Synthesis and characterization of polypyrrole-coated iron oxide nanoparticles

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Keywords: polymer composites, polypyrrole, Fe3O4, chemical precipitation, Raman spectroscopy, x-ray photoelectron spectroscopy

Abstract

Conducting polymers are gaining importance in recent years for their remarkable electrical and ionic properties and so, in order to further improve the fundamental properties, they are being integrated with iron oxide (Fe3O4) nanoparticles (NPs). Therefore, in the present study, polypyrrole (PPy) doped with iron oxide NPs to form PPy@Fe3O4 nanocomposite by adopting a simple chemical precipitation method of in situ polymerization. The various spectroscopic (UV–vis, FTIR, Raman, XRD, and XPS), and electron microscopic (FESEM and HRTEM) analysis were employed to study the effects of Fe3O4 NPs onto the polymer mixture. The analysis of results revealed the successful doping of Fe3O4 NPs onto the PPy polymer and also, the Raman spectral studies confirmed not only for the stabilization of doped nanocomposites in its polaronic form but also prevented from the auxiliary oxidation of polymer.

1. Introduction

In recent years, conductive polymers (CPs) have significantly attracted the attention of many researchers from both academics and industrial point of view for the potential properties to have applications in the manufacturing sector like rechargeable batteries, smart windows, sensors, light-emitting diodes (LED), and nonlinear optical (NLO) devices [1, 2]. When these organic polymers get combined with magnetic materials, the formed hybrid polymer nanocomposites possess the properties of both conducting and magnetism, where they can find applications in molecular electronics, electromagnetic shields, electrochemical display devices, and microwave-absorbing probes [3, 4]. The iron oxide (Fe3O4) nanoparticles (NPs) for example stands first among all other magnetic materials and offers the additional properties of maintaining the superparamagnetic behaviour, large surface area, enhanced electrochemical activity, catalytic nature, stability, and very low toxicity [5]. The most attractive feature of this compound is that the iron ore is highly abundant in nature and can be extracted directly as iron oxide in its most stable form [6]. Also, the Fe3O4 NPs have been demonstrated to maintain a promising effect in various applications of the biomedical sector as an effective probe for the construction of drug-delivering systems and contrasting agents of magnetic resonance imaging (MRI), hyperthermia-based cancer therapy, DNA separation, and purification, etc [7]. The applications of this material...
in the biological and clinical field are supported by the low toxicity, biocompatibility, high magnetic susceptibility, chemical stability, high saturation magnetization values, and cost-effectiveness [8].

The main issues concerning the use of Fe₃O₄ NPs in the biomedical sector is that their rapid agglomeration owing to the size growth and decreased passage through the cell membranes, in addition to their high oxidative properties towards the cellular proteins. One approach to control the two effects of agglomeration and surface toxicity is by means of coating the magnetic Fe₃O₄ particles with that of surfactants or polymers including polyethylene glycol (PEG) 6000 [9, 10], dextran [11, 12], carbon nanotubes (CNTs) [13], polypyrrole (PPy) [14, 15], etc. For example, in a study, the Fe₃O₄–PEG particulate system was tested for the control of SKOV-3 ovarian cancer cells using hyperthermia (magnetic field) and photo-thermal (light irradiation) therapy. The results confirmed the successful induction of anticancer activity with no/minimal effects on the enzymes that support the regular functions of the liver, lung, and spleen [9]. A similar study with the use of PEG–Fe₃O₄ NPs towards in vivo breast cancer cells was able to fully control their growth with the induction of mitochondrial damage and reduced levels of NF-κB translocation [10]. Also, in a different study, the folic acid-targeted, dextran-conjugated Fe₃O₄ NPs were able to fully localize the vinblastine drug into the sites of pancreatic cancer cells, resulting in a significant reduction to the cancer cells count with the induction of apoptotic pathway [11, 12]. These reports provide the information that the polymer-coated Fe₃O₄ NPs formed by the use of polymer as a template can allow the generation and fine-tuning the properties such as controlled size, well-defined morphologies, enhanced surface area, and other performance characteristics. In that view, PPy is a type of polymer that belongs to the class of CPs, which can be prepared mainly by electrochemical polymerization or via chemical oxidative polymerization method [14]. Besides, the conductive properties of PPy have certain limitations that particularly restrict their use for a wide range of applications like poor durability, solubility, thermal stability, and processability [15]. Moreover, the monomeric units of PPy undergo oxidation and make them soluble in water and this particular property is of the highest importance because of its natural ability and easy decomposition in contrast to other counter polymers and inorganic materials such as lithium (Li), nickel (Ni), and nickel–cadmium (Ni-Cd) [16].

