

Full Paper

PVP- and PEG-grafted Ni Doped Iron Oxide Nanoparticles for Biomedical Applications: Electrochemical Synthesis and Characterization

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Abstract- Here, an electrochemical synthesis method is reported for the facile preparation of Ni doped iron oxide grafted with biocompatible polymers (i.e. PVP and PEG). PVP- and PEG coated Ni doped iron oxides (i.e. PVP-Ni-IOs and PEG-Ni-IOs) were fabricated through cathodic electrochemical deposition. The aqueous electrolyte containing 2.4 g Fe(NO₃)₃, 1g FeCl₂, 0.2NiCl₂ and 0.5 g PVP or 0.5 g PEG was used as the deposition media. The crystal structure, morphology, chemical composition, purity, and magnetite properties of the prepared PVP-Ni-IOs and PEG-Ni-IOs samples were scrutinized through XRD, FTIR, FE-SEM/EDAX and VSM techniques. The presence of PVP and PEG on the surface of the IOs was confirmed via EDS and FTIR analyses. XRD and FE-SEM probes showed that the products are magnetite crystal structure with the particle size about 20 nm. EDAX results verified that the samples have metal ion doped Fe₃O₄ (about 7%Ni cations) composition. In addition, VSM measurement confirmed that the both PVP-Ni-IOs and PEG-Ni-IOs samples have superparamagnetic nature, showing the saturation magnetizations of 52.98 and 48.51 emu/g, respectively.

Keywords- Iron oxide, Ni doping, Surface coating, Nanoparticles, Electrochemical synthesis

1. INTRODUCTION

There is a great interest in the development of new nanomaterials for multimodal applications in biology, environment, energy and medicine. Magnetic nanomaterials have a range of unique properties and can offer new attractive options in many applications [1]. In this regards, surface coated iron oxides (IOs) are proper candidates for uses in various biomedical and environmental applications including magnetic resonance imaging (MRI), drug delivery systems, biological imaging, cytometry, medical diagnostics, cell tracking and magnetic separation, contaminant removal, remediation, and water treatment [2-8]. Surface modification of IOs by polymers, proteins, amino acids or other biocompatible molecules is usually investigated to grant these magnetic nanoparticles physiological stability and biocompatibility [9-14]. In this regard, it was reported that co-modifying with poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG) offer to the IOs proper steric hindrance and better colloidal stability [15]. PEG is a water soluble polymer and has been widely used to enhance the water solubility of hydrophobic inorganic nanoparticles [16,17]. PVP polymer has been also well applied in the synthesis of IOs, due to its good aqueous dispersing ability and biocompatibility [18-20]. As an electrochemical preparation method, cathodic electrochemical synthesis provides facile and cheap route for preparation of metal oxides and hydroxides with particle-, plate-, rod- and wire-like morphologies [20-27]. Until now, electrochemical synthesis has been used for preparation of magnetite NPs in both bare and surface coated forms. For example, IOs grafted with PEG [28,29], chitosan [30,31], PEI [32], PVA [33,34], saccharides [35,36] and PVP [37,38] have been fabricated using cathodic electrochemical synthesis and their physico-chemical properties have been also investigated. Furthermore, this electrochemical strategy has been also applied for fabricating fine nanoparticles of metal cations doped iron oxides [39-50]. The results of these works have proven that the magnetic (i.e. saturation magnetization, remanent magnetization and coercivity) of the doped IOs are improved as a result of metal ions doping into the magnetite crystal structure.

Here, we report iron oxide NPs doped by metal ions and also surface modified with PVP and PEG polymers prepared by cathodic electrodeposition method. The morphological properties and crystal structure of the fabricated sample could be easily changed through altering the simple electrochemical conditions like applied current, voltage and electrolyte composition [51-53]. In this work, we used one-step cathodic deposition method for the preparing the PVP coted Ni^{2+} doped IOs (PVP-Ni-IOs) and PEG coated Ni^{2+} doped IOs (PEG-Ni-IOs) nano-particles. The obtained magnetite NPs are characterized through by FT-IR, FE-SEM, XRD and VSM techniques.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Iron (II) chloride tetrachloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), gadolinium chloride hexahydrate ($\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$), polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$), were purchased from Sigma-Aldrich. The graphite plates and stainless steel sheets (316 L) were provided from local companies.

