Development and characterization of a novel conductive polyaniline-g-polystyrene/Fe$_3$O$_4$ nanocomposite for the treatment of cancer

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**ABSTRACT**

The goal of this study is to synthesize, characterize and investigate some physicochemical properties of conductive polyaniline-g-polystyrene/Fe$_3$O$_4$ (Fe$_3$O$_4$/PSt-g-PANI) nanocomposites. For this purpose, initially, Fe$_3$O$_4$ nanoparticles were synthesized by a co-precipitation method. Then, the desired nanocomposite was synthesized in two steps. First, the atom transfer radical polymerization (ATRP) of styrene was performed using an ATRP initiator attached to the surface of Fe$_3$O$_4$ nanoparticles, followed by functionalization of the Fe$_3$O$_4$-PSt with amine groups (–NH$_2$). Second, surface oxidative graft copolymerization of aniline was accomplished using the –NH$_2$ moieties on the Fe$_3$O$_4$/PSt-NH$_2$ as the anchoring sites. The prepared materials were characterized by various instruments, including TEM, SEM, TGA, EDX, FT-IR, XRD and conductivity measurements. The results indicated that the synthesized conductive polymer/Fe$_3$O$_4$ nanocomposites had higher electrical conductivity and thermal resistance than those of the corresponding homopolymers.

**Introduction**

In recent decades, inorganic/organic composites have attracted the attention of scientists in both scientific and industrial fields. These composites possess unique properties (such as thermal stability) and have various functional groups within a single material. These composite/hybrid materials present novel and wonderful properties (e.g. mechanical, chemical, electrical, rheological, magnetic, optical, catalytic and so on). They have different applications in areas such as drug delivery systems, diagnostics, coatings and catalysis [1–10].

Conducting polymers (CPs) are significant because of their relatively easy processability, thermal and environmental stabilities and tunable electrical conductivities, for example, polyaniline (PANI) [11], polypyrrole (PPy) [12] and polythiophene (PTP) [13,14]. Conducting polymers may have potential applications in areas such as composite materials, tissue engineering, separation membranes, surface-activation materials, supercapacitor, electronic and electro-optic devices, as well as molecular motors [15–17]. Novel advances in polymer engineering have certainly increased the investigation of nanostructured CPs [18,19]. A new challenge in this area of nanotechnology is the capability to synthesize relatively small monodispersed CPs nanostructures, and their composites with metal oxide nanoparticles that have multifunctional properties [11,20–23].

Encapsulation of nanoparticles, such as metal oxides into conducting polymers, leads to nanohybrid organic/inorganic composites that demonstrate high thermal resistance, catalytic, electrochemical, optical, mechanical, electrical properties [24–27]. Also, metal oxide nanoparticles in conducting polymeric matrices allow for the development of products in many applications in sensors, microelectronics, cancer therapy, etc [28–31]. The unique properties of such compositions are essentially dependent on their size and shape. Diverse conducting polymer/inorganic particle composites have been synthesized by different methods and their properties and applications studied [32–37]. For example, Sadek et al. have reported In$_2$O$_3$–PANI composites as sensors for H$_2$, NO$_2$ and CO gases [33,38]. Xu et al. published the synthesis of a Pt–PANI composite and its application in detecting glucose [34]. De et al. studied TiO$_2$–PANI nanocomposites that can be used as electronic gadgets like capacitors [35]. V$_2$O$_5$–PANI composites have remarkable promise for their use as a...
cathode material for lithium secondary batteries [36]. One of the distinctive applications of polyaniline is its use in photothermal therapy of cancer. Xia et al. [39], Hong et al. [40] and Zhou et al. [20] have reported polyaniline as drug carriers for the photothermal therapy of cancer.

With the expansion of magnetic materials, significant research attempts have been made to synthesize conjugated polymers with magnetic materials to generate new magnetic and electrically conducting organic/inorganic materials, that can be used in electromagnetic interposition shielding, data storage and biomedical applications [41–49]. Different methods have been improved to make conducting magnetic nanocomposites, such as through the precipitation of iron salt in a polymer matrix [50,51], the in situ synthesis of the polymer by oxidative [52] or electrochemical [53] processes in the presence of well-dispersed magnetic nanoparticles and polymerization of the monomer [54–56].

