

Full Paper

A Simple Electrochemical Fabrication and Characterization of Superparamagnetic Nanocomposite of Iron Oxide Nanoparticles Grown onto Amine-Functionalized Porous Graphene

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Abstract- In this research, Co-doped Fe₃O₄/NH₂-graphene nanocomposite is produced by direct current electrodesposition technique from an aqueous electrolyte containing the iron/cobalt chloride/nitrate salts and amine-functionalized porous graphene. The applied electrochemical parameters were $i=5$ mA/cm², $T_{bath}=25^{\circ}\text{C}$ and $t_{deposition}=15$ min. The electrochemical growth of magnetic particles onto graphene layers and formation of Co-IONPs/f-PG composite were tuned through XRD, FT-IR, FE-SEM, VSM and EDAX analyses. The magnetite phase and particle morphology of the deposited iron oxide onto graphene layers was indicated by XRD pattern and FE-SEM images. The cobalt content of deposited iron oxide was clearly revealed in the EDAX data. The magnetic measurement by vibrating sample magnetometer (VSM) technique exhibited superparamagnetic nature with saturation magnetization and retentivity values of 47.65 emu g⁻¹ and 2.26 emu g⁻¹ for the electro-synthesized magnetic nanocomposite. In final, direct cathodic electrodeposited is proposed as simple procedure for production of iron oxides with various graphene-based materials.

Keywords- Nanocomposite, Iron oxide, cobalt doping, Functionalized graphene, Electrochemical synthesis

1. INTRODUCTION

Recently, many studies have been performed to investigate potential uses of nanostructured materials (in both pristine and composite forms) in various practical fields [1-

7]. In this regard, the nanocomposites of graphene-based structures with metal oxides/hydroxides have been topic of many works [8-12]. For instance, composition the nanoparticles (NPs) with graphene/graphene oxide has recently received more attention as results of the novel and/or enhanced performances that cannot be gained by each part of composite in pristine forms, and it was proved that the fabricated metal oxides/hydroxides@graphene nanocomposites exhibit improved capabilities in a wide variety of application fields, including catalysis, bio-sensing, energy storage, and etc. [13-22]. Among them, magnetic NPs/graphene nanocomposites, especially iron oxides nanoparticles (IONPs), have shown very promising potential applications in biology, drug delivery, energy storage and contaminants removing from waste water [23-29]. For example, IONPs have mentioned as valuable promising SC electrode materials because of their low cost, easy synthesis, natural abundance, and safety. On the other hand, it has been confirmed that IONPs doping with transition metal cations could be boosted up their abilities in the biomedical and supercapacitive uses [30-38]. Although, Fe_3O_4 NPs have enticed more attention as compared with Fe_2O_3 in the capacitive applications of iron oxides, due to the better metallic electrical conductivity, however, they suffer from aggregation problems, poor cycle life and low conductivity, where reduce their practical capabilities. Fortunately, it has proven that the conductivity problems could be refined through compositing with graphene-based nanomaterials [39-42]. As facile method, electrochemical syntheses i.e. both anodic and cathodic electrodeposition, have been well developed in the recent years and recommend by researchers as an easy preparation method for the fabricating of various nanomaterials, where this method has benefits of simple set-up, low temperature, multi-functionality, controllable and inexpensive [43-52]. Hence, this method can be alternative easy route for preparation of IONPs/graphene nanocomposite. The loading of IONPs onto graphene not only refine the problems related to the graphene aggregation/restacking but also improve the IONPs conductivity [53,54]. Therefore, the preparation of graphene based IONPs composite becomes extremely important [55-60], and so that various methods have been developed to prepare high surface area and well-defined IONPs/graphene nanocomposites. In the present study, the nanocomposite of functionalized porous graphene (f-PG)/ Co^{2+} -doped IONPs is synthesized though cathodic electrodeposition method. To the best of our knowledge, this type composite has not reported until now. Notably, cathodic electrodeposition has been recently applied in many studied to fabrication metal-ion doped iron oxide nanoparticles [61-63]. However, the electrochemical synthesis has not been reported for the fabrication of IONPs/f-PG composite.

2. EXPERIMENTAL

2.1. Synthesis of Co-IONPs/f-PG composite

A simple two-electrode electrochemical set-up was chosen to perform electrodeposition experiments. The electrodes were steel 316L foil cathode and graphite plate anode, with same sizes of 5cm*10cm. The deposition bath was also the one-litter Beaker containing an aqueous electrolyte. For preparation of deposition electrolyte the following steps were followed; first, 3g iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich, 99.9%), 1.5g iron(II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich, 99%) and 0.5g cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.5%) were dissolved in 500cc deionized H_2O , second, The 100mg functionalized porous graphene (f-PG) was dispersed into 500cc deionized H_2O through probe ultrasonic. Notably, functionalized porous graphene was purchased from local company. In the last step, the prepared solution were added into one-litter beaker and mixed with magnetic stirrer for 2h. The composite synthesis was carried out in the galvanostatic regime with applied current of 0.5 A for 15min. Then, the deposit was collected form the cathode and dried at 80°C for 1h. The dried powder was final product.