2.2. Preparation procedure

The cathodic electrochemical synthesis was chosen for the preparation of samples. The electrolyte solution was prepared by dissolving the iron(II) chloride/iron(III) nitrate/nickel chloride (1 g:2.4 g:0.2 g) salts in 1 L deionized water. 0.5 g PVP/ or 0.5 g PEG was then added in this electrolyte and stirred for 1 h. The synthesis experiments were done in two-electrode system including a 10 cm*5 cm stainless steel cathode centered between two graphite plates (10 cm*5 cm). A typical current density of 5 mAcm^{-2} was applied for 30 min at RT condition, and black thin film was formed on the cathode surface. After each synthesis run, the purification process was followed as; (a) the cathode were removed from the electrolyte and washed several times with deionized water, (b) the deposited black film was scraped from the cathode surface and dissolved in 50 cc ethanol, and then (c) the black powder was washed with ethanol several times to remove free and un-reacted polymers, (d) the powder was then dispersed in ethanol and centrifuged at 6000 rpm for 10 min, and (e) finally, the black powder was separated by magnet and dried at 80°C in vacuum oven for 1h. The obtained dry powder were labeled PVP-Ni-IOs and PEG-Ni-IOs samples and characterized by various techniques.

2.3. Characterization techniques

The powder XRD was performed at room temperature with a Phillips PW-1800 X-ray diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda=0.154056 \text{ nm}$). The IR spectra were provided using Bruker Vector 22 IR spectrometer in the frequency range $4,000\text{--}400 \text{ cm}^{-1}$. Field-emission Scanning Electron Microscope (FE-SEM, model Mira 3-XMU with accelerating voltage of 100 kV), attached with Energy Dispersive X-ray Spectroscopy (EDAX, for measuring elemental composition) were used for observing the surface morphology and collecting elemental data. Magnetization measurements were performed at room temperature with vibrating sample magnetometer (VSM, Lake Shore 7307).

3. RESULTS AND DISCUSSION

3.1. Crystal structure

The XRD diffraction patterns of the prepared samples are shown in Fig. 1. It is clear that the both XRD patterns of our samples are completely similar to the pure magnetite XRD patterns reported in the literature [54,55], which has been prepared through electrochemical synthesis. The characteristic diffraction peaks of (111), (220), (311), (400), (422), (422), (511), (440) and (533) are agreement with those of the inverse cubic spinel structure of Fe_3O_4 (JCPDS No. 85-1436). No additional XRD peak was seen, revealing the preparation of pure magnetite phase.

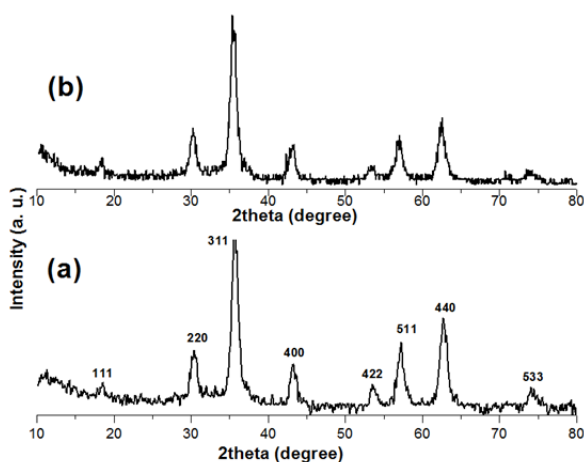


Fig. 1. XRD patterns of the prepared (a) PVP-Ni-IOs and (b) PEG-Ni-IONs samples

3.2. FT-IR

To evaluate the presence of grafted PVP and PEG polymers onto the surface of Ni-IOs NPs, FT-IR spectra were recorded and shown in Fig. 2. In both spectra; (a) the absorption peaks at 578 and 587 cm^{-1} are related to the stretching vibration mode of Fe–O/Ni–O bonds, (b) the peaks at 1635 and 1637 cm^{-1} are attributed to the bending vibration of water adsorbed on the surface of Ni-IOs and (c) the peaks at 3420 and 3425 cm^{-1} are due to the –OH present on the surface of Ni-IOs nanoparticles [57-60]. These data proved the magnetite phase for both prepared PVP-NI-IOs and PEG-NI-IOs samples.

