-1} , 1448 cm^{-1} , 1624 cm^{-1} , 2925 cm^{-1} , 2874 cm^{-1} , 2814 cm^{-1} and 3345 cm^{-1} . The characteristic vibrations for these observed IR bands are as follow; the band at 2874 cm^{-1} is attributed to the symmetric carbon-hydrogen stretching vibration, the peak at 3345 cm^{-1} can be ascribed to the nitrogen-hydrogen stretching mode, the IR band at 2925 cm^{-1} is due to the asymmetric stretching vibration carbon-hydrogen bond, the band appear at 885 cm^{-1} indicates the NH_2 wagging, the absorption at 1624 cm^{-1} is related to the bending vibration mode of amine group (i.e.- NH_2), also NH_2 scissoring mode is seen at 1448 cm^{-1} , the band located at 1245 cm^{-1} represents the carbon-carbon stretching mode, the peak at 1377 cm^{-1} indicates the bending vibration of CH_2 group, carbon-nitrogen stretching vibration is also seen at 1207 cm^{-1} , the band located at 1163 cm^{-1} proved the carbon-carbon skeletal stretching, and the absorption band at 1070 cm^{-1} can be corresponded to the carbon-nitrogen stretching vibration mode. All these observed IR bands proved the presence of PEI coat on the Cu-IOs NPs.

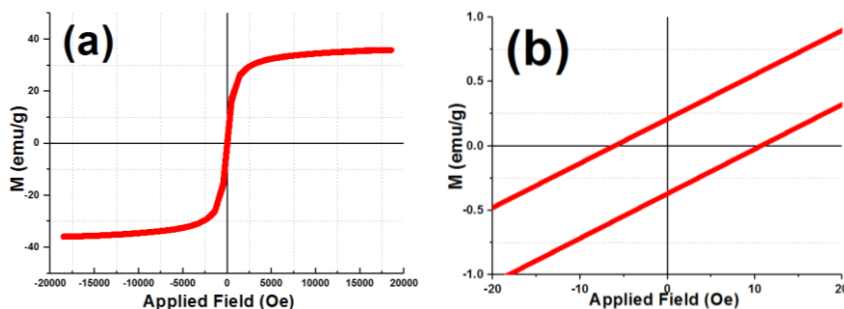


Fig. 4. Hysteresis loops for the prepared PEI coated Cu-IOs sample

The magnetic properties of the fabricated PEI/Cu-IOs sample were analyzed by VSM measurement. Fig. 4 shows the VSM curves of PEI coated Cu-IOs powder at RT. It is seen that the prepared powder exhibits reversible hysteresis profile, revealing its superparamagnetic property (Fig. 4a). Furthermore, low residual magnetization (M_r) and coercivity (H_{ci}) value are also observable in Fig. 4b for the fabricated powder, which proved its superparamagnetic nature. The magnetic data i.e. saturation magnetization (M_s), residual magnetization (M_r) and coercivity (H_{ci}) values for the fabricated PEI/Cu-IOs powder were measured to be: $M_s=35.87$ emu/g, $M_r=0.36$ emu/g and $H_{ci}=8.54$ G. From these magnetic values, it is revealed that the prepared powder exhibits very low residual magnetization and coercivity values, and hence the suitable magnetic properties of the prepared sample were qualified for biomedical aims.

4. CONCLUSION

In summary, a simple electrochemical preparation procedure was established for facile fabrication of polyethylenimine-coated Cu^{2+} doped iron oxide nanoparticles. The superparamagnetic nature of the prepared nanoparticles was observed by VSM measurements. XRD and IR analyses exhibited the magnetite (i.e. Fe_3O_4) crystal nature of the prepared sample and PEI coat on the surface of iron oxide nanoparticles, respectively. The results of analyses showed that the prepared magnetic nanoparticles have all physic-chemical requirements for applications like as hyperthermia, drug delivery and etc.

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