2.2. Sample characterization

FE-SEM images were provided by a field-emission scanning electron microscopy (FE-SEM, Mira 3-XMU with accelerating voltage of 100 kV). The FTIR spectrum were collected at a wavenumbers of 400 to 4000 cm^{-1} using a Bruker Vector 22 Fourier transformed infrared spectroscope. The crystal structure of the prepared nanocomposite was analyzed through X-ray diffraction (XRD, Phillips PW-1800). The VSM profile of the nanocomposite was recorded by lakeshore 7400 vibrating sample magnetometer (VSM) instrument.

3. RESULTS AND DISCUSSION

Surface morphological characteristics (FE-SEM observations) and elemental weight percentages of the synthesized composite (Co-IONPs/f-PG sample) are shown in Fig. 1. For better specifying the composite morphology, the FE-SEM image of the pristine functionalized porous graphene powder is also presented in Fig. 1a. For f-PG sample, the sheet-like morphology is obviously seen in FE-SEM image. The observed sheets have pores onto their surfaces, revealing the porous nature of the graphene layers (Fig. 1a). The composite only exhibits the uniform particle morphology in the FE-SEM observations (Fig. 1 b and c). These findings indicated that the iron oxide particles have uniformly deposited onto the f-PG sheets, and completely covered all surfaces of the graphene layers. The iron oxide particles have complete spherical shape and at the range of 20nm (Fig. 1c). The elemental graph in Fig. 1d showed that the prepared sample has the carbon, oxygen, cobalt and iron elements in its composition (Fig. 1d). For the detected elements, the weight percentages of 41.73 wt% (for iron), 9.99 wt% (for cobalt), 2.1wt% (for nitrogen), 10.14 wt% (for carbon) and 36.03 wt% (for oxygen) are measured, as seen in Fig. 1e. From these data, the magnetite

phase of iron oxide was proved and is in agreement with XRD data (Fig. 2). Also, the 10% doping of cobalt cations into Fe_3O_4 crystal structure was revealed. The graphene existence in the prepared sample was proven from the carbon weight percentage. The nitrogen content of the prepared sample was also proved the amine functional group of the applied porous graphene.