A new method for the synthesis of organic/inorganic materials is controlled/living radical polymerization (CRP). CRP is a strong method for the synthesis of well-defined organic polymers because of a controlled molecular weight, narrow molecular weight distribution, combination and performance [57]. One of the methods of CRP is atom transfer polymerization (ATRP). ATRP has been commonly used for the preparation of polymers with a well-defined structure [58] by surface-initiated polymerization of various monomers, such as styrene, methacrylates, acrylates and dienes [59–63].

In the present study, we report a novel route for the synthesis of a brush polymer from the surface of Fe₃O₄ as core/shell nanoparticles. Therefore, we used the combination of two methods of ATRP of styrene and in situ chemical oxidation of aniline from the surfaces of the magnetic nanoparticles (Scheme 1). Characterization of this well-defined brush polymer has been investigated by performing FT-IR, thermogravimetric analysis, energy-dispersive X-ray (EDX), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Considering the properties of the conductive polymer/Fe₃O₄ nanocomposite, it has potential applications in the treatment of cancer.

**Experimental**

**Materials**

Aniline and styrene monomers (Merck) were distilled under reduced pressure and stored below 0 °C. 2,2'-bipyridine (bpy), ammonium persulfate (APS), sulphuric acid, nitric acid, chloroform, FeCl₃·6H₂O, FeCl₂·4H₂O, NaOH, methanol and tin (II) chloride dihydrate were obtained from Merck. All chemicals were used as supplied without further purification. Copper chloride (I) (CuCl) (Merck) was stirred 12 h in acetic acid. Then, it was filtered, washed with absolute ethanol, and dried 24 h under a vacuum at 60 °C. 2-bromo-2-methyl propionic acid (Br-MPA) was obtained from Sigma Aldrich.

**Preparation of the Fe₃O₄ nanoparticles**

Fe₃O₄ nanoparticles were prepared using a co-precipitation path; it was synthesized without any additional stabilizer according to the following procedure. In summary, in this way, 0.79 M FeCl₃·6H₂O and 0.4 M FeCl₂·4H₂O were added to 25 ml of 0.4 M HCl. This solution of mixed iron salts was added dropwise to 250 ml of 1.5 M NaOH with stirring under an N₂ atmosphere. The obtained colloid solution was centrifuged at 5000 rpm, washed with an excess of deionized water and then dried in an oven for 6 h at 60 °C. A black fine powder (Fe₃O₄) was generated [64].

**Preparation of an ATRP initiator onto Fe₃O₄ nanoparticles**

2-bromo 2-methyl propionic acid (Br-MPA) (2.5 ml) and 1.5 g of Fe₃O₄ nanoparticles were dispersed in 50 ml methanol with the aid of ultrasound for 1 h. The dispersed solution was
then transferred to a 100 ml round bottom flask equipped with a condenser and a magnetic stirrer under nitrogen. The solution temperature was maintained at 65 °C under stirring for 24 h and then the solution was decanted and rinsed numerous times with methanol to remove non-chemisorbed Br-MPA; the solid product was dried overnight under vacuum at 60 °C (Scheme 2).

**ATRP of styrene with Fe₃O₄/Br-MPA as the initiator**

In the ATRP polymerization, functional nanoparticles with Br-MPA (25 mg) were mixed with a styrene monomer (2.5 ml). After purgation of the mixture with nitrogen for 10 min, it is transferred to a bottle with CuCl (4.9 mg) and 2,2'-bipyridine (19 mg). The reaction temperature was raised to 120 °C. After finishing the reaction time (20 h), the mixture was diluted with tetrahydrofuran (THF). The final products were precipitated with methanol. For further characterization, it was dissolved in toluene to form a clear yellowish solution [65] (Scheme 3).

**Preparation of poly(p-amino styrene)-coated Fe₃O₄ (Fe₃O₄/PS-NH₂)**

First, the nitroxide group is produced on polystyrene backbone using strong nitric acid and sulphuric acid. In a round-bottomed flask containing strong nitric acid (15 ml), which was placed in the ice-water bath, the polystyrene coated iron oxide nanoparticles (Fe₃O₄/PS) (0.75 gr) was suspended in it. Then, 23 ml of strong sulphuric acid was slowly added to it and the temperature was enhanced to 30 °C and continued for 10 h. After the desired time, the product was filtered and washed with sufficiently of water. It was transferred to a Soxhlet's extraction apparatus for reflux-extraction in 96% ethanol for 10 h. The product obtained in this step was Fe₃O₄/PS-NO₂ (Scheme 3).

