

*Full Paper*

# **Polyvinylpyrrolidone-grafted Gadolinium Cations Doped Iron Oxide Nanoparticles for Biomedical Applications: One-step Cathodic Electrochemical Synthesis and Characterization**

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**Abstract-** In this paper, magnetic iron oxide nanoparticles (MIOs) of controlled size distribution were electrochemically fabricated through applying typical galvanostatic deposition conditions from dissolved iron(II) chloride, iron(III) nitrate, Gd(III) chloride salts in aqueous media. The produced deposit was MIOs doped with ~19% Gd<sup>3+</sup> cations (i.e. Gd-MIOs). *In situ* surface grafting of the deposited Gd-MIOs with polyvinylpyrrolidone (PVP/Gd-MIOs) polymer was also achieved through only addition of PVP into the deposition bath without using any supporting electrolyte. The presence of PVP-grafted layer onto the Gd-MIOs surface was supported *via* EDS and FTIR data. The magnetic evolution results indicated that the prepared PVP/Gd-MIOs powder has all the magnetic qualification requirements and hence could be a potential candidate for use in bio-medicine.

**Keywords -** Iron oxide, Nanoparticles, Doping, Surface coating, Electrochemical synthesis

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## **1. INTRODUCTION**

Development of new magnetic nano-particles and their facile preparation strategies has been recently gained great interest in application areas of bio-medicine, energy, nanotechnology, and environment [1-3]. Magnetic nano-particles (MNPs) exhibit a range of unique properties and can present novel attractive capabilities in various uses [4-6]. For

instance, naked- and surface grafted magnetic iron oxides (MIOs) are interest potential candidates for applications like as contrast agents for MRI [7,8], hyperthermia [9,10], stem cell [11], drug delivery [12], chemotherapy [13], supercapacitors and batteries [14-18], contaminant removal [19,20], bio-sensing [21], and cancer diagnostics [22,23]. Among these different application domains, the biomedical application of MIOs has been widespread research field, and there is great focus in this context to provide clinical use of MIOs [24]. Furthermore, several preparation methods have been established for production of magnetic nanoparticles, including hydrothermal [25,26], electrochemical [27-32] solvothermal [33,34], co-precipitation [35-37], microemulsion [38], thermal decomposition [39-41], sol-gel [42,43], and pyrolysis [44] methods. Using the electrochemical route, many oxides and hydroxides with various morphologies like as particle, rod, plate, tube and sphere has been successfully produced in a simple two-electrode set up [45-57]. In biomedical uses, surface of MIOs should be grafted with bio-compatible materials including PEG, PVP, chitosan, dextran, saccharides, amino acids, organic acids, etc. to supply the physiological stability and biocompatibility [58-62]. Electrochemical production through base electro-generation has been recently introduced as an easy, simple and fast technique for the fabrication of bare MNPs [63], surface capped  $\text{Fe}_3\text{O}_4$  [64], and metal-ion doped MIOs [65-70]. In this study, surface grafted iron oxide nanoparticles with PVP polymer and doped with gadolinium cations (PVP/Gd-MIOs) are prepared by cathodic base electro-generation process. The obtained magnetite NPs are characterized through by EDAX, FT-IR, FE-SEM, XRD and VSM techniques.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of iron oxide samples

Electrochemical synthesis (deposition) processes were performed in typical two-electrode cell. The cathode electrode was selected to be a stainless steel plate (361 L) with a geometric area of  $50 \text{ cm}^2$ . The anode electrode was graphite plate with area of  $100 \text{ cm}^2$ . An aqueous electrolyte of 2.4 g Iron (III) nitrate nonahydrate, 0.8 iron (II) chloride tetrachloride, 0.6 gadolinium chloride hexahydrate and 0.5 g polyvinylpyrrolidone (PVP) was prepared for the electro-synthesis of PVP/Gd-MIOs samples. All of the used salts and PVP polymer were obtained from Sigma-Aldrich Company. The mentioned materials were dissolved in 1 liter deionized water and the pH was fixed at 6.7. In the deposition experiments, cathodic current of 1A was applied into the electrochemical cell for 15 min at RT condition. And a black film was observed on the steel cathode at the end of deposition time. After synthesis, the steel cathode was washed with ethanol and the black film was collected from its surface as the deposition product. The drying of deposit was carried out at  $90 \text{ }^\circ\text{C}$  in vacuum oven for 60 min. In final, the dry black powder was obtained and subjected to characterization techniques.

