

Full Paper

Electrochemical Synthesis of Dextran- and Polyethyleneimine-Coated Superparamagnetic Iron Oxide Nanoparticles and Investigation of their Physico-chemical Characters

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Abstract- In this paper, with manganese doping into the crystal structure of iron oxide and then surface coating with dextran/PEI layers, two novel types of superparamagnetic particles are fabricated. A simple one-step cathodic electrochemical synthesis is developed for preparation of these magnetic nanoparticles. The deposition and surface coating are simultaneously performed from the dextran or PEI added aqueous solution of 0.1M Fe(II) chloride, 0.2M Fe(III) nitrate and 0.05M manganese nitrate. FT-IR, EDAX and FE-SEM analyses showed nano-size of the prepared iron oxide particles and the polymer layers onto their surface. Negligible remanence and coercivity values exhibited by the prepared iron oxide particles verified their excellent superparamagnetic behavior. Based on the analyses results, it was proven that the prepared magnetic particles are good candidates for biomedical applications.

Keywords- Iron oxide, Dextran, PEI, Magnetic powder, Electrochemical synthesis

1. INTRODUCTION

Recently, iron oxides-based nanomaterials (magnetite, magnetite and mixed ferrites) have found potential interest for use in various bio-medicine [1-5], charge storage devices [6-8], heavy metal removal [9,10], bio-chemistry and biology [11]. Surface modified iron oxides-based particles have also found widespread list of applications including magnetic resonance

imaging, tissue repair, magnetic separation, bio-separation hyperthermia, bio-sensing and targeted delivery of various drugs [12-20].

As a preparation procedure, electrochemical syntheses have been extensively applied for synthesis of nanostructured materials and it was reported that the quality (i.e. crystal structure, chemical composition and morphology) of the deposited product is easily tailored by parameters of pH, bath composition, deposition mod, temperature, salt and bath type [21-30]. In the case of iron oxides (IOs), cathodic electrodeposition has been used to fabricate surface-grafted IOs, and it was reported that the IOs formation and surface coating are concurrently occurred in this method [31,32], where these advances establish CED method to be competitable with common chemical methods e.g. solvothermal, co-precipitation and thermal decomposition [33-39]. Notably, these chemical methods use high temperature, expensive precursors, high pressure, long synthesis time, multistep process to produce pristine and surface capped IONs, where CED route exhibits one-step process, room temperature, *in situ* capping and mild conditions for fabricate IOs. In all biomedical application fields, magnetic particles should be present; (i) large saturation magnetization (M_s) values at the presence of external field, (ii) negligible coercivity (H_{ci}) and remanence (M_r) at the absence of applied field, (iii) surface coated with biocompatible molecules, (iv) low toxicity and (v) biocompatibility [40,41]. On the other hand, preparation of metal-ion doped IOs has been investigated using CED method, and Co-, Dy-, Zn-, La-, Sm- and Gd-doped IOs with improved magnetic behavior have been synthesized through cathodic deposition [25-55]. In this paper, two new types of superparamagnetic surface coated iron oxides (Dextran-coated Mn^{2+} -doped IOs and PEI-coated Mn^{2+} -doped IOs) are reported for the first time. These IOs are deposited through constant current deposition from the PEI /or dextran dissolved Fe(III)nitrate/Fe(II)chloride/Mn chloride electrolyte. The characterizations of electrodeposited DEX/Mn-IOs and PEI/Mn-IOs powders are followed by DSC-TGA, XRD, FT-IR, FE-SEM, EDAX and VSM analyses.

2. EXPERIMENTAL

2.1. Chemicals

Iron(III) nitrate (Sigma Aldrich, 99.9%), iron(II) chloride (Sigma Aldrich, 99%), manganese nitrate (Sigma Aldrich, 99.5%), polyethylene imine (PEI, $[H(NHCH_2CH_2)_nNH_2]$, Sigma Aldrich, $M_w \sim 25,000$) and dextran (Sigma Aldrich, average $M_w = 70,000$) were purchased and used as received without any purification.