Next, the nitroxide group was reduced to an amino group. In a round-bottomed flask containing 20 ml of hydrochloric acid (6M) and 23 ml of absolute ethanol, the Fe₃O₄/PS-NH₂ (0.1 g), aniline monomers (0.01 mol) were added into the aqueous solution of hydrochloric acid (1.0 M). The oxidant solution (2.6 mol of (NH₄)₂S₂O₈ in 20 ml of 1.0 M HCl) was added into the reaction mixture at 75 °C and continued for 12 h. After the desired time, the product was washed with 10% NaOH solution, distilled water and absolute ethanol. To wash the Fe₃O₄/PS-NH₂, it was transferred to a Soxhlet's extraction apparatus for reflux-extraction in absolute ethanol for 10 h. The Fe₃O₄/PS-NH₂ obtained was dried under vacuum at 40 °C for 48 h (Scheme 3).

**Preparation of Fe₃O₄/polystyrene-g- polyaniline, core/shell nanoparticles**

For surface oxidative graft copolymerization of aniline is the same as in Abbasian et al [65]. Briefly, the Fe₃O₄/PSt-NH₂ (0.1 g), aniline monomers (0.01 mol) were added into the aqueous solution of hydrochloric acid (1.0 M). The oxidant solution (2.6 mol of (NH₄)₂S₂O₈ in 20 ml of 1.0 M HCl) was added into the reaction mixture at 0 °C. The oxidative graft copolymerization was performed for 8 h. The PSt-NH₂ was used as the anchoring sites for polyaniline. The final product was dispersed into 1-methyl-2-pyrrolidone and centrifuged to remove the PANI homopolymer (Scheme 4).

**Instrumentation**

FT-IR spectra were recorded using a Shimadzu FT-IR-8101M; the spectrum was recorded at room temperature. The thermal properties of the Fe₃O₄/PSt-g-PANI nanocomposite measurement were determined by TGA-PL (England). XRD spectra were obtained using a Siemens D 5000 (Berlin, Germany), X-ray generator (CuKα radiation with λ = 1.5406 Å) with a 2θ scan range of 2 to 80° at room temperature. The size and morphologies of the products were examined by scanning electron microscopy (SEM; Cam Scan MV 2300). The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. Transmission electron microscopy (TEM) images were performed on a Philips EM208 microscope (Philips, Eindhoven, Netherlands) with a 100 kV accelerating voltage. The conductivity of the samples was measured at room temperature by a standard four-probe apparatus (Azar Electric Co., Urmia, Iran). Electrochemical experiments were conducted using Auto-Lab PGSTA T302N.
Results and discussion

Preparation and surface modification of the magnetic nanoparticles

The Br-MPA attached to the surface of the iron oxide nanoparticles were used for ATRP polymerization. In addition, Br-MPA helps to stabilize nanoparticles in an organic solvent.

The XRD spectrum of Fe$_3$O$_4$ is displayed in Figure 1(a). The XRD spectrum indicated that the nanoparticles do not have any impurities. The average size of the Fe$_3$O$_4$ nanoparticles was calculated as \( \sim 11 \) nm using the Debye–Scherrer’s formula and the peak from 311 reflection [66].