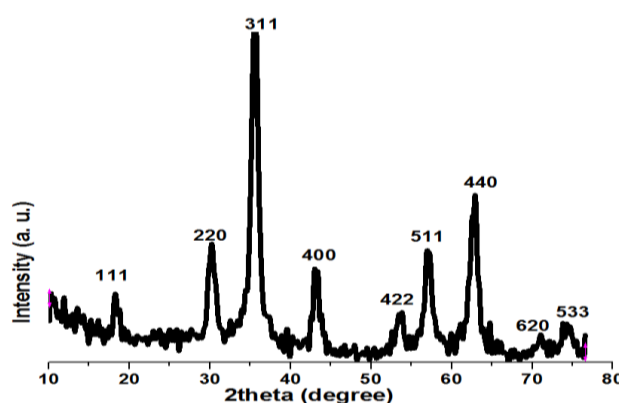
## 2.2. Characterization of samples

XRD pattern of the fabricated powder was collected using a Philips PW-1800 X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda=0.154056$  nm). Particle size determination was obtained from X-ray diffraction line broadening and electron microscopy (FE-SEM). The IR analysis was done on the Bruker Vector 22 IR spectrometer in the wavenumbers between 4000–400  $\text{cm}^{-1}$ . Energy Dispersive X-ray Spectroscopy (EDAX) was used to identify the elemental composition of sample. And morphology observations of the prepared sample were provided by Field-emission Scanning Electron Microscope (FE-SEM, model Mira 3-XMU with accelerating voltage of 100 kV). Magnetization evaluation was carried out through vibrating sample magnetometer (VSM, Lake Shore 7307).

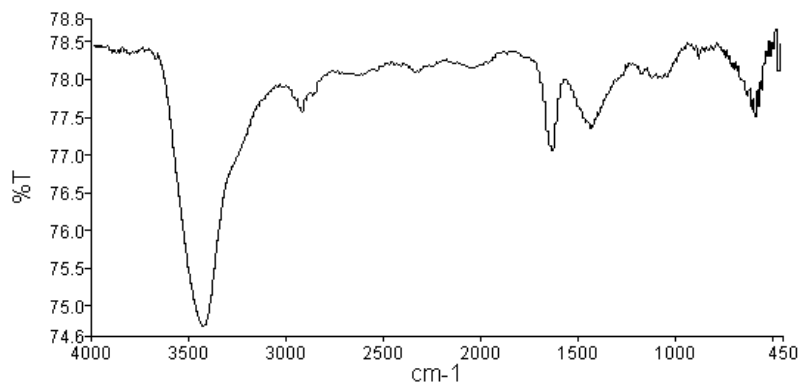
## 3. RESULTS AND DISCUSSION

### 3.1. Crystal phase of PVP-grafted Gd-MIOs powder

XRD on a dried deposit was performed to determine the crystallographic structure of the obtained sample. The diffractogram of PVP/Gd-MIOs is shown in Fig. 1. For the prepared powder, the well-defined diffraction peaks of (111), (220), (311), (400), (422), (511), (440), (620) and (533) are located at the  $2\theta$  of 19.05°, 30.95°, 35.43°, 44.12°, 54.33°, 58.16°, 63.42°, 72.65° and 74.21°, respectively. The XRD pattern of PVP/Gd-MIOs powder is very identical to those reported for pure magnetite phase of iron oxide [32-36], and it can be stated that the prepared powder has magnetite crystal nature. No additional diffraction is detected in XRD pattern (Fig. 1), indicating preparation of pure magnetite product *via* applied electrochemical method. Furthermore, all the above diffractions are fully matched with the reported diffractions for inverse cubic spinel crystals of  $\text{Fe}_3\text{O}_4$  with reference number of 85-1436 [52-55]. As a result, it is verified that the prepared PVP/Gd-MIOs powder by cathodic deposition procedure has magnetite crystal structure. Through the Debye- Scherrer relation, the average grain size of 11.36 nm was estimated for the PVP/Gd-MIOs powder.



