Hybrid Nanocomposite Based on $CoFe_2O_4$ Magnetic Nanoparticles and Polyaniline

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ABSTRACT: *$CoFe_2O_4$ Magnetic Nano Particles (MNPs) were synthesized by an efficient method in aqueous medium with the particle sizes of about 20-50 nm. Then, a hybrid nanocomposite of polyaniline (PANI)-$CoFe_2O_4$ MNPs has been electrodeposited directly on a stainless steel wire by the potentiostatic method. Microscopic images of electrodeposited PANI and PANI-$CoFe_2O_4$ nanocomposite coatings were obtained by scanning electron microscope. The scanning electron microscopic images of polyaniline and its nanocomposite pointed out the influence of $CoFe_2O_4$ nanoparticles in the electrodeposition of polyaniline. Dispersion of $CoFe_2O_4$ nanoparticles in electrolyte solution during the electrodeposition, creates a nanocomposite with a more surface area than pure polyaniline.*

KEY WORDS: *Nanoparticle, Conductive polymer, Nanocomposite, Electrodeposition.*

INTRODUCTION

Over the past decade, nanoscale metal oxide particles have attracted a great attending for their interesting properties and novel applications [1-3]. These nanoparticles often display very interesting magnetic, optical, electrical and chemical properties different from their bulk counterparts [1]. Due to their unusual size and shape dependent properties, they have been suggested to technological applications in various fields. For example, their high surface-to-volume ratio causes the presence of large fractions of atoms accessible for catalytic reactions [4-6].

Magnetic Nano Particles (MNPs) and their dispersion in various media have recently been receiving growing attention. MNPs are inorganic materials that can be inserted into a polymeric matrix. Magnetic measurements of small particles show that the magnetic moment of nanoparticles can be improved by a factor of 1.3 per atom in accordance to comparison with the bulk materials [7]. MNPs are very important for their application in magnetic memory devices [8]. We could also find them in biomedical applications such as Magnetic Resonance Imaging (MRI)

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1021-9986/10/4/173 7/$/2.70

enhancers, hyperthermia, drug delivery, separation of biological entities, and medical diagnosis [9, 10].

Heterogeneous-conducting polymer nanocomposites have been the topic of great interest over the last few years [11]. Although various kinds of conducting polymers have been developed, polyaniline has emerged as one of them for the synthesis of polyaniline /inorganic particle composite, such as conducting polyaniline/carbon nanotube [12], polyaniline/V_2O_5 [13], polyaniline-$BaTiO_3$ [14], polyaniline-ZnO fibers [15], polyaniline/platinum [16], polyaniline/palladium [17, 18]. The insertion of platinum and palladium to the polymeric system is possible when the high electron density of polymer is accessed through the single electron pair on the nitrogen head groups. Hybrid nanocomposite based on $NbWO_6$ nanosheets and polyaniline was also investigated by sonication method [19]. Such new nanocomposite cover a great range of application like photosensitive materials, electrochromic devices, light-emitting diodes and etc. Also, the polyaniline nanocomposite with TiO_2 was synthesized by the in situ polymerization of aniline using $(NH_4)_2S_2O_8$ as an oxidant [20, 21].

The magnetic nanoparticles have been employed extensively in the preparation of magnetic nanocomposite based on various polymers such as, polyacrylate [22], polyethylene glycol-acrylamide [23], polystyrene [24], poly(o-anisidine) [25], chemically polymerized polyaniline sulphate and phosphate [26], poly (butyl acrylate-styrene) [27,28], epoxy [29], sodium alginate [30], polystyrene/ poly(isopropylacrylamide-co-methyl acrylate acid) [31], polyvinyl alcohol [32], poly(oligo(ethylene glycol) methacrylate-co-methacrylic acid) [33] and poly(N-vinyl-2-pyrrolidone) [34]. Hybrid nanocomposites present the properties of both nanomaterials and the polymer by combining mechanical strength, thermal stability, optical or electrical properties [35].

In the present work we synthesized the $CoFe_2O_4$ MNPs and reported the electrochemical coating of stainless steel (SS) wire with PANI and its nanocomposites with $CoFe_2O_4$ MNPs as PANI-$CoFe_2O_4$ MNPs. In addition to, we investigated the influence of $CoFe_2O_4$ MNPs in the electrolyte solution on the polymer growth.

EXPERIMENTAL SECTION

Chemical reagents

Aniline monomer (reagent grade, Merck) was kept below 0 ºC. The other reagents, such as H_2SO_4, $FeCl_3.6H_2O$ and $Co(CH_3COO)_2.4H_2O$ were prepared from Merck. The solution of 1.0 M sulfuric acid was prepared from concentrated sulfuric acid by suitable dilution. Distilled water was applied for all synthesis and treatment processes.