2.2. Synthesis of samples

The well-known electrochemical method i.e. cathodic synthesis via base generation was selected to prepared iron oxide samples. The two biocompatible agents of dextran and PEI were used to in situ surface capping of iron oxide nanoparticles during their cathodic deposition. Furthermore, the iron oxides were doped with manganese cations during their electrochemical synthesis. A simple two-electrode electrochemical set up was used for preparing the iron oxide nanoparticle with PEI- and DEX-surface coated and crystal structure doped with Mn^{2+} cations. The electrodeposition cell was one-liter beaker, which two electrodes of stainless steel (as cathode and anode with size of 5cm*10cm) have immersed into the electrolyte. The bath electrolyte was prepared by mixing the 0.1M Fe(II) chloride, 0.2M Fe(III) nitrate and 0.05M Mn nitrate in 1L deionized H_2O . Notably, two series of this solution bath were prepared and the 1g/L capping agent (i.e. dextran or PEI) was added to these baths and stirred for 2h, and then were used as the deposition baths. The electrodeposition was ran with applying dc condition ($i=0.2 A dm^2$) for 30min. After this experiment, the deposit was collected from the cathode surface and dissolved in ethanol. Then, this mixture was centrifuged at 6000 rpm for 10 min to remove the excess of polymer. In final, the iron oxide product was collected from the ethanol solution by magnet and dried to obtain black powders (i.e. DEX/Mn-IOs and PEI/Mn-IOs).

2.3. Sample characterization

The morphologies of the prepared DEX/Mn-IOs and PEI/Mn-IOs samples were observed using field-emission scanning electron microscopy (FE-SEM, Mira 3-XMU with accelerating voltage of 100 kV). And the elemental data of both DEX/Mn-IOs and PEI/Mn-IOs samples were provided on this FE-SEM instrument through EDAX analysis. Thermal behaviors (DCS-TG analysis) of samples were investigated by thermo-analyzer instrument (STA-1500) at the conditions of atmosphere= N_2 gas $T=25-500$ °C and heating rate= $5^\circ C/min$. The XRD patterns were taken by Phillips PW-1800. The FTIR spectra of DEX/Mn-IOs and PEI/Mn-IOs samples were collected through a Bruker Vector 22 FT-IR spectroscope at the wavenumbers of $4 cm^{-1}$ from 400 to $4000 cm^{-1}$. The VSM curves were also provided using Lake Shore Cryotronics 7400 series instrument and the related magnetic data were obtained from the VSM profiles.

3. RESULTS AND DISCUSSION

3.1. Crystal structure

XRD patterns of the synthesized DEX/Mn-IOs and PEI/Mn-IOs samples are presented in Fig. 1. Both samples exhibited crystal planes (111), (220), (311), (400), (442), (511) and (440), which are easily indexed to the iron oxide with magnetite phase with a cubic unit cell (JCPDS 01-088-0315, $a=0.83980$ nm). No extra XRD plane was seen verifying the pure magnetite structure and also the Mn^{2+} substitution in the Fe^{2+} sites of Fe_3O_4 . The average

crystallite sizes (D) of 9.2nm and 9.6nm were calculated (*via* the Scherrer's equation) for the prepared DEX/Mn-IOs and PEI/Mn-IOs samples, respectively.