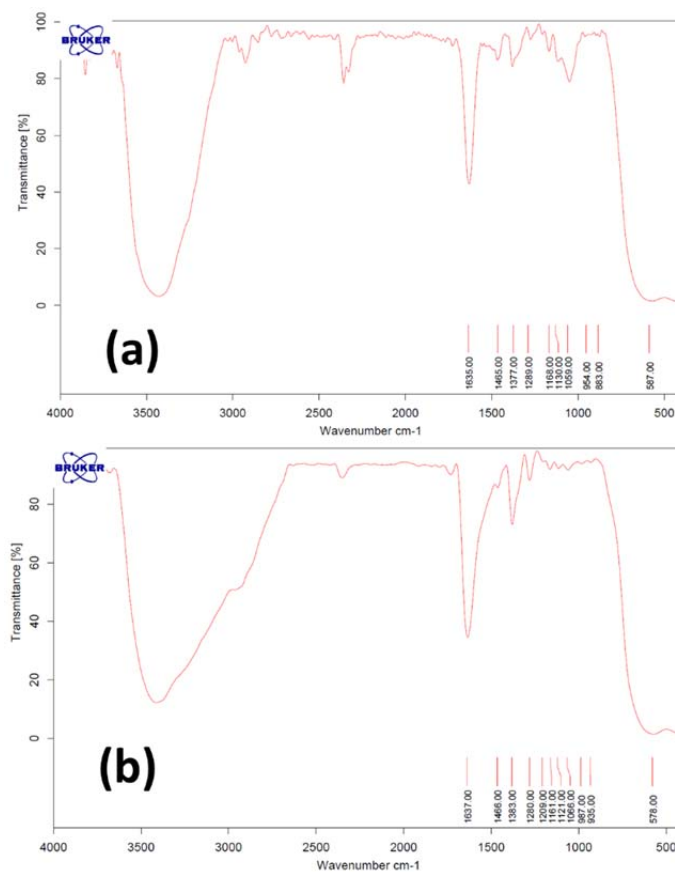


Fig. 2. IR spectra of the prepared (a) PVP-Ni-IOs and (b) PEG-Ni-IONs samples

For the prepared PVP-NI-IOs sample (Fig. 2a); vibration modes of CH₂ groups at 2917, 2870, 1466, 1382 and 1209 cm⁻¹ [61,62], stretching modes of C-N bond at 1280 and 1066 cm⁻¹ [63,64], stretching mode of C-C bond at 1121 cm⁻¹ [65,66] and vibration of C=O group at 1637 cm⁻¹ [64,67]. These IR bands confirmed the presence of PVP on the surface of the synthesized nanoparticles.

For the prepared PEG-NI-IOs sample (Fig. 2b); C-H stretching vibrations around 2916 cm⁻¹ and 954 cm⁻¹ [68,69], CH₂ vibrations at 1289 cm⁻¹ and 1465 cm⁻¹ [70], C-O-C stretching at 1130 cm⁻¹ and 1377 cm⁻¹ [71], CH out-of-plane bending vibrations at around 2889 cm⁻¹ and 954 cm⁻¹ [71,72], -OH stretching and bending vibrations at 3415 cm⁻¹ and 1405 cm⁻¹ and C-H wagging at 890 cm⁻¹ [73,74]. The presence of these characteristic peaks of PEG proved the successful formation of PEG grafted Ni doped Fe₃O₄ nanoparticles.