The equation uses the reference peak width at angle \( \theta \), where \( \lambda \) is the X-ray wavelength (1.54060 Å), \( b \) is the width of the XRD peak at half height and \( k \) is a shape factor, about 0.89 for magnetite.

\[
D_c = \frac{k \lambda}{b \cos \theta}
\]

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The atom transfer radical polymerization (ATRP) initiator, Br-MPA, was attached on the Fe$_3$O$_4$ nanoparticles through the esterification reaction. The evidence showed that Br-MPA was chemically bonded to Fe$_3$O$_4$ nanoparticles. The FT-IR spectrum of Fe$_3$O$_4$ nanoparticles was showed in Figure 2(a). The peak at 3417 cm$^{-1}$ is related to the stretching vibrations of OH or water molecules adsorbed onto the surface of the Fe$_3$O$_4$ nanoparticles, and the peak at 565 cm$^{-1}$ is attributed to the stretching vibration mode of Fe–O. In Figure 2(b), due to the structure of functional carboxylic acid (Br-MPA), there are characteristic absorptions bands in the FT-IR spectrum. The peak at 2944–2843 cm$^{-1}$ region is attributed to stretching vibration of C–H, the band around 1700 cm$^{-1}$ is due to the stretching vibration of C=O, and the peak at 3008 cm$^{-1}$ is ascribed to the stretching vibrations of the OH group.

ATRP polymerization of styrene with modified Fe$_3$O$_4$ nanoparticles

One of the preferences of ATRP [67,68] is that an alkene monomer like styrene can be polymerized with molecular weight and PDI control, either in bulk or in solution [69]. FT-IR, SEM and XRD can prove that the “grafting from” reaction proceeds successfully.

Figure 3 and Table 1 showed the energy-dispersive X-ray (EDX) analysis spectrum of Fe$_3$O$_4$-Br-MPA. The presence of C, O, Fe and Br signals presented that the nanoparticle surfaces were modified by 2-bromo2-methyl propionic acid (Br-MPA).

Figure 4(a) shows the FT-IR spectrum of Fe$_3$O$_4$/PSt. According to the FT-IR spectrum the characteristic absorption groups (–OH) on the nanoparticle surface appeared in 3326 cm$^{-1}$. The strong band at 2925 cm$^{-1}$ (asymmetric) and 2850 cm$^{-1}$ (symmetric) is related to the –CH$_2$ stretching vibrations.

Figure 2. FT-IR spectra of (a) Fe$_3$O$_4$ nanoparticles (b) Br-MPA and (c) Fe$_3$O$_4$/Br-MPA.
vibration at 2935 and 2852 cm\(^{-1}\), the phenyl ring stretching vibration at 1445, 1511, the ring in phase C–H stretching vibration at 1014 cm\(^{-1}\), and 1600 cm\(^{-1}\) corresponding to the C=C stretching of the aromatic ring and the ring out-of-plane bend at 699 cm\(^{-1}\). The FT-IR spectrum of Fe\(_3\)O\(_4\)/PSt established with the PSt standard.

The morphology of the Fe\(_3\)O\(_4\) nanoparticles and Fe\(_3\)O\(_4\)/PSt were probed using SEM. As shown in Figure 5(a), the Fe\(_3\)O\(_4\) nanoparticles are spherical in shape with about 30 nm diameter. With the growth of the polystyrene chain on the Fe\(_3\)O\(_4\) surface using initiators of ATRP polymerization, Br-MPA attached to Fe\(_3\)O\(_4\) nanoparticles, larger particles were obtained (Figure 5(b)). Therefore, the Fe\(_3\)O\(_4\) nanoparticle was coated with polystyrene and becomes core/shell nanocomposite. These materials with chemically bonds between organic and inorganic have improved properties.

Figure 1(b) shows the X-ray diffraction pattern after growth of polystyrene on the Fe\(_3\)O\(_4\) nanoparticles. The appearance of peaks at 2\(\theta\) = 10–24\(^{\circ}\) is related to polystyrene. This shows that the polystyrene has an amorphous structure. The characteristic peak at 2\(\theta\) = 35.5\(^{\circ}\) is attributed to the presence of Fe\(_3\)O\(_4\) nanoparticles.

**Preparation of poly(p-amino styrene) grafted onto Fe\(_3\)O\(_4\)**

FT-IR spectrum confirmed the structural characteristics of the obtained polymer-coated Fe\(_3\)O\(_4\). In the spectrum line of Fe\(_3\)O\(_4\)/PSt-NO\(_2\), the absorption bands at 1515 cm\(^{-1}\) and 1346 cm\(^{-1}\) were attributed to the –NO\(_2\) group (Figure 4(b)), which, suggested that the nitration reaction occurred and –NO\(_2\) groups were attached to a benzene ring. After a reduction reaction and the production of amino groups, the bands at 3363 cm\(^{-1}\) and 1608 cm\(^{-1}\) became stronger because of the stretching vibration of N–H as shown in the FT-IR spectra of Fe\(_3\)O\(_4\)/PSt-NH\(_2\) (Figure 4c). Furthermore, we found that the characteristic bands of –NO\(_2\) at 1515 and 1346 cm\(^{-1}\) apparently became weaker, suggesting that –NO\(_2\) groups were reduced to –NH\(_2\).