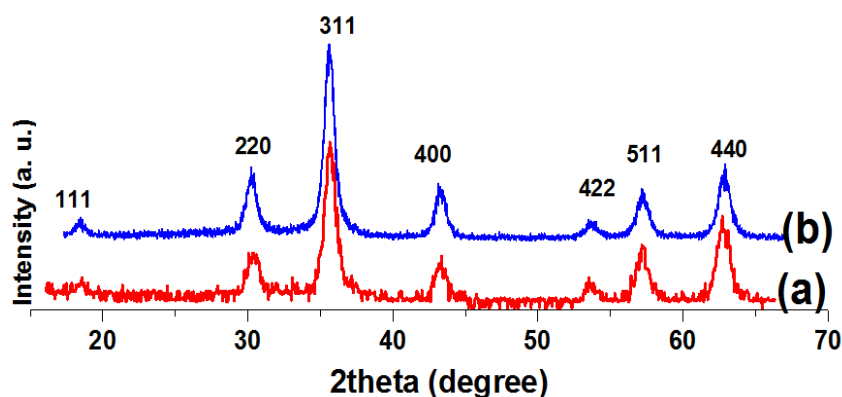


Fig. 1. XRD pattern of the prepared iron oxide/porous graphene composite

3.2. Morphological evolution

FE-SEM observations of the prepared DEX/Mn-IOs and PEI/Mn-IOs samples are shown in Figs. 2a and b. For both samples, particle morphology is seen with average size of 15nm. The elemental graphs of the DEX/Mn-IOs and PEI/Mn-IOs samples are also given in Figs. 2c and d. For the DEX/Mn-IOs powder, the existence of carbon (30.65%wt), oxygen (25.11%wt), iron (35.02%wt) and manganese (9.22%wt) were observed (Fig. 2c). These data confirmed two facts about DEX/Mn-IOs sample; (i) doping with manganese cations, and (ii) surface coating with dextran. For the PEI/Mn-IOs powder, the presence of carbon (30.97%wt), oxygen (24.52%wt), nitrogen (2.95%wt), iron (33.26%wt) and manganese (9.22%wt) were proved (Fig. 2d). These elemental data clearly indicated the PEI coating the surface of the electrodeposited iron oxides and also their crystal structure doping with 9.22% Mn^{2+} ions.

3.3. FT-IR

IR spectra of the prepared iron oxides samples are shown Fig. 3. For the DEX/Mn-IOs sample, the following vibrations are seen in Fig. 3a: $\nu_{as}(C-H)$ at 2936 cm^{-1} , $\nu_{sy}(C-H)$ at 2886 cm^{-1} , $\nu(C-C)$ at 1022 cm^{-1} , $\nu(CH_2)$ at 1466 cm^{-1} , $\nu(C-O-C)$ at 1153 cm^{-1} , $\nu(C-OH)$ at 1378 cm^{-1} and $\nu(O-H)$ at 875 cm^{-1} [56,57]. These IR bands clearly indicated the vibrations of various chemical bonds located at the dextran chains. The IR adsorptions at the wavenumbers below 700 cm^{-1} are also related to the Fe(III)-O-Fe(II) and Fe(II)-O-Mn chemical bonds [58,59]. Hence, the dextran surface coat layers onto the prepared Mn-IOs particles are proved.