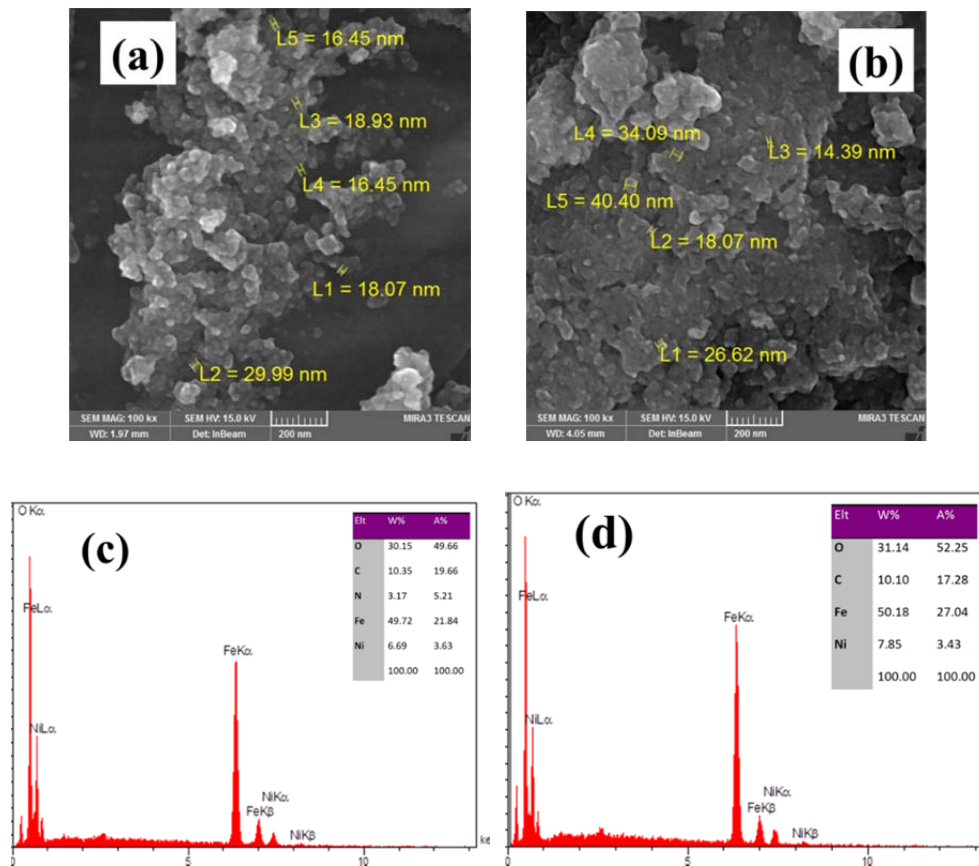


Fig. 3. FE-SEM images and EDS data of the prepared (a,c) PVP-Ni-IOs and (b,d) PEG-Ni-IOs samples

3.3. Morphological characterization

FE-SEM images and the elemental analysis data are shown in Fig. 3. For both fabricated PVP-Ni-IOs and PEG-Ni-IOs samples, the particle-like morphology is observed in the FE-SEM images (Figs. 3a and b). The average particle size for the PVP-Ni-IOs sample was calculated to be 20 nm and also for the PEG-Ni-IOs sample, this size was 25 nm. The findings revealed that the prepared sample in the presence of PVP has smaller size than those fabricated in the PEG presence. The EDAX diagrams and the extracted data are presented in Figs. 3c and d. For the PVP-Ni-IOs sample, the elements of oxygen, carbon, nitrogen, iron and nickel with weight percentage of 30.15%, 10.35%, 3.17%, 49.72% and 6.69% are obtained, respectively. The Ni element presence in EDAX data confirmed the metal ion doping of magnetite during its cathodic electrochemical synthesis. Furthermore, the presence of C and N elements confirmed the attached PVP polymer onto the Ni-IOs nanoparticles. For the PEG-Ni-IOs sample, the elements of oxygen, carbon, iron and nickel with weight percentage of 31.14%, 10.10%, 50.18% and 7.58% are observed respectively. The C content in the chemical composition of this sample proved the attachment of PEG coat layer onto the surface of deposited iron oxides, and Ni content deal with the doped iron oxides. Hence, the

FE-SEM and EDAX analyses confirmed the successful electrochemical preparation of polymer grafted metal ion doped iron oxide nano-particles.