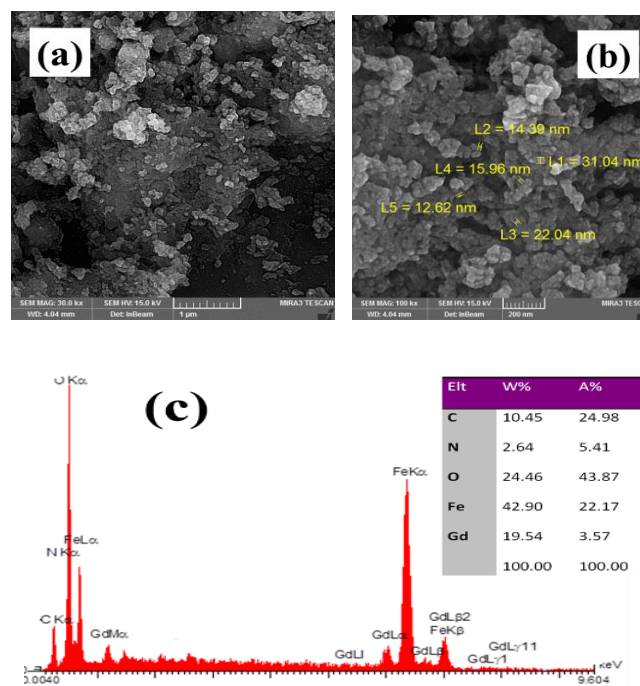
**Fig. 1.** XRD pattern of the prepared PVP-grafted Gd-MIOs powder



**Fig. 2.** IR spectrum of PVP-grafted Gd-MIOs powder

**3.2. FT-IR analysis of PVP-grafted Gd-MIOs powder**

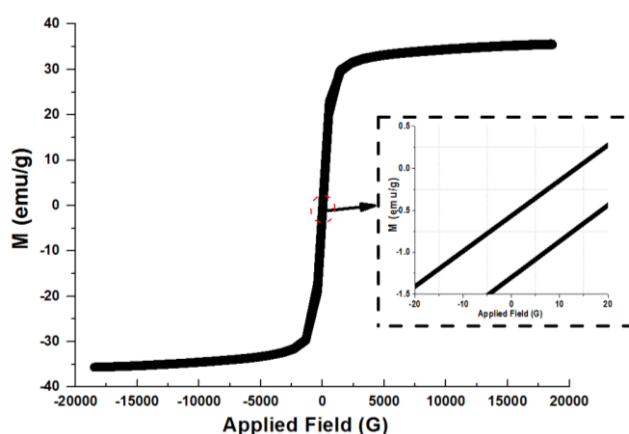
The recorded FT-IR spectrum for the Gd-MIOs powder is shown in Fig. 2. In this Fig, several IR adsorptions are observed, which are due to the following chemical bond vibrations; (i) C=O vibration at  $1643\text{ cm}^{-1}$  [71,72], (ii) the -OH vibrations at  $3437\text{ cm}^{-1}$ , (iii) stretching vibration mode of Fe-O/Gd-O bonds at  $551$  and  $434\text{ cm}^{-1}$  [73,74], (iv) stretching vibration of carbon-nitrogen at  $1211\text{ cm}^{-1}$  [75], (v) C-H stretching mode at  $2923\text{ cm}^{-1}$ , (vi) stretching of carbon-carbon bond at  $1155\text{ cm}^{-1}$  [65,66], (vii) carbon-hydrogen bending at  $2861\text{ cm}^{-1}$  [72], (viii) C-H wagging at  $892\text{ cm}^{-1}$  [71,75]. The existence of these IR adsorptions verified the formation of PVP-grafted Gd-MIOs powder.