Apparatus

Electrochemical experiments were performed using an electrochemical analyzer (μAutolab type III). The measurements were carried out in a conventional single compartment electrochemical cell consisting of a stainless steel wire (length=2.0 cm, diameter= 250 μm) or glassy carbon (disk, 3.14 mm^2 geometrical area exposed to the solution) as working electrodes assembled in the electrochemical cell, a platinum wire as the counter electrode and Ag/AgCl/KCl (3 M) as reference electrode. All potentials are reported with respect to this reference electrode. Furthermore, the Scanning Electron Microscope (SEM) images were obtained using a Philips model X-30. Transmission Electron Microscope (TEM) images were recorded using a Zeiss EM 10 C.

Synthesis of $CoFe_2O_4$ magnetic nanoparticles

The mixed solution containing 100 mL of 0.08 M $FeCl_3.6H_2O$ and 0.04 M $Co(CH_3COO)_2.4H_2O$ (with Co:Fe atomic ratio of 1:2) were arranged in distilled water. This solution was added little by little into the 100 mL of 0.64 M NaOH under strongly stirring. The temperature of the reaction beaker kept at 55 ºC. During the procedure, the color of solution in beaker changed from the initially brown to dark brown and precipitation happened. The digestion were completed at 55 ºC for 120 min afterward, the precipitates were filtered and carefully washed with distilled water. The precipitates were dried at 80 ºC in air. The powder was dispersed in ethanol, and sonicated for 5 min finally, the suspension filtered and then dried at 150 ˚C for 50 min to obtain the final $CoFe_2O_4$ nanoparticles.

Electrodeposition of PANI and PANI-$CoFe_2O_4$ nanocomposite coatings

Prior to electropolymerization, surface of the SS wire was polished with emery paper and glassy carbon surface was polished with 0.3 μm alumina powder and then, washed with distilled water. The electrode was then sonicated (5 min) in ethanol to remove the adsorbed particles.

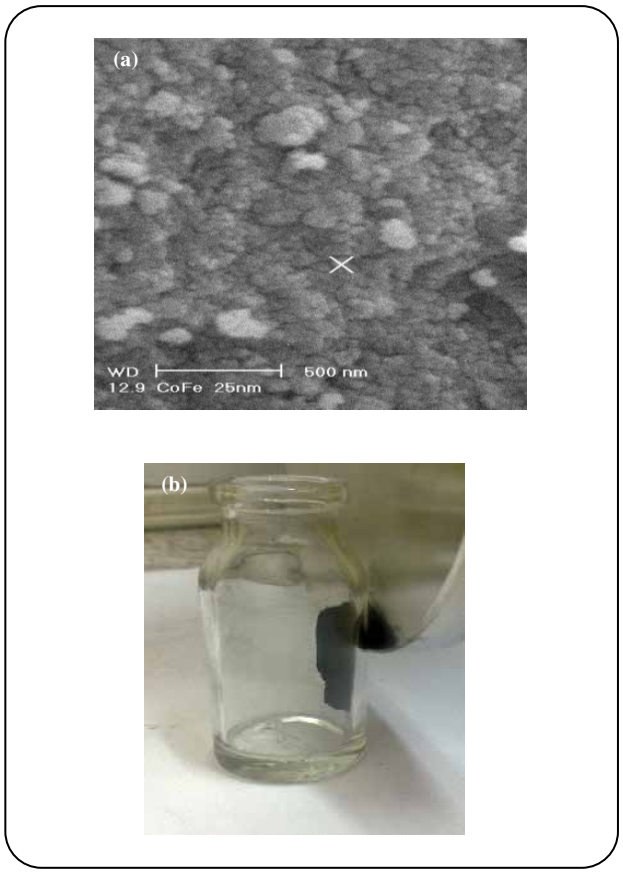


Fig. 1: (a) SEM image of $CoFe_2O_4$ magnetic nanoparticles, (b) photograph showing magnetic property of $CoFe_2O_4$ nanoparticles.