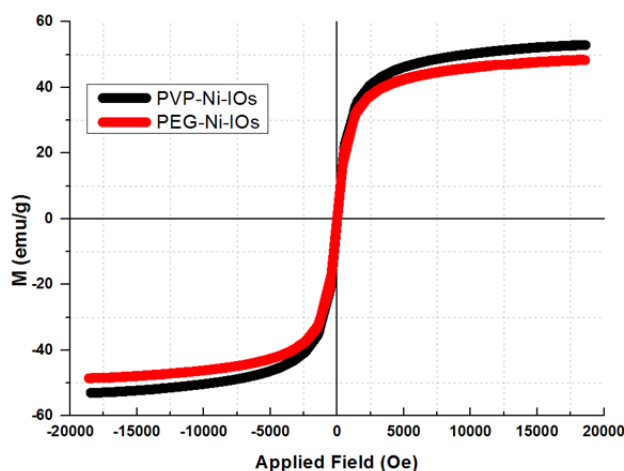


Fig. 4. Hysteresis loops for electro synthesized samples

3.4. Magnetic evaluation

The magnetic properties of the electro synthesized samples were obtained via VSM analysis. Fig. 4 shows the hysteresis loops of PVP-Ni-IOs and PEG-Ni-IOs samples at room temperature. The obtained data from the VSM graphs is also listed in Table 1. As it can be seen in Fig. 4, for this case the magnetization curve is totally reversible because of the fast magnetic relaxation which causes the system to be remained at thermodynamic equilibrium [75]. Also, both samples showed a typical superparamagnetic behavior suggesting that the IOs surface modified with PEG and PVP preserved their superparamagnetic nature. As listed in Table 1, the saturation magnetization (M_s) values for the fabricated PVP-Ni-IOs and PEG-Ni-IOs samples are observed to be 52.98 and 48.51 emu/g, respectively. These values indicated the proper magnetic response of the prepared samples in the presence of applied field. Also, the M_r values of 0.001 and 0.017 emu/g were observed for PVP-Ni-IOs and PEG-Ni-IOs samples, respectively.

Table 1. Magnetic data for the prepared samples

Sample name	M_s (emu/g)	Coercivity (Hci)G	Positive (Hci) G	Negative (Hci) G	Negative M_r (emu/g)	Positive M_r (emu/g)	Retentivity M_r (emu/g)
PVP-Ni-IOs	52.95	0.17	10.14	9.89	-0.51	-0.48	0.001
PEG-Ni-IOs	48.51	4.16	-9.64	-1.32	0.38	0.05	0.017

These M_r data clearly proved the suitable superparamagnetic nature of these samples. Notably, the M_s values for the bare undoped and Ni doped Fe_3O_4 NPs have been reported to be: $M_s=41.47$ emu/g, $M_r=0.17$ emu/g for bare IOs [76], and $M_s=72.9$ emu/g, $M_r=1.21$ emu/g for bare Ni-IOs [77]. Comparing these data indicated that the superparamagnetic behavior of iron oxide is improved by metal ion doping and also surface modifying with polymers.

4. CONCLUSION

In summary, a simple fabrication method was proposed to prepare polymer coated metal ion doped iron oxide. Using the proposed method, the PVP- and PEG coated Ni doped magnetite NPs were prepared and characterized through XRD, FE-SEM and VSM techniques. The analyses results proved the successful formation of PVP-Ni-IOs and PVP-Ni-IOs nano-particles. The obtained products have particle size of about 20 nm. The PVP and PEG coats on the surface of Ni-iron oxides were specified through FT-IR and EDAS data. Magnetic evaluation revealed that the prepared products have superparamagnetic properties.

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