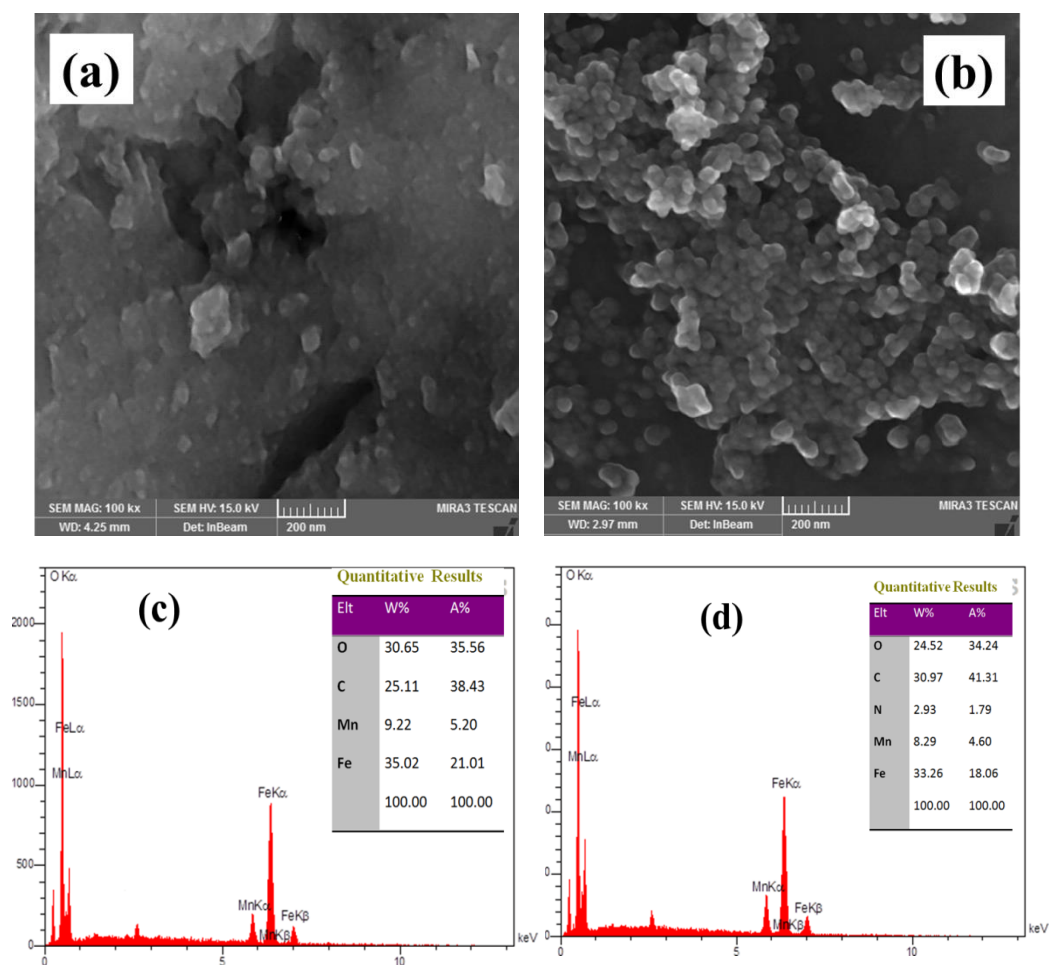


Fig. 2. (a,b) FE-SEM images and (c,d) EDS data of the synthesized DEX- and PEI-coated Mn^{2+} -doped IOs

For the PEI/Mn-IOs sample, the following vibrations are also existed in Fig. 3b: $\nu_{\text{as(C-H)}}$ at 2944 cm^{-1} , $\nu_{\text{sy(C-H)}}$ at 2872 cm^{-1} , $\nu_{\text{(N-H)}}$ at 3395 cm^{-1} , $\nu_{\text{(NH}_2\text{)}}$ at 1624 cm^{-1} , $\nu_{\text{(C-N)}}$ at 1070 cm^{-1} , $\nu_{\text{(C-C)}}$ at 1163 cm^{-1} , $\nu_{\text{(CH}_2\text{)}}$ at 1466 cm^{-1} , $\nu_{\text{(C-N)}}$ at 1207 cm^{-1} , $\nu_{\text{(C-OH)}}$ at 1377 cm^{-1} and $\nu_{\text{(O-H)}}$ or $\nu_{\text{(N-H)}}$ at 905 cm^{-1} [56-59]. These IR bands are related to PEI polymer layer onto the surface of Mn-IOs particles.