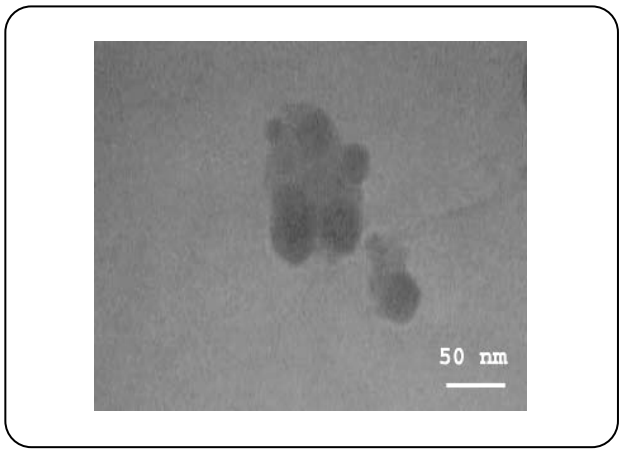


Fig. 2: TEM image of $CoFe_2O_4$ magnetic nanoparticles.

For electrodeposition of PANI and PANI-$CoFe_2O_4$ nanocomposite coatings on the surface of glassy carbon electrode, certain amount of $CoFe_2O_4$ MNPs (10 mg in 50 mL) were dispersed in 1.0 M sulfuric acid containing of 0.025 M aniline. Then PANI-$CoFe_2O_4$ nanocomposite coating was electrochemically polymerized by applied repetitive Cyclic Voltammograms (CVs) to glassy carbon working electrode at 50 mV/s. In addition, for electrodeposition of PANI-$CoFe_2O_4$ nanocomposite coating on the surface of SS wire, the constant potential of 0.8 V were applied to SS working electrode for 15 min in aqueous solution in which 25 mg $CoFe_2O_4$ MNPs were dispersed in the 50 mL of 1.0 M sulfuric acid containing of 0.05 M aniline. For comparison, pure PANI coating was also electrodeposited in the same conditions as mentioned above on the surface of both glassy carbon and SS wire.

RESULTS AND DISCUSSION

PANI growth in the absence and presence of the $CoFe_2O_4$ MNPs by repetitive cyclic voltammetry

The morphology of synthesized $CoFe_2O_4$ MNPs was investigated using SEM. Part (a) of Fig. 1 shows the typical scanning electron micrograph of the $CoFe_2O_4$ MNPs. This micrograph demonstrates that a bulk quantity of spherical $CoFe_2O_4$ MNPs. Part (b) of Fig. 1 confirms magnetic properties of $CoFe_2O_4$ nanoparticles, as indicated by its attraction to a permanent hand magnet. Fig. 2 shows the transmission electron micrograph of spherical $CoFe_2O_4$ MNPs exists with the particle sizes of about 20-50 nm.

The inner curves of parts (a) and (b) of Fig. 3 show the 20th and 30th cyclic voltammograms which were recorded during repetitive voltammograms in a solution of 0.025 M aniline in 1.0 M sulfuric acid on a glassy carbon electrode. This way, consists of the conventional synthesis with voltammogram shapes, is well-defined as assigned in previous works [36, 37]. While, the outer curves in Fig. 3 show the voltammograms in same conditions in the presence of $CoFe_2O_4$ MNPs (10 mg in 50 mL). After comparing the voltammograms of Fig. 3, influence of $CoFe_2O_4$ MNPs in the electropolymerization of aniline is observable. It demonstrates that $CoFe_2O_4$ MNPs in the electrolyte solution plays an important role in the subsequent electropolymerization and polymer growth.

Potensiostatic deposition of PANI in the absence and presence of $CoFe_2O_4$ MNPs on the surface of SS wire

An inset of Fig. 4 on the upper left corner shows the *I-t* (current versus time) curve of SS wire in 1.0 M sulfuric acid solution without aniline in which the applied potential was 0.8 V. Fig. 4 shows the *I-t* curve of SS wire