In this study, the magnetite Fe₃O₄ NPs is combined with PPy for excellent absorption conferring stability for a broad range of biomedical applications. A few of the research investigations about the synthesis of Fe₃O₄ NPs surface-functionalized first with PPy followed by the conjugation with folic acid for potential applications in nanomedicine have also been reported [17]. Further works on PPy@Fe₃O₄ (PPy-coated Fe₃O₄) are significantly used in magnetic guided treatments [18]. Therefore, the present work is aimed to investigate the influence of surface coated PPy on the physicochemical and morphological characteristics of Fe₃O₄. For that, we first formed the Fe₃O₄ NPs by a wet chemical precipitation route and this follows the surface coating of PPy to form PPy@Fe₃O₄ nanocomposite. The formed PPy@Fe₃O₄ was subjected to various characterizations such as the FTIR, Raman, powder XRD, UV–vis, FESEM, HR TEM and XPS to fully understand the surface, electronic, and morphological characteristics.

2. Experimental procedure

2.1. Preparation of Fe₃O₄ NPs

The Fe₃O₄ NPs were prepared by chemical precipitation method as follows: Initially, 800 ml of deionized water was taken in a four-necked round-bottom flask equipped with the condenser, a nitrogen gas inlet, and a mechanical stirrer. Then, FeCl₃·6H₂O (AR grade, HiMedia, India) and FeCl₂·4H₂O (AR grade, HiMedia, India) were taken in 2:1 molar ratio to the flask. The following mixture was stirred using a magnetic stirrer under nitrogen atmosphere for 30 min, followed by the addition of 1.5 mol⁻¹ ammonium hydroxide (NH₄OH, AR grade, HiMedia, India) aqueous solutions until the pH of the reaction mixture reached 8. The reaction was continued for another 2 h in the same experimental condition and finally, the Fe₃O₄ NPs are produced.

2.2. Synthesis of PPy@Fe₃O₄ nanocomposite

The Fe₃O₄ NPs prepared in the first step were taken into a 500 ml round-bottom flask equipped with a mechanical stirrer. The PPy monomer and dodecylbenzene sulfonic acid (NaDBS) was dissolved in 200 ml of deionized water with vigorous stirring at room temperature in the flask. An aqueous acidic FeCl₃·6H₂O solution was then added to the reaction mixture and stirred. Then the polymerization was allowed to proceed for 12 h at room temperature under constant stirring and the products obtained were washed with deionized water and ethanol several times and dried under vacuum at 60 °C for 24 h.

2.3. Characterization techniques

The PPy@Fe₃O₄ nanocomposite was analyzed via Cary 50 UV–vis spectrophotometer (Varian, US) in the spectral range of 200–800 nm. The crystal phases of the prepared samples were analyzed by powder x-ray
diffraction (XRD) using Rigaku mini flux-II diffractometer, Japan equipped with Cu-Kα radiation (λ = 1.5408 Å). It was operated at 30 mA, 30 kV with a continuous scanning speed of 2° min⁻¹ in the 2θ range of 10°–80°.

The interference, influence, and interplay of functional groups involved in the reaction were analyzed by the Fourier transform-infrared (FTIR) spectrophotometer (Spectrum 100 FT-IR, Perkin Elmer, USA). For the FTIR studies, the pellet was prepared from homogenous mixing of a requisite amount of the samples with KBr (1:3) for complete removal of moisture. Then by using a hydraulic press, the pellets generated were tested under ambient conditions. The field-emission scanning electron microscopy (FESEM; FEI-Quanta FEG 200F, Thermo Fisher Scientific, USA) was used to determine the size and morphology of particles by sputter coating of gold. The images were captured in back-scattered electrons (BSE) mode with a detector at an accelerating voltage of 5 kV and a beam current of 30 pA.