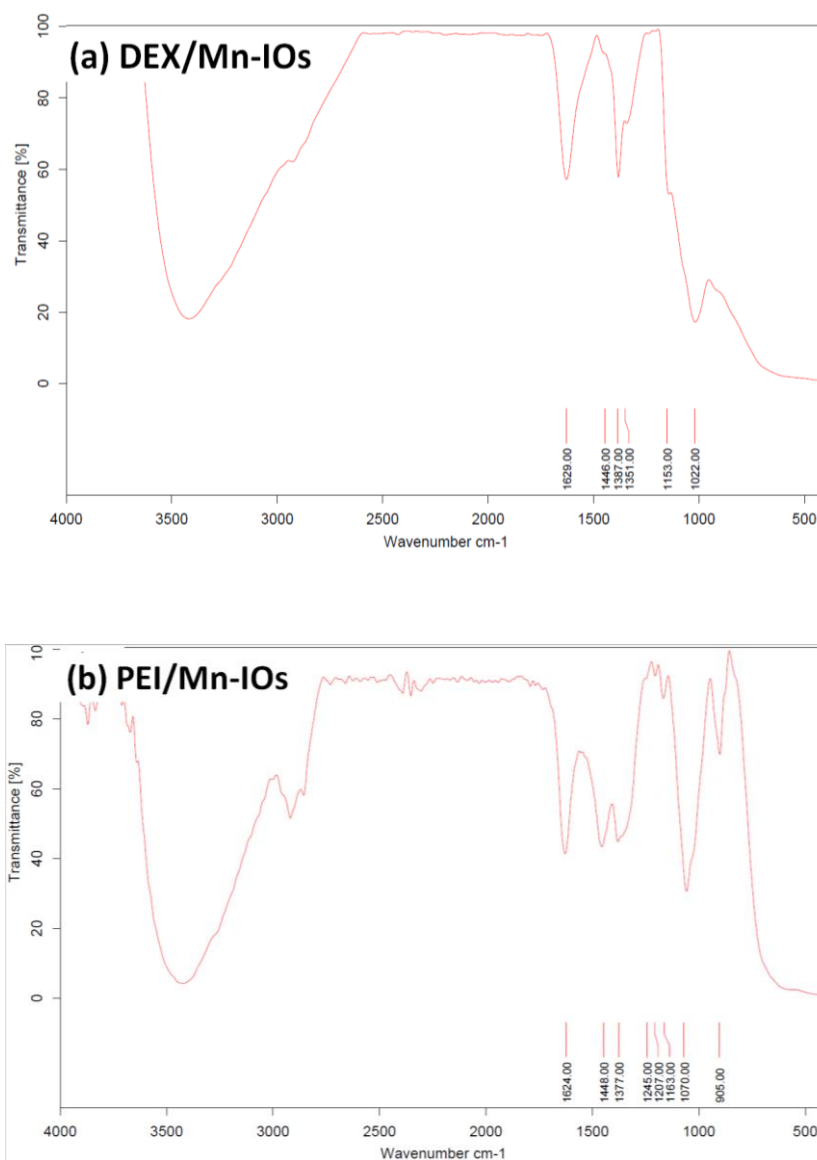


Fig. 3. FTIR spectra of the surface coated iron oxides

3.4. TG analysis

Fig. 4 shows the TG curve of the prepared DEX/Mn-IOs sample. In the TG curve, there is a weight loss of 8.5% at $T < 150^{\circ}\text{C}$ due to the remove of OH^- groups linked to the Mn-IOs surfaces. For this step DSC shows a small endothermic peak. For pure dextran powder, the organic skeleton breakdown of dextran was reported to be observed at $245\text{-}250^{\circ}\text{C}$ [60,61]. For our powder, a sharp weight loss (31.5% wt.) is observed at the 265°C , which is due to the remove of dextran from the particle surfaces. The DSC curve is also indicated the strong endothermic peak for this temperature range. These observations proved the dextran later onto the deposited Mn-IOs particles.