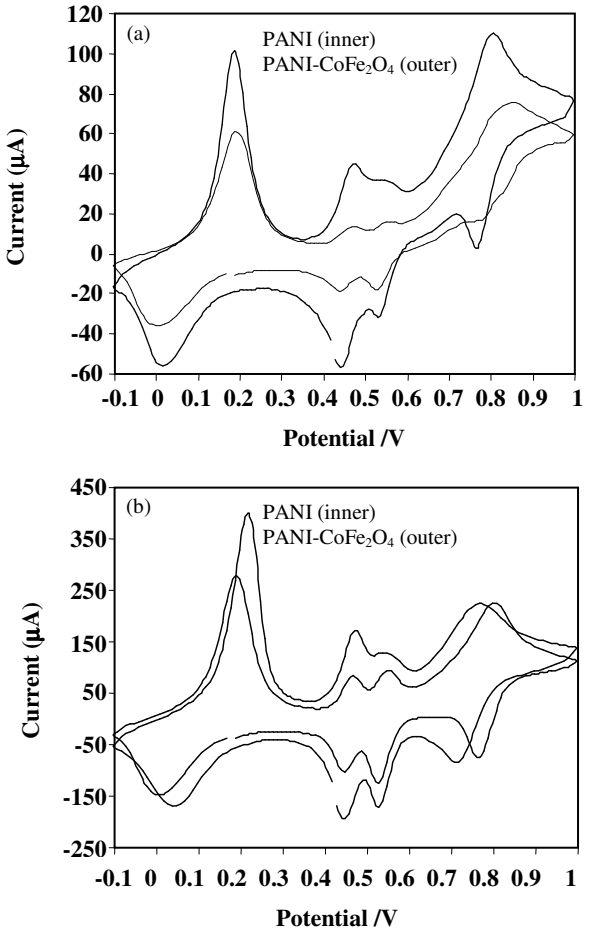


Fig. 3: (a) 20th and (b) 30th comparative cyclic voltammograms during the growth of PANI (inner voltammograms) and PANI-$CoFe_2O_4$ (outer voltammograms) coatings at 50 mV/s.

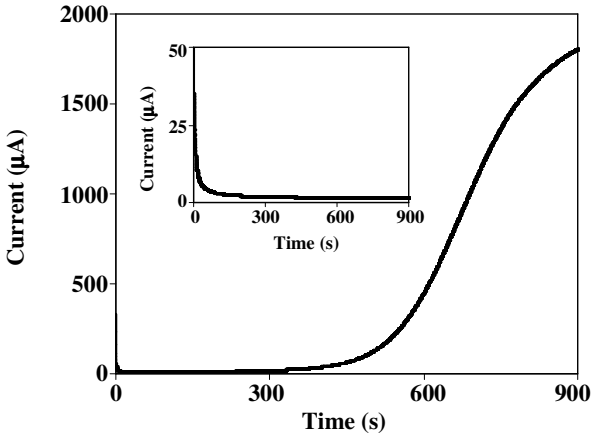


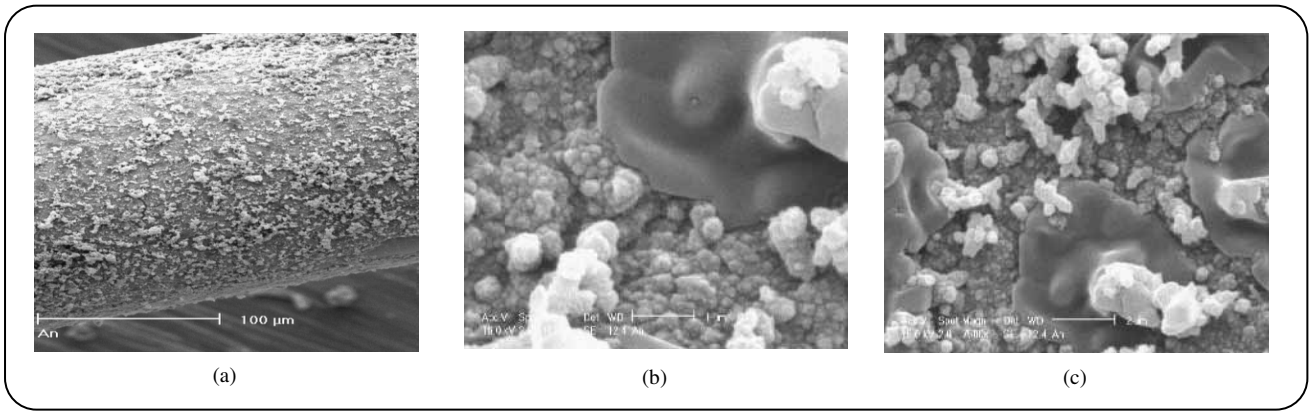
Fig. 4: The curve of current versus time of SS wire during the potentiostatic deposition of PANI-$CoFe_2O_4$ nanocomposite coating. Inset: The curve of current versus time of SS wire in same condition in the absence of aniline.