3. Results and discussion

In this work during the synthesis of PPy@Fe3O4 nanocomposite, the Fe3O4 NPs reacted with PPy and NaDBS mixture, where the NaBDS can serve as a dopant as well as a surfactant. Also, the mechanical blending in the form of vigorous stirring allows for the oxidative polymerization of PPy and this on contact with the Fe3O4 NPs generates fully grown PPy@Fe3O4 nanocomposite [19]. Figure 1 demonstrates the comparison of powdered XRD patterns of Fe3O4 NPs, PPy, and PPy@Fe3O4 nanocomposite; From the figure, the diffraction peaks exhibited by Fe3O4 NPs were determined at 29.6°, 35.2°, 42.7°, 56.7°, 62.3° corresponding to the diffraction planes of (200), (311), (400), (511), and (440) (respectively) and are related to the face-centered cubic (fcc) spinel symmetry (JCPDS card number 65-3107). Similarly, the PPy sample showed an amorphous structure with a broad XRD peak around 21.8° corresponding to the Miller index of (220) lattice. In the case of PPy@Fe3O4, apart from the broad peak of PPy, the peaks of Fe3O4 were similarly observed in the nanocomposite, suggesting that the surface functionalization of PPy by its addition does not alter the crystal structure of Fe3O4 or induces any changes to its phases [20]. Further, the mean grain size of PPy@Fe3O4 nanocomposite is estimated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where D represents the crystalline size, k the Scherrer constant, λ, x-ray wavelength, β, the full width at half maximum (FWHM), and θ represents the Bragg angle as 28.96 nm [21].

Figure 2 illustrates the morphology of PPy (A1, A2, A3), Fe3O4 (B1, B2, B3), and PPy@Fe3O4 (C1, C2, C3) nanocomposite at different scales (2 μm, 1 μm, and 500 nm) when observed through a FESEM microscope. Figures 2(A1)–(A3) shows that the micrograph of PPy reveals the presence of globular particles having an irregular shape. Similarly, the FESEM images of Fe3O4 NPs (figures 2(B1)–(B3)) illustrate the presence of rod-shaped and homogenous arrangement of magnetite NPs. Figures 2(C1)–(C3) represents the formation of PPy@Fe3O4 nanocomposite with its surface structure in a spherical shape. Further, the SEM image indicates the spherical composites have a smooth surface and narrow size distribution, which is a typical and suitable
structure of a template. Based on the above analysis, it can be inferred that the Fe3O4 incorporated PPy has been successfully synthesized and also indicated for the presence of interaction between the two components using the formation of the final composite in a different shape than that of the individual ones. This further confirms that the PPy has been efficiently decorated on to the surface of Fe3O4 NPs.

Figures 3(a)–(b) shows the HRTEM images of PPy@Fe3O4 nanocomposite at different scale bars indicating the size, shape, and dispersive nature of the formed nanocomposite. It can be elucidated from the images that there is a thin (light shaded) layer of PPy layer in the range of 2–4 nm at the surface of Fe3O4 NPs. This confirms that the Fe3+ is successfully getting adsorbed onto the Fe3O4 NPs, facilitating the encapsulation of the PPy layer onto them. Secondly, there is no apparent aggregation among the Fe3O4 NPs in the nanocomposite as the PPy layer inhibited the aggregate formation, but with little thickening of the layer up to 15 nm. Further, the crystal properties of as-synthesized PPy@Fe3O4 nanocomposite when observed by the HRTEM revealed the interplanar spacing of \( \sim 0.519 \) Å (figure 3(b)). The corresponding SAED pattern as shown in figure 3(c), indicates an amorphous phase.

Figure 4 shows the comparison of FTIR spectrums of PPy@Fe3O4, PPy, and Fe3O4 NPs, where the absorption peak at 1300 cm\(^{-1}\) in PPy@Fe3O4 and PPy attribute for C–N ring stretching band of PPy in contrast to the Fe3O4 NPs. Also, a small band at 1544 cm\(^{-1}\) formed could be due to the C–C stretching vibration, and the dull peak at 1642 cm\(^{-1}\) attributes to the C=C ring stretching of PPy. In order to differentiate the FTIR spectrum of PPy, the peak at 1300 cm\(^{-1}\) was not found in the PPy@Fe3O4 nanocomposite, confirming that the PPy has been successfully polymerized and decorated on the surface of Fe3O4 NPs. Further, the peak observed at 1072.2 cm\(^{-1}\) in PPy and PPy@Fe3O4 nanocomposite showed C-O-C absorption as a function of a shift in the stretching vibrations when PPy was added. The changes associated with energy levels could well be deciphered upon the interaction between the PPy and Fe3O4.

Figure 5 shows the Raman spectra of Fe3O4, PPy, and PPy@Fe3O4 nanocomposite and from the graph, the Raman scattering peak for PPy@Fe3O4 nanocomposite observed at 673 cm\(^{-1}\) corresponds to the typical vibrational modes of Fe3O4 NPs. Further, the spectrum corresponding to PPy nanotubes showed a broad peak at 1065 cm\(^{-1}\) which corresponds to the characteristic of C–H in-plane deformity. Also, two small peaks (aromatic

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**Figure 2.** FESEM images of PPy (A series), Fe3O4 (B series), and PPy@Fe3O4 nanocomposite (C series).
form) near 921 and 980 cm\(^{-1}\) represented the vibrational modes of quinoid, polaronic, and bipolaronic structure suggesting the existence of moderate polymeric oxidation between aromatic and quinoid structures. The Raman spectra at 1560 cm\(^{-1}\) correspond to the C=\(\text{C}\) conjugated bonds, which brings in all the delocalized electrons to build up accounting for its conductivity. Accordingly, it is concluded from the Raman spectra that the Fe\(_3\)O\(_4\) NPs are not simply mixed or blended but conjugated with the PPy polymer via chemical interaction as evident from the conjugate bond formation [25].