**Characterization of Fe\(_3\)O\(_4\)/polystyrene-g-polyaniline nanocomposites**

The Fe\(_3\)O\(_4\)/polystyrene-g-polyaniline nanocomposite was characterized by FT-IR. Figure 6 shows the FT-IR spectrum of Fe\(_3\)O\(_4\)/polystyrene-g-polyaniline. The formation of polyaniline was shown by an absorption band at 3379 cm\(^{-1}\) which can be attributed to the N–H stretching mode; 1587, 1500 cm\(^{-1}\) is related to the C=N stretching mode for quinoid and C=C stretching mode for benzenoid units; and 1303, 1168 cm\(^{-1}\) can be attributed to the C–N stretching mode for the benzenoid unit. 1118 and 825 cm\(^{-1}\) can be attributed to the C–H in the benzene plane.

Figure 1(c) displays the X-ray diffraction pattern for the Fe\(_3\)O\(_4\)/PSt-g-PANI nanocomposite. This is characterized by the

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C       | 46.43    | 73.09    |
| O       | 11.57    | 11.74    |
| Fe      | 8.47     | 7.59     |
| Br      | 33.53    | 7.58     |
| Totals  | 100      |          |
appearance of peaks extending over the 2θ range of 5° to 30°. This shows that the polymer has an amorphous structure and is a completely coated nanoparticle.

SEM was used to study the morphology of Fe₃O₄/PSt-g-PANI as shown in Figure 7. Much larger particles were obtained when the polymer chains grew from the Fe₃O₄/PSt surface (Figure 5(b)). The compacted and large amounts of polyaniline chains “clothe” the Fe₃O₄/PSt nanocomposite to become bulk materials.

Figure 8 shows the thermal behavior and thermogravimetric analysis (TGA) of the Fe₃O₄, Fe₃O₄/PSt and Fe₃O₄/PSt-g-PANI nanoparticles. As shown in Figure 8(a), the Fe₃O₄ nanoparticles exhibit high stability in the range of 50–800°C. These nanoparticles have lost about 6% of their total weight. Probably the evaporation of absorbed water on the surface of nanoparticles had led to weight loss. Figure 8(b) is related to PST-grafted Fe₃O₄ that shows a sharp weight loss (61%) at 300–350°C. This weight loss is attributed to evaporation of solvent trapped between the polymer chains and the burning-up of the grafted polystyrene.

Figure 8(c) shows the thermal behavior of Fe₃O₄/PSt-g-PANI nanocomposite, i.e. 41% weight loss at 50–800°C. The initial weight loss is about 3.6% at 127°C that can be assigned to the decomposition of solvent molecules trapped between the polymer chains. The rapid weight decrease is in the second region at ~340°C, which is attributed to the decomposition of homo-PANI. Moderate rate of weight loss in Fe₃O₄/PSt-g-PANI could be related to the presence of the polyaniline chain on the backbone of polystyrene.

Figure 9(a) shows the TEM image of the Fe₃O₄ nanoparticles. The TEM image determines the size distribution and...
morphology of the Fe₃O₄ nanoparticles. The Fe₃O₄ nanoparticles show high aggregation due to the large specific surface area. The TEM image in Figure 9(b) shows the Fe₃O₄/PSt-g-PANI nanocomposite. This image illustrated that aggregation and the dispersion were decreased and improved, respectively. The Fe₃O₄/PSt-g-PANI nanocomposite exhibited very good dispersion in the solvent.