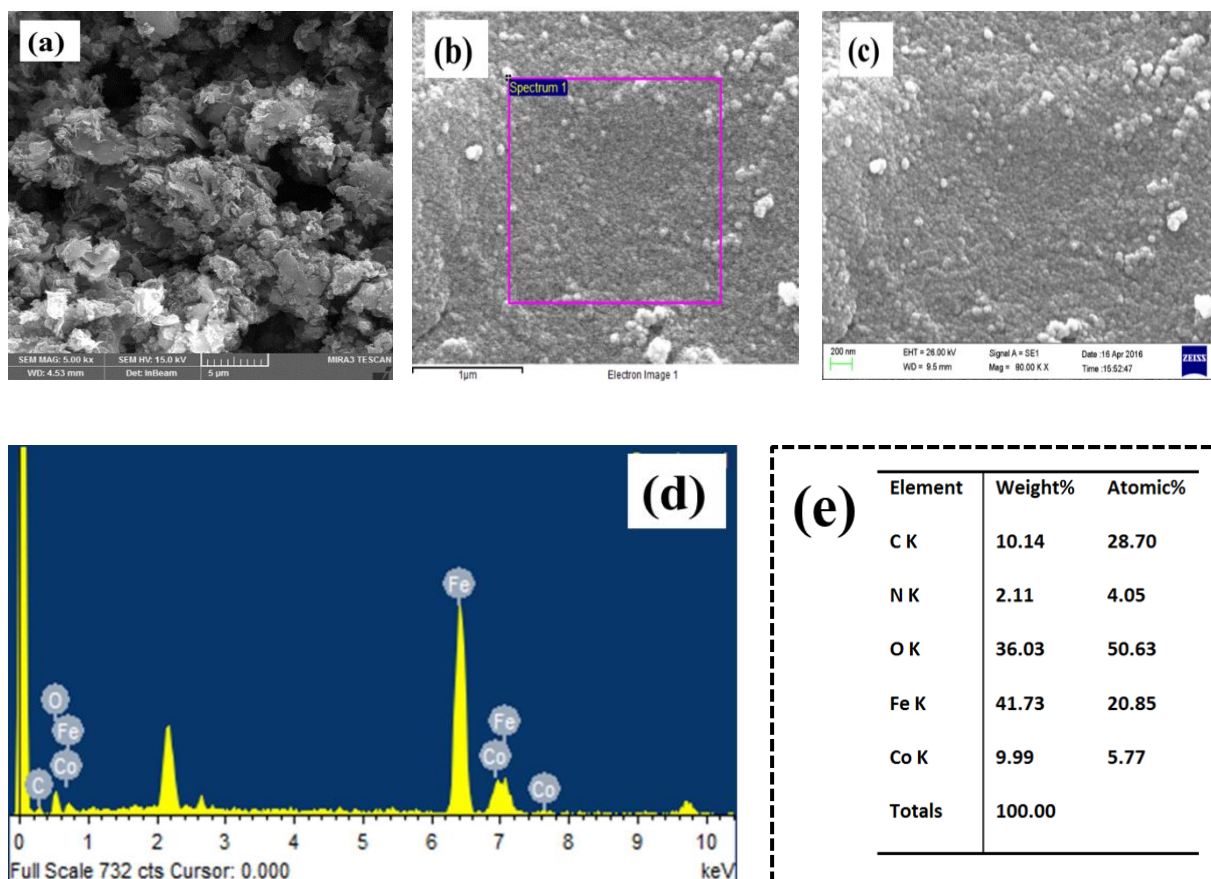


Fig. 1. FE-SEM images of functionalized porous graphene, (b,c) and the fabricated nanocomposite, (d) its EDS profile and (e) elemental weight percentages.

Fig. 2 indicates the XRD pattern of the electro-synthesized composite. The sample presents specific diffraction peaks of (220), (311), (400), (422), (511), (440), (620) and (622), which are related to the magnetite crystal structure reported in the literature [64,65]. In fact, the pattern of our sample is fully matched with the cubic spinel iron oxide structure with JCPDS number of 01-088-0315. These findings indicated that the prepared composite has only magnetite phase, and no additional phase was observed.

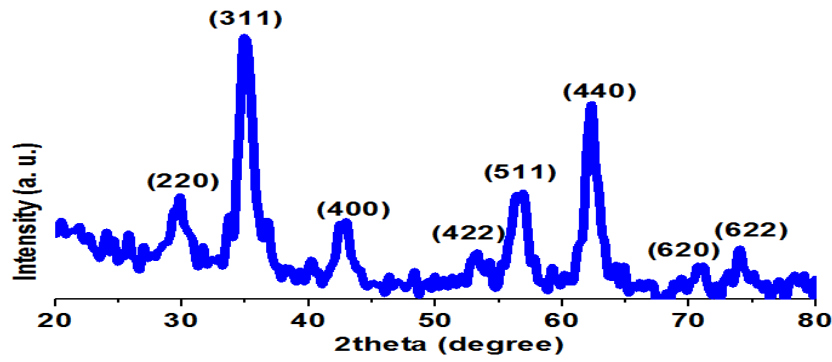


Fig. 2. XRD pattern of the prepared iron oxide/porous graphene composite

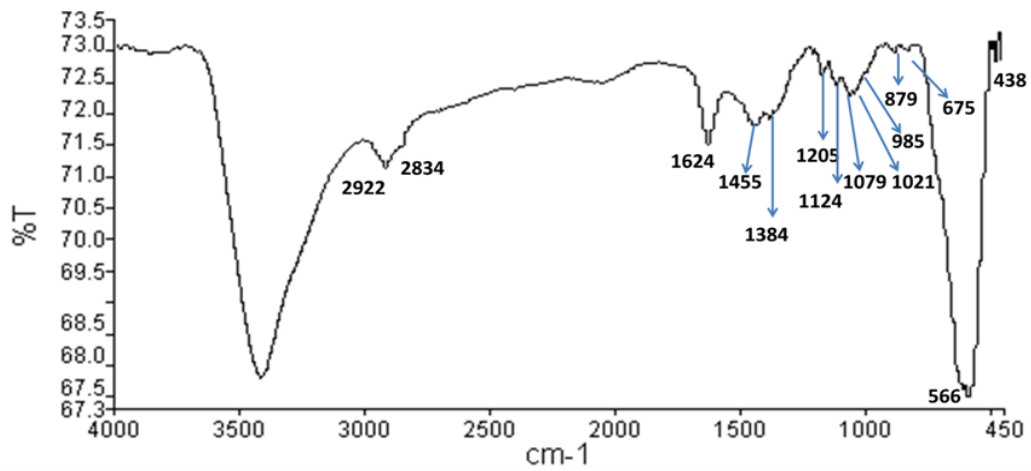


Fig. 3. IR spectrum of the synthesized iron oxide/porous graphene nanocomposite

IR spectrum of the deposited iron oxide/porous graphene sample is shown in Fig. 3. For the sample, the two IR adsorptions at 657 cm^{-1} and 566 cm^{-1} are related into the Fe-O-Fe and/or Fe-O-Co vibrations, which come from splitting the main band at 545 cm^{-1} and its shifting to higher bands [62].