in 1.0 M sulfuric acid solution containing of 0.05 M aniline that 25 mg of $CoFe_2O_4$ MNPs were dispersed in 50 mL of electrolyte solution and then sonicated to obtain the uniform dispersion. The increasing of current after the 500 s related to the oxidation of aniline and its electropolymerization on the surface of SS wire. The amounts of consumed charge (Q) during the applied potential (0.8 V) to SS wire in the absence (Fig. 4, inset) and presence (Fig. 4) of 0.05 M aniline were 0.002 and 0.4183 coulomb (C), respectively. It indicates the electrooxidation and deposition of PANI nanocomposite coating on the surface of SS wire. The SEM images of PANI coating on SS wire are shown in parts (a) to (c) of Fig. 5, while Fig. 6 shows the SEM images of PANI-$CoFe_2O_4$ nanocomposite coating on the surface of SS wire from parts (a) and (b). Differences in the morphology of PANI-$CoFe_2O_4$ nanocomposite and pure PANI related to the presence of $CoFe_2O_4$ MNPs. The $CoFe_2O_4$ MNPs act as an incorporating agent. The presence of $CoFe_2O_4$ MNPs results the polymer coating with more porosity in comparison with pure PANI. So, the PANI-$CoFe_2O_4$ nanocomposite has larger surface area than pure PANI. On the other hand, there is a direct relation between the current intensity and surface area of electroactive substrate [38]. As a result, higher voltammetric current for nanocomposite in comparison with pure polymer (parts (a) and (b) of Fig. 3) related to the larger surface area of nanocomposite than pure polymer.

The enhanced surface area of conductive polymer nanocomposites can be useful for the immobilization of biomacromolecules (proteins and enzymes) for biosensor applications [39, 40]. It is clear that the properties of a wide variety of materials and performance of different devices depend strongly on their surface characteristics. Surface chemistry could therefore be significant to physical properties of nanomaterials and their applications [41]. However, it is simple to control the composite structure using different amounts of $CoFe_2O_4$ MNPs.

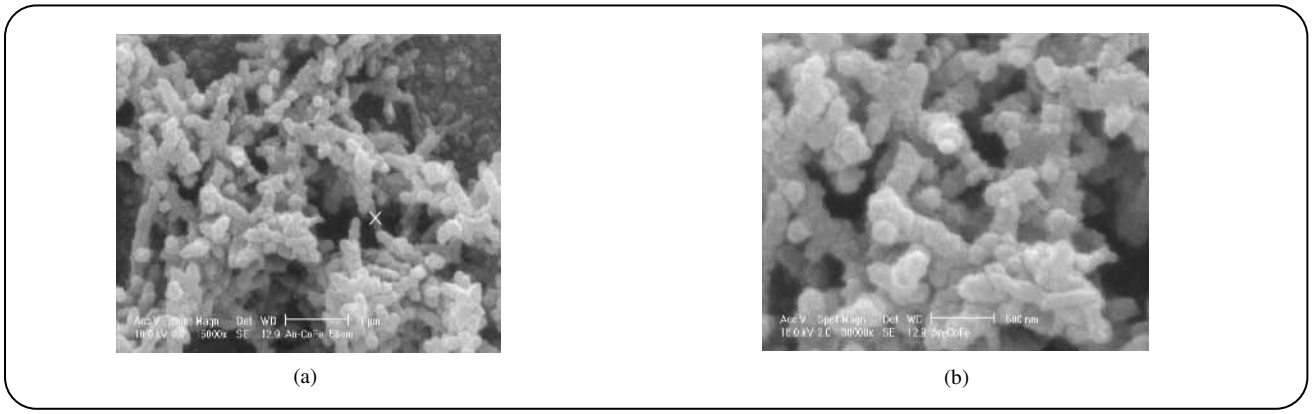
CONCLUSIONS

We hereby present a case in which we successfully synthesized $CoFe_2O_4$ nanoparticles. PANI-$CoFe_2O_4$ nanocomposite was deposited directly on the surface of stainless steel wire by the potentiostatic method. Polymerization and morphology of the polyaniline coatings are discussed in a comparative manner for



(a) (b) (c)

Fig. 5: (a)-(c) SEM images of the PANI coating on the surface of SS wire.



(a) (b)

Fig. 6: (a) and (b) SEM images of the PANI-$CoFe_2O_4$ nanocomposite coating on the surface of SS wire.

finding the key role of $CoFe_2O_4$ nanoparticles in the polyaniline nanocomposite synthesis. An extensive sample examination with the help of the SEM presented. The results indicated that synthesized $CoFe_2O_4$ MNPs can affect the electropolymerization process by production a porous nanocomposite and increasing surface area in comparison with pure polyaniline. This effect occurs when $CoFe_2O_4$ MNPs acts as incorporating agent. Of course, composition of such nanostructures can be changed by controlling the amount of dispersed nanoparticles. Since composites made from $CoFe_2O_4$ nanoparticles display essential stability and this method can be effectively used for practical purposes.

Acknowledgment

This work was supported by the Research Institute of Applied Sciences (RIAS)-ACECR.

Received : Nov. 4, 2009 ; Accepted : Feb. 28, 2011

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