**Conductivity measurements**

The electrical conductivity of polyaniline and its composites makes it suitable for electrical applications. Conductivity measurements were carried out by a four-point probe method. The blends of PANI nanocomposites were compacted into pellets for measurement. All measurements were done in air at room temperature and converted to conductivity by the following equation:

\[
\rho = \frac{1}{\delta} = \frac{V}{I \omega l \ln 2}
\]

In this equation, \(\rho\) is the resistivity (\(\Omega\ cm\)), \(\delta\) is the conductivity (\(s/cm\)), \(V\) is the potential difference (mV), \(I\) is the applied constant current (mA), and \(\omega\) is the thickness (cm). The conductivity of the nanocomposite was high compared to that of PANI. The improved conductivity of the composite is possibly due to the charge transfer between Fe₃O₄ nanoparticles and PANI. The conductivity values of the pure PANI and its nanocomposites were 1.32 and 1.25 Scm⁻¹, respectively (Table 2).

As shown in Figure 10, the effect of the potential scanning rate (V) on the peak currents for the chemically synthesized homo and nanocomposite of PANI were investigated under cyclic voltammetric (CV) conditions in the range of 10 to 90 mVs⁻¹, in DMSO between -0.20 and +1.00 V. All potentials are given versus the reference (Ag/AgCl) electrode. The polymer film was prepared on glassy carbon (GC) microelectrode by casting the polymeric solution of samples in THF by ultrasonic treatment for 10 min.

Typical cyclic voltammograms (CVs) of the homoPANI film are shown in Figure 10(a). As seen, the CVs of the homoPANI indicated two anodic peaks at around 0.31 and 0.52 V versus the reference electrode. Moreover, as can be realized, the anodic peaks shifted in the direction of a positive potential with increasing scan rate, which indicated that the electrochemical doping/dedoping of the casted polymer film was chemically reversible. In Figure 10(b), the CVs of the nanocomposite of the PANI film exhibited two typical redox couples with anodic peaks at about 0.26 and 0.47 V against the Ag/AgCl electrode. A similar voltammogram of pure polyaniline for the nanocomposites of PANI showed that the anodic peaks currents linearly increased with increasing scan rate. Also, Figure 10(b) shows that despite the polystyrene chains, the PANI nanocomposite is electrically conductive.

**Conclusion**

A Fe₃O₄/PSt-g-PANI nanocomposite was successfully synthesized with a core-shell structure and a new path, combining surface-initiated atom transfer radical polymerization of styrene with pattern-guided oxidative polymerization of aniline. Immobilization of an ATRP initiator on the Fe₃O₄ surface allowed for the subsequent surface-initiated ATRP to produce polystyrene grafted polymers. Then, functionalization of the polystyrene grafted to the amino group was completed. The resulting macroinitiator (Fe₃O₄/PSt-NH₂) was used for in-situ chemical oxidating of aniline. FT-IR and TGA data verify that the surface modification of Fe₃O₄ by a chemical grafting approach was indeed successful. FT-IR, XRD, TGA, TEM, and SEM confirmed the success of the synthesis and polymerization processes. The synthesized Fe₃O₄/polystyrene-g-polyaniline showed better electrical conductivity and better thermal stability relative to homopolymers. Moreover, morphological studies by SEM and TEM presented direct and clear evidence for grafting of polystyrene and polyaniline to the Fe₃O₄ surface nanoparticles. The method presented for the preparation of the Fe₃O₄/polymer nanocomposite is attractive because the chemical grafting of the polymers to Fe₃O₄ has benefits over a composite prepared by the simple mixing of components.

**Table 2. Characteristics of the conductive nanocomposite.**

| sample          | Polymerization time(h) | Particle size (nm) | Shell thickness (nm) | Conductivity (\(\sigma\) S/cm) |
|-----------------|------------------------|--------------------|----------------------|-------------------------------|
| Fe₃O₄           |                        | 10–21              | –                    | –                             |
| Fe₃O₄/PSt-g-PANI| 8                      | 12–50              | 7–14                 | 1.32                          |

![Figure 10. Cyclic voltammetry curves (CVs) of the chemically synthesized (a) homo-PANI (b) Fe₃O₄/PSt-g-PANI.](image-url)
Due to improved physicochemical properties relative to the homopolymers, the synthesized nanocomposite could be beneficial for numerous applications from supercapacitors or other electronic devices to medicine. This nanocomposite showed high electrical conductivity of about 1.25 S cm⁻¹.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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