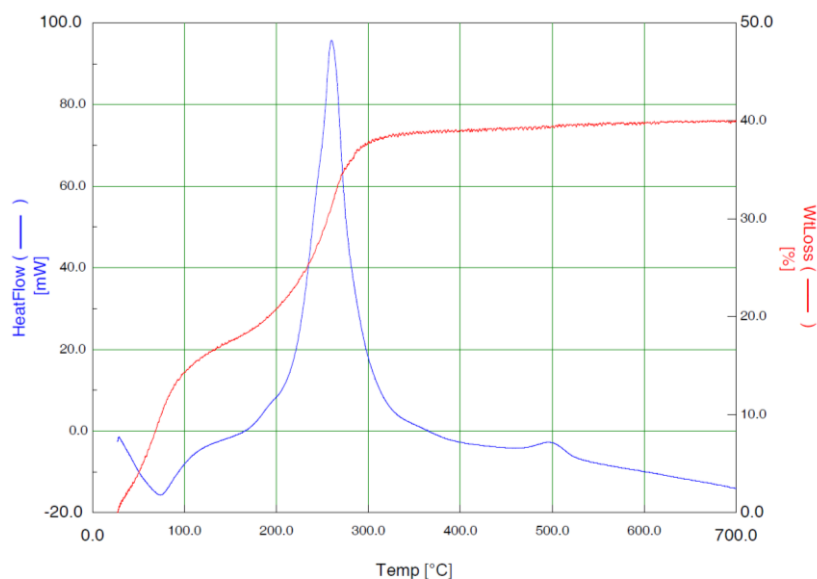


Fig. 4. DSC curve and related TG profile for the prepared DEX/Mn-IOs particles

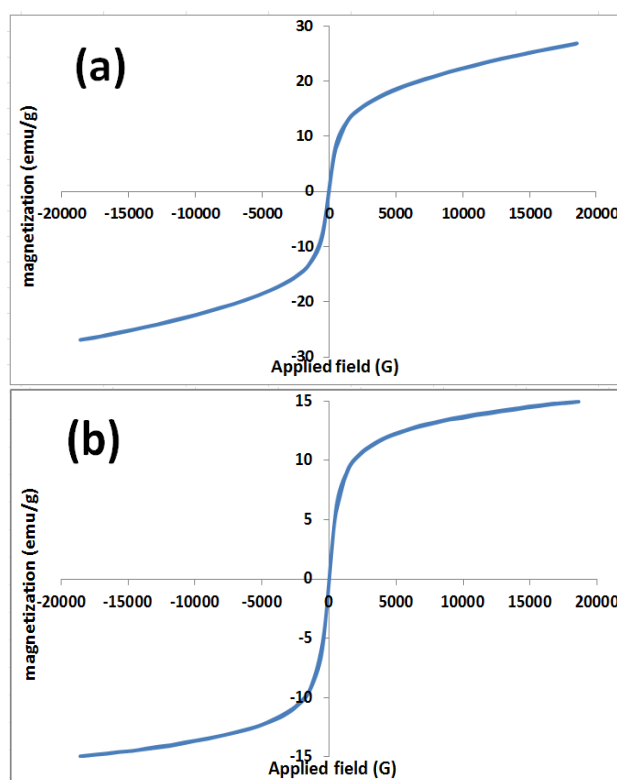


Fig. 5. Hysteresis profile and the related magnetic data for the prepared DEX- and PEI-coated Mn²⁺-doped IOs

3.5. Magnetic evaluation

VSM profiles of the prepared samples are presented in Fig. 5. The saturation magnetization (M_s) values of 26.75 emu g⁻¹ and 14.59 emu g⁻¹ were observed for DEX- and PEI-coated Mn²⁺-doped IOs samples, respectively. The remanence (M_r) values of 0.14 emu

g^{-1} and 0.21 emu g^{-1} DEX- and PEI-coated Mn^{2+} -doped IOs samples, respectively. These data implied the supervising magnetic behavior of both prepared samples, where the very low (or negligible remanence of both sample indicated their superparamagnetic nature. Furthermore, very low coercivity (H_{ci}) values were also observed for both samples with removing the applied field i.e. $H_{ci} = 3.41 \text{ G}$ (for DEX/Mn-IOs) and $H_{ci} = 1.871 \text{ G}$ (for PEI/Mn-IOs). As compared with the reported magnetic data (remanence and coercivity values) in the literature [42-46,62], an improvement in the magnetic behavior of iron oxide nano-particles was obtained. Also, the observed magnetic performances of DEX- and PEI-coated Mn^{2+} -doped IOs samples are the suitable for biomedical aims and hence the prepared samples have proper magnetic conditions for biomedical applications like hyperthermia.

4. CONCLUSION

In summary, DEX- and PEI-coated Mn^{2+} -doped iron oxide particles were simply fabricated through galvanostatic electrochemical deposition method. It was found that Mn-doping and surface coating improved the magnetic behavior of iron oxide. The TG data indicated about 32%wt dextran coat on the deposited iron oxide particles. Also, the EDAX data showed the fabricated iron oxide powders have ~10% doped Mn cations in their crystal structures. Superparamagnetic behaviors were observed for the prepared nanoparticles.

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