



Composite nanofibers prepared from metallic iron nanoparticles and polyaniline: High performance for water treatment applications



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ABSTRACT

Presented here is a simple preparation of metallic iron nanoparticles, supported on polyaniline nanofibers at room temperature. The preparation is based on polymerization of interconnected nanofibers by rapid mixing of the aniline monomer with Fe(III) chloride as the oxidant, followed by reductive deposition of Fe⁰ nanoparticles, using the polymerization by-products as the Fe precursor. The morphology and other physico-chemical properties of the resulting composite were characterized by scanning and transmission electron microscopy, Brunauer–Emmett–Teller method, X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and vibrating-sample magnetometry. The composite fibers were 80–150 nm in diameter and exhibited the expected ferromagnetic behavior. The composite rapidly and efficiently removed As(V), Cr(VI), and also Congo red dye, from aqueous solutions suggesting their usefulness for removal of toxic materials from wastewater. The composite fibers have high capacity for toxin removal: 42.37 mg/g of As(V), 434.78 mg/g of Cr(VI), and 243.9 mg/g of Congo red. The fibers are easily recovered from fluids by exploiting their ferromagnetic properties.

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1. Introduction

In recent years, conducting polymers nanostructures have attracted special attention in the fields of nanoscience and nanotechnology due to their unique combination of the electronic properties of conductive polymers and the large surface area of nanomaterials [1]. Specifically, the synthesis and applications of one dimensional (1D) nanostructured conducting polymeric materials with controllable morphology that includes nanotubes, nanowires and nanofibers, have been explored over the past few years [2–5].

Among 1D conducting polymer nanostructures, nanofibers of polyaniline (PANI) have stimulated research interest as they can be easily synthesized in bulk quantities and have a large surface area to volume ratio, with good redox properties, high conductivity and excellent environmental stability [6]. This has resulted in

potential applications in sensors, actuators, super capacitors, field effect transistors and in separation or purification systems [7–11].

Moreover, to improve the functionality of 1D conducting polymer nanostructures metal nanoparticles (with unique electronic, catalytic, magnetic and optical properties) were incorporated [12], as a secondary component, to form 1D nanocomposites. This incorporation can be considered as a constructive technique because the combination of metal particles with a conducting polymer offers an attractive route to reinforce the polymer as well as introduce electronic properties, based on morphological modification or electronic interaction between the two components [13].

Consequently, efforts have been devoted to attach various metal nanoparticles onto 1D conducting polymer supporting matrices and manufacturing multifunctional 1D composite nanostructures with enhanced physico-chemical properties. In particular, a series of noble metal nanoparticles including Ag, Au, Pt and Pd were produced inside or on the surface of PANI nanofibers via *in situ* redox reactions and/or by reduction processes in the presence of other reducing agents such as ethylene glycol or HCOOH, respectively [14–18]. Although noble metal nanoparticle supported on 1D PANI nanofibers have been studied extensively, magnetic nanoparticles such as zero valent iron (Fe⁰), with increased reactivity, supported on PANI nanofibers have not been widely investigated.

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In this work, a simple and facile chemical strategy to synthesize Fe^0 nanoparticles supported on PANI nanofibers (PANI/ Fe^0) at room temperature is demonstrated. A simple synthesis protocol based on rapid-mixing polymerization method was employed first for the production of PANI nanofibers using ferric chloride (FeCl_3) as oxidant [19]. After completion of the polymerization reaction, the PANI nanofibers and reaction by products (FeCl_2 or any unreacted FeCl_3) could be found in the polymerization solution. After addition of sodium borohydride (NaBH_4) solution, as an external reducing agent, Fe^0 nanoparticles were grown on the PANI nanofibers matrix.

The present synthesis strategy represents a new type of 1D conducting polymer nanocomposite with several advantages. Firstly, the synthesis method is very simple and executed at room temperature without employing an external means such as template or surfactant. Secondly, no external metal precursor is used as the source of metal nanoparticles; rather a polymerization by-product is used as the precursor of Fe^0 nanoparticles. Finally the physico-chemical properties of the PANI/ Fe^0 composite nanofibers can easily be tuned by varying the Fe^0 nanoparticle-loading in the PANI nanofibers.

The as-synthesized PANI/ Fe^0 composite nanofibers are expected to display enhanced physico-chemical properties obtained synergistically from both components of the composite nanofibers. They could be used as multifunctional materials in various fields of nanotechnology and for environmental remediation. It is already well established that because of the presence of large amounts of amine and imine functional groups, PANI has interactions with some heavy metal ions and toxic dye molecules that have strong affinity to nitrogen. Consequently, the application of PANI for the removal of heavy metals and dyes has been studied intensively [11,20,21].

