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Synthesis, characterization and antibacterial effect of new magnetically core–shell nanocomposites

Alireza Allafchian [a,*], Hamid Bahramian [b], Seyed Amir Hossein Jalali [c], Hossein Ahmadvand [b]

[a] Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan 84156 83111, Iran
[b] Department of physics, Isfahan University of Technology, Isfahan 84156 83111, Iran
[c] Institute of Biotechnology and Bioengineering, Isfahan University of Technology, Isfahan 84156 83111, Iran

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ABSTRACT

A new magnetically responsive three-component nanocomposite consisting of $NiFe_2O_4$, Poly Acrylonitrile Co Maleic Anhydride (PAMA) and nanosilver was synthesized and characterized and then its antibacterial activities were tested. For the preparation of $NiFe_2O_4$@Ag, $NiFe_2O_4$ was coated by Ag and for the synthesis of $NiFe_2O_4$@PAMA@Ag, $NiFe_2O_4$ was first covered by PAMA and then silver nanoparticles were immobilized on the surface of the PAMA shell. The nanocomposites were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The antibacterial activity of the synthesized nanocomposite against some gram positive and gram negative bacteria was studied and compared with that of naked $NiFe_2O_4$, $NiFe_2O_4$@Ag and $NiFe_2O_4$@PAMA. The $NiFe_2O_4$@PAMA@Ag had better antibacterial activity and could be readily isolated from the aqueous solution via magnetic decantation, thereby avoiding the contamination of the environment.

1. Introduction

Nanotechnology continues to grow with the synthesis of novel polymer nanocomposites and the associated products in the commercial market. Polymer nanocomposites are produced from nanoparticles dispersed inside the polymeric matrix [1–3] or coated by polymer [4,5]. Polymers are the manipulating materials with a specific chemical and structural nature, long chains and functional groups permitting the incorporation and dispersion of nanoparticles [6]. Recently, core–shell nanocomposites comprising magnetic nanoparticles and polymers have been noticed in several investigations. However, the produced core–shell nanocomposites are expected to show the properties of original materials and exhibit novel functionality [7].

Among the numerous nanoparticles used as the biocidal agent, silver nanoparticles have been the famous antibacterial agent due to their higher antimicrobial activities against gram-positive and gram-negative bacteria since many years ago [8]. Although silver nanoparticles have been extensively investigated in the colloidal systems, their use may result in some unwanted effects [9,10]. Some attempts have been made to immobilize silver nanoparticles on synthetic polymers to make composite materials with antimicrobial activity. Sometimes, there is the need to entrap silver nanoparticles on various metrics and surfaces for numerous practical applications and prevent the undesired effect of using pure silver nanoparticles [11,12]. Kong et al. synthesized silver nanoparticles/poly (methyl methacrylate) (PMMA). The new nanocomposite could be used as a semi-transparent antimicrobial coating [13]. Melaiye et al. prepared the nanocomposite by the formation of silver nanoparticles inside the electrospun Tecophilic fiber. The nanocomposite showed the bactericidal and fungicidal effects by using the disk diffusion technique [14].

Many studies have shown that silver nanoparticles have a potential toxicity for human and environment in a concentration-dependent manner [15]. Therefore, it is necessary to separate the Ag based disinfectants from water solution after treatment. Among different methods used to tackle these problems, one approach is to use nanomagnetic system as a core and polymer nanocomposites as the shell, and utilize these nanostructures for the treatment of the media. Magnetic nanoparticles can be manipulated by an external magnetic field; therefore, magnetic nanoparticles coated with polymer nanocomposites and AgNPs could be readily separated from the bulk solution. Finally, using a static magnetic field with a silver nanocomposite combined with nanosize ferromagnetic can prevent the uncontrolled waste disposal of silver nanoparticles [16–18]. The separation of magnetic composite by a

* Corresponding author. Fax: +98 3133919014;
E-mail address: Allafchian@cc.iut.ac.ir (A. Allafchian).

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magnetic field is more effective than filtration or centrifugation. One of the most common methods for synthesizing magnetic nanocomposite materials is coating spinel ferrites, such as Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $MnFe_2O_4$, and $ZnFe_2O_4$ with polymer [19]. Spinel ferrites magnetic composites with Ag have been successfully synthesized by many groups and the antibacterial performance has also been investigated [20,21]. Although spinel ferrites are a suitable candidate for the preparation of magnetic nanocomposites, the amount of AgNPs combined with spinel ferrites is inadequate [22,23]. Therefore, some researchers have found that if a layer of polymer coat is formed on the surface of spinel ferrites, the immobilization of AgNPs may be easily achieved [19,24].

In this study, we prepared a new silver magnetically core–shell nanocomposite, $NiFe_2O_4$@PAMA@Ag, and evaluated it by Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and Field emission scan electron microscope (FESEM). Finally, the resulting core–shell nanocomposite was tested for releasing Ag^+ in water and assessed against both gram negative, *Escherichia coli* and *Salmonella typhimurium,* and gram positive, *Staphylococcus aureus* and *Bacillus cereus*, bacteria.