A typical XPS spectrum of PPy@Fe\(_3\)O\(_4\) nanocomposite depicting the core–shell structure is shown in figure 6. From the figure, the broad XPS spectrum of Fe 2p indicates the presence of O (1s) and C (1s) peaks.
corresponding to the Fe$_3$O$_4$ NPs. The corresponding binding energies of deconvoluted Fe 2p showed the presence of Fe 2p$_{3/2}$ peaks between 709.3 and 710.2 eV for the FeO. Further, the broad superposed peaks corresponding to the Fe$_3$O$_4$ were observed between 723.1 and 724.4 eV. Also, the peaks corresponding to Fe 3þ were observed between 724.4 and 712.3 eV revealing the banding between Fe$^{2+}$ and Fe$^{3+}$. The decollated peaks

Figure 5. Comparison of Raman spectra of Fe$_3$O$_4$, PPy, and PPy@Fe$_3$O$_4$ nanocomposite.

Figure 6. XPS spectral comparison of O, C, and Fe elements in the PPy@Fe$_3$O$_4$ nanocomposite.
of O (1s) corresponding to three peaks viz. 530.7, 532.0, and 533.8 eV were also identified. These O peaks were bonded with neighboring atoms such as vacancy of oxygen and the surface groups of H2O and OH accordingly. In the PPy@Fe3O4 nanocomposite’s XPS spectrum, there was a strong CT (charge-transfer) satellite peak appearing as a shoulder peak between 284.0 and 285.5 eV indicating the etching of PPy with Fe3O4. Fe and C and C–N group of PPy. It is this satellite signature that emphasizes the Fe3O4 integration with the PPy. Alternatively, O1s peaks were observed at 530.73 eV (lattice O, Fe–O), 532.01 eV (C–O), and 533.89 eV (Fe–C–O) which are in agreement with the XRD pattern [26].

Figure 7 illustrates the UV–vis spectral comparison of Fe3O4 NPs, PPy, and PPy@Fe3O4 nanocomposite samples where the PPy sample exhibits a characteristic peak at 230 nm. The characteristic peak of PPy at \( \lambda_{\text{max}} = 230 \text{ nm} \) reveals that the soluble PPy was synthesized successfully. Moreover, the Fe3O4 NPs show a wide range absorption peak in the range of 300–350 nm, typically correlating with absorption maxima of magnetic NPs [27]. Notably, the PPy@Fe3O4 nanocomposite demonstrated the characteristic absorption peak of both Fe3O4 NPs and PPy in the range of 330–450 nm and typically at 460 nm. It was inferred from the UV–vis spectroscopic analysis that there was a transition from the valence band to the antibonding polaron state attributing to effective doping. Upon successful doping, there might be a slight change in the morphology of the nanocomposite with a slight red shift attributing polaron-p transition. This suggests that the interaction between the PPy and Fe3O4 is occurring via quinoid ring structure [25–28].

4. Conclusion

In this work, the synthesis of Fe3O4 NPs and their doping efficacy on the polymeric matrix (PPy) was successfully investigated by Raman spectroscopy, XPS, and electron microscopic (FESEM and HRTEM) studies. The interaction between the NPs and the polymer was explored using changes associated with morphological and electronic properties when compared to Fe3O4 NPs and PPy. The evidence on the charge-transfer between the PPy and Fe3O4 NPs in the event of stabilization of polaronic segments has been demonstrated using Raman spectra and XPS. The occurrence of such an interaction has led to enhanced conductivity and reduced resistance of the composite upon etching Fe3O4 NPs thereby preserving the conductive properties. The as-synthesized multifunctional nanocomposite with their magnetic properties fine-tuned thereby regulating the transferability and structural stability would find its application in designing nano-architectures with special magnetic properties.

Acknowledgments

The authors would like to acknowledge the financial support provided by a Research University grant from University of Malaya (RU001–2020). The King Saud University author is grateful to the Deanship of Scientific Research, King Saud University for funding through Vice Deanship of Scientific Research Chairs.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare no conflict of interest.

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