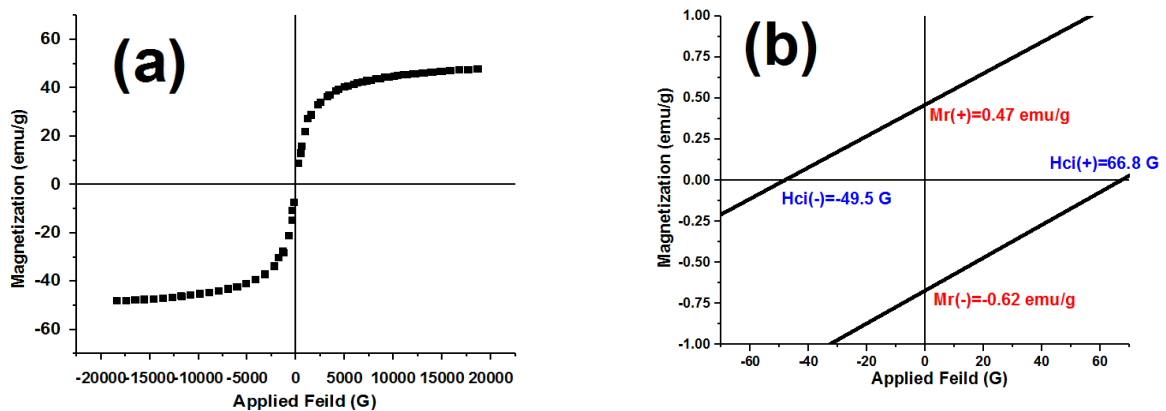


Fig. 4. Hysteresis profile for the prepared composite at room temperature

Furthermore, the IR band located at 438 cm^{-1} is due the Fe-O-Fe vibration [62,63]. Some other IR adsorptions are also seen in Fig. 3, which listed below; C–C bonds vibration at 1079 cm^{-1} , $-\text{CH}_2$ vibrations at 2834 cm^{-1} and 2922 cm^{-1} , N–H vibration at 1385 cm^{-1} , C–N stretching vibration at 1205 cm^{-1} , O–H stretching vibration located at 3400 cm^{-1} and 3500 cm^{-1} , skeletal vibrations at 1624 cm^{-1} , C–C stretching vibrations at 879 cm^{-1} and C–OH stretching at 1455 cm^{-1} [64-69]. These IR bands clearly proved the electrochemical grown of the Co-doped magnetite onto amine-functionalized graphene.

The magnetic study of the prepared nanocomposite was performed on the vibrating sample magnetometer (VSM) instrument via recording the magnetization of composite sample at the applied field of -2000 to 2000Oe in RT conditions and the data were plotted in Fig. 4. From the VSM profile in Fig. 4a, it is observable that the prepared composite sample exhibited superparamagnetic properties with magnetization (M_s) and retentivity (M_r) values of 47.65 emu/g and 2.26 emu/g , respectively. This M_s value are lower than those reported to the magnetic IONPs [70-72], which is related to the non-magnetic part of the prepared composite. The other magnetic parameters for the prepared nanocomposite (i.e. Co-IONPs/f-PG) could be extracted from Fig. 4b. As it can be seen in Fig. 4b, the composite exhibited the positive M_r , negative M_r , positive H_{ci} and negative H_{ci} of $+0.47\text{ emu/g}$, -0.62 emu/g , $+66.8\text{ G}$ and -49.5G , respectively. These data implied the suitable magnetic properties for the nanocomposite obtained by electrochemical grown of Co^{2+} doped Fe_3O_4 onto amine-functionalized porous graphene.

4. CONCLUSION

In summary, the nanocomposite of cobalt cations doped iron oxide nanoparticles with NH_2 -functionalized porous graphene was successfully synthesized through simple two-electrode deposition. The fabricated composite exhibited suitable magnetic characters with $M_s=47.65\text{ emu/g}$ and $M_r=2.26\text{ emu/g}$. The particle size of Fe_3O_4 in the composite was measured to be 20 nm via FE-SEM observations. The presence of 10% wt cobalt cations in composite structure was revealed by EDAX analysis and it was also found that Co^{2+} doping has no essential on the crystal structure of magnetite phase. IR data was also confirmed the connection of magnetic particles to the surface of porous graphene layers via the amine groups. In final, the developed method could be simple route for fabrication of magnetic-graphene based composites.

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