2. Experimental

2.1. Materials and methods

All the chemicals, including $Ni(NO_3)_2$, $Fe(NO_3)_3$, $Ag(NO_3)$, $K_2S_2O_8$, Na_2SO_3, NaOH and other chemicals, were provided from Merck and used without further purification. Doubly distilled and deionized water were used as a solvent in all reactions. Acrylonitrile and dimethyl formamide (DMF) were commercial products that had been purified by vacuum distillation before they were used. Fourier transform infrared (FT-IR) spectrum was obtained using an FT-IR Jasco Japan spectrophotometer. X-ray diffraction (XRD) patterns of the synthesized samples were taken with a Philips X-ray diffractometer over a 2θ range from 10° to 80°, using Cu K_α radiation (λ=0.154 nm) in the step size of 0.02. The scanning electron microscopy (FE-SEM) images were obtained using a Hitachi Japan S4160 field emission scanning electron microscope. Tarnsmision electron microscope analysis was done using cm30 Philips machine. Magnetic properties of the as-prepared composites were studied using a vibrating sample magnetometer (VSM) from Meghnatis Daghigh Kavir Company (Iran). The surface area of the materials was studied using single-point Brunauer–Emmett–Teller (BET; Nano Sord, Iran) method.

2.2. Preparation of $NiFe_2O_4$

Nickel ferrite nanoparticles were prepared by a citrate gel method using nickel (II) and iron (III) nitrates with a known amount of citrate [25]. First, 20 ml of 1.0 mol L^{-1} citric acid was mixed with 20 ml solution of the analytical grade of 0.5 mol L^{-1} $Ni(NO_3)_2 \cdot 6H_2O$ and 1.0 mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ (in which the Ni: Fe molar ratio was maintained at 1:2) and dissolved in distilled water. Then, the pH value was reached to 9.0 using 0.10 mol L^{-1} ammonium hydroxide solution. The mixture was also stirred at 30 °C for 2 h to complete the reaction. The produced mixture was dried in an oven at 100 °C for 24 h. The produced substance was calcinated at 600 °C for 2 h in argon atmosphere.

2.3. Preparation of Ag

The synthesis of silver nanoparticles is well understood and several methods have been developed that can offer good control over particle size and morphology [26,27]. In this work, silver nanoparticles were synthesized by reducing silver nitrate in a sodium borohydrate solution. Experiments were carried out by following a procedure described in Ref. [27]. In a typical synthesis of silver nanoparticles, 50 ml of 5.0 mmol L^{-1} of $AgNO_3$ was added drop-wise to 50 ml of 10.0 mmol L^{-1} of sodium borohydrate in a beaker and allowed for 2 h to reduce the silver ions into AgNPs. The produced AgNPs was washed with distilled water several times to remove any excess protecting agent. The final product was dried in an oven at 50 °C for 2 h.

2.4. Preparation of $NiFe_2O_4$@Ag

To prepare $NiFe_2O_4$@Ag, appropriate amounts of $NiFe_2O_4$ were reacted with 0.189 g $AgNO_3$. First of all, 0.10 g of $NiFe_2O_4$ nano particles was added to deionized water and sonicated for 10 min as the materials were completely dispersed. Then 0.189 g $AgNO_3$ was added to the mixture. After vigorous stirring of this mixture for 30 min to ensure the adsorption of Ag^+ by $NiFe_2O_4$, 50 ml of the reducing agent 10.0 mmol L^{-1} was added drop-wise into the reaction vessel. The prepared $NiFe_2O_4$@Ag was washed with distilled water several times and put in an oven at 60 °C for 6 h [23].

2.5. Synthesis of PAMA and $NiFe_2O_4$@PAMA nanocomposite

The synthesis of PAMA polymers was performed by water-phase precipitation copolymerization process. As a general method of PAMA preparation, 3 ml of acrylonitrile, 0.8 g maleic anhydride and 0.1 mass% of $K_2S_2O_8$–Na_2SO_3 as the polymerization initiator [28] were intensively mixed. The product was then heated at 60 °C in nitrogen atmosphere for 4 h. This was followed by a drying treatment at 90 °C. The final products were lightly ground using a centrifugal mill with stainless steel knives.

The $NiFe_2O_4$@PAMA composite was prepared by coating PAMA on the surface of $NiFe_2O_4$ nanoparticles. To fulfill this goal, 1.0 g PAMA was added in 2.0 ml of DMF at 40 °C. The mixture was stirred for 6 h until all PAMA polymer was dissolved. Then, 1.0 g $NiFe_2O_4$ was added to the solution. After that, the mixture was further sonicated for 10 min. Finally, the collected sample was dried in an oven at 60 °C for 6 h.

2.6. Synthesis of $NiFe_2O_4$@PAMA@Ag nanocomposite

A reduction chemical method was employed for the immobilization of Ag nanoparticles onto the surface of $NiFe_2O_4$@PAMA composite to prepare the three-component $NiFe_2O_4$@PAMA@Ag nanocomposite. In the first step, 1.0 g of $NiFe_2O_4$@PAMA was dispersed in 20 ml $AgNO_3$ aqueous solution (0.1 mol L^{-1}). After vigorously stirring this mixture, a solution of sodium borohydride, as the reducing agent, was introduced into the reaction vessel. After the fixed period of reaction time, the prepared $NiFe_2O_4$@PAMA@Ag nanocomposite was separated by magnetic decantation and washed several times with water to remove any excess protecting agent. Finally, the $NiFe_2O_4$@PAMA@Ag nanocomposite was dried in an oven at 60 °C for 6 h.

2.7. Antibacterial tests

The antibacterial activity of materials was evaluated by Kirby–Bauer disk diffusion method [29]. This is the standard method for assessing antibacterial activity of new synthesized materials. Briefly, four or five colonies of the bacteria were selected by using a sterile inoculating loop and suspended in 2 ml of sterile phosphate buffer saline (PBS). The tested bacteria were gram positive and gram negative, including *Staphylococcus aureus* (ATCC 29213) and *Bacillus cereus* (ATCC 14579), *Escherichia coli* (ATCC 35218), and *Salmonella typhimurium* (ATCC 14028). Turbidity of the