In addition, Fe^0 nanoparticles with excellent electron donating capacity have been effectively used over the past few years to remediate surface and ground water contaminated with inorganic ions and organic compounds [22]. The large specific surface area

and greater density of the highly reactive surface sites of Fe^0 nanoparticles have been proposed to result in a rapid and cost-effective water treatment system compared to conventional iron-based technologies [23]. Therefore, due to enhanced surface area, highly reactive surface sites and greater electron donor property, derived synergistically from both components of the PANI/ Fe^0 composite nanofibers, these are expected to perform efficiently in the removal of contaminants from water.

Herein, the contaminant removal behavior of the obtained PANI/ Fe^0 nanofibers is studied by considering two heavy metal pollutants, arsenic(V) [As(V)], one of the most toxic ground water pollutants, chromium(VI) [Cr(VI)], the most common heavy metal pollutant in industrial wastewater and one organic pollutant, Congo red (CR), a carcinogenic anionic azo dye released into waste effluents of different dyeing industries. Due to the toxic and carcinogenic effects of As(V), Cr(VI) and CR on human health and on the environment [24–26], their removal from water is important. Evaluation of the performance of the PANI/ Fe^0 composite nanofibers toward contaminant removal from water exhibited enhanced removal performance compared to the PANI nanofibers counterpart.

2. Experimental section

2.1. Materials

Aniline (ANI, 99% acquired from Sigma–Aldrich, USA) was purified using vacuum distillation. Distilled ANI was stored in a refrigerator prior to use for polymerization. Anhydrous iron (III) chloride (FeCl_3), sodium borohydride (NaBH_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium arsenate heptahydrate ($\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$) and Congo red (CR) were purchased from Sigma–Aldrich, USA. Ultrapure water (type-2, resistivity- $17.4 \text{ M}\Omega \text{ cm}^{-1}$), collected from an EASYpure[®] II, UV-ultrapure water system, was used for polymerization media and preparation of all aqueous solutions. All other chemicals used were of reagent grade.

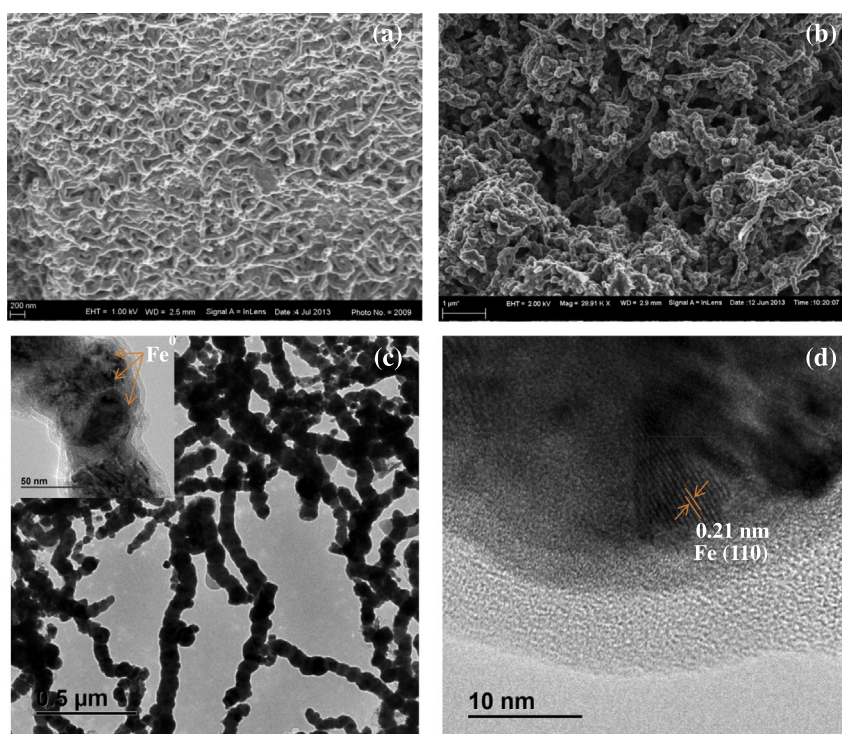


Fig. 1. FE-SEM images of (a) PANI nanofibers and (b) PANI/ Fe^0 composite nanofibers and HR-TEM images of (c and d) PANI/ Fe^0 composite nanofibers at two different magnifications.

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