**Fig. 3.** (a,b) FE-SEM images and (c) EDS data of PVP-grafted Gd-MIOs powder

### 3.3. Morphology of PVP-grafted Gd-MIOs powder

Morphology and elemental data of the fabricated PVP/Gd-MIOs are presented in Fig. 3. The particle-like morphology with relative agglomerated form is detected by the scanning microscopy (Figs. 3a and b). The average particle size for the PVP/Gd-MIOs powder was measured to be 20nm. The EDAX profiles and the resulted data are given in Fig. 3c. For the PVP/Gd-MIOs powder, the elements of O, C, N, Fe and Gd were detected with weight percentage of 24.46%, 10.45%, 2.64%, 42.9%, and 19.54%, respectively. Hence, for the fabricated PVP/Gd-MIOs sample, the elements of carbon, oxygen, iron, Gd and nitrogen are seen in its chemical composition. The carbon content in chemical composition of PVP/Gd-MIOs powder was obtained to be 10.45%wt, which come from the PVP grafted layer on the surface of the deposited film onto the cathode. The N weight percentage in the prepared PVP/Gd-MIOs was found to be 2.64%wt, indicating the PVP presence onto the surface of PVP/Gd-MIOs nano-particles. Furthermore, the Gd cations value on the composition of PVP/Gd-MIOs powder was 19.54%wt. The  $Gd^{3+}$  existence in chemical formula of the prepared Gd-MIOs sample was proved the doping of the iron oxide deposit with  $Gd^{3+}$  ions during their deposition preparation. Finally, observation of Fe (42.9%wt) and O (24.46%wt) elements in the composition of PVP/Gd-MIOs powder supported the magnetite crystal nature of the fabricated deposit on the steel cathode. These data fully asserted the successful electro-chemical production of  $Gd^{3+}$  ions iron oxide nano-particles *via* the applied conditions in this paper.



**Fig. 4.** VSM diagram for the PVP-grafted Gd-MIOs powder

### 3.4. Magnetic evaluation of PVP-grafted Gd-MIOs powder

The magnetic analysis of the prepared PVP-grafted Gd-MIOs powder was done by VSM measurements and the obtained profile is shown in Fig. 4. In this Figure, a typical superparamagnetic performance at the presence of external field is seen for the prepared powder.

No hysteresis loop was observed at the VSM curve, revealing the proper magnetism of PVP-grafted Gd-MIOs powder at room temperature. The measured magnetic data including saturation magnetization ( $M_s$ ), negative and positive remanent magnetization (negative  $M_r$  and positive  $M_r$ ), remanent magnetization ( $M_r$ ), negative and positive coercivity (negative  $H_{ci}$  and positive  $H_{ci}$ ), and coercivity ( $H_{ci}$ ) for the prepared PVP-grafted Gd-MIOs powder are;  $M_s=35.61$  emu/g,  $M_r=0.41$  emu/g, negative  $M_r=-1.32$  emu/g, positive  $M_r=-0.55$  emu/g, negative  $H_{ci}=13.4$  G, positive  $H_{ci}=30.24$  G and  $H_{ci}= 8.4$  G. For these magnetization values, it can be said that the prepared Gd-MIOs powder exhibits high  $M_s$  value at the external field, and hence could be a good candidate for possible biomedical uses. Furthermore, Gd-MIOs powder showed very low  $H_{ci}$  and  $M_r$  values, where these two magnetic quantities are very important role in hyperthermia.

#### 4. CONCLUSION

In summary, an easy and simple electrochemical fabrication method was reported for synthesis of polymer-grafted magnetic iron oxide nanoparticles. Using this method, *in situ* doping with  $Gd^{3+}$  cations and PVP grafting of MIOs were easily achieved. The obtained magnetic nanoparticles have particle size of about 20 nm. The magnetic crystal phase was revealed by XRD pattern, and the PVP-grafted layer on the MIOs was also confirmed by IR data. In addition, VSM measurements confirmed that the prepared PVP-grafted Gd-MIOs powder exhibited proper magnetization characters; i.e. high saturation magnetization, negligible remanent magnetization and low coercivity values.

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