



Recyclable magnetite-silver heterodimer nanocomposites with durable antibacterial performance

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ABSTRACT

There is a significant need for magnetite-silver nanocomposites that exhibit durable and recyclable antimicrobial activity. In this study, magnetic iron oxide nanoparticles (Fe_3O_4 NPs) coated with ethylenediamine-modified chitosan/polyacrylic acid copolymeric layer ($\text{Fe}_3\text{O}_4@ECS/PAA$) were fabricated. Subsequently, directly deposited silver (Ag) NPs procedure was carried out to form the antibacterial heterodimers of $\text{Fe}_3\text{O}_4@ECS/PAA-Ag$ NPs. The composition and morphology of the resultant nanostructures were confirmed by FT-IR, XRD, TEM and TGA. The overall length of the heterodimers was approximately 45 nm, in which the mean diameter of $\text{Fe}_3\text{O}_4@ECS/PAA$ NPs reached up to 35 nm, and that of Ag NPs was around 15 nm. The mass fraction of silver NPs in the nanocomposites was about 63.1%. The obtained $\text{Fe}_3\text{O}_4@ECS/PAA$ NPs exhibited good colloidal stability, and excellent response to additional magnetic field, making the NPs easy to recover after antibacterial tests. In particular, the $\text{Fe}_3\text{O}_4@ECS/PAA-Ag$ NPs retained nearly 100% biocidal efficiency (10^6 – 10^7 CFU/mg nanoparticles) for both Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus* throughout ten cycles without washing with any solvents or water, exhibiting potent and durable antibacterial activity.

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1. Introduction

Silver nanoparticles (Ag NPs) have been extensively used over the past decade in various applications including catalysts, metal electrodes, biotechnology and bioengineering, medicine, and water treatment due to their unique electronic, optical, and catalytic properties [1–4]. Furthermore, they have also attracted considerable attention because of their excellent antibacterial property [5–7]. Currently, Ag NPs or their composites have been employed as effective antibacterial agents in a diverse range of consumer products. It is reported that the antibacterial properties of silver are closely related to the size of nanoparticles [8]. Unfortunately, Ag NPs synthesized using conventional methods aggregate easily, which greatly decreases their antibacterial activity [9]. To solve this problem, Ag NPs have been loaded onto suitable matrix, such as silicon dioxide [10,11], cellulose fiber [12,13], carbon nanotube [14,15,18] and graphene oxide [16–18].

Thanks of the large surface area and superparamagnetism,

Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have found a lot of applications in various fields [19–21]. Combining Fe_3O_4 NPs and Ag NPs can not only prevent the coalescence of Ag NPs, but also achieve recycling of nanosized silver to avoid contamination of surroundings. Bhupendra Chudasama et al. [22] synthesized Fe_3O_4 -Ag core-shell nanostructures and studied their antimicrobial activity and molecular mechanism. In their work, hydrophobic Fe_3O_4 -Ag nanostructures realized phase transfer via ligand exchange, improving the dispersibility in water. Xia et al. [9] synthesized $\text{Fe}_3\text{O}_4@C@Ag$ nanocomposites with a mean diameter of 250 nm. The intermediate carbon layer protected magnetic core and improved the antibacterial activity of the Ag NPs. Compared to the Fe_3O_4 NPs, the decrease in the saturation magnetization for as-prepared samples can be attributed not only to the decreased content of the magnetic core, but also the Ag shell and the intermediate carbon layer. Tamim Mosaib et al. [23] coated Fe_3O_4 NPs with poly (vinyl pyrrolidone) conjugated catechol (PVP-CCDP). Afterwards, silver nanoparticles were deposited onto PVP-CCDP coated iron oxide NPs by using remain catechol. The as-made nanoparticles could be removed easily through a magnet after antibacterial test and make it repeatable use. After five repeated uses, the antibacterial activity was declined by 20%.

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The magnetic nanocomposites mentioned above possess Fe_3O_4 @Ag core/shell structures. Gu et al. [24] described a methodology to form Fe_3O_4 -Ag heterodimers based on the reactions on the colloidosome of organic solvent/water. The resultant heterodimeric nanostructures are composed of two distinct particles bound as a single entity and possess two different applied surfaces. The dual nature of heterodimeric nanostructures confers upon them fascinating properties [25,26]. To the best of our knowledge, using magnetic heterodimeric NPs as antibacterial agents has not been reported yet.

Chitosan (CS), which is produced by deacetylation of chitin, is a natural, biodegradable and biocompatible polysaccharide with high content of amino ($-\text{NH}_2$) groups [27–29]. Moreover, it exhibits “contact-killing” antibacterial activity, which functions similarly to general polycation compounds [30,31]. In this study, we fabricated recyclable antibacterial heterodimer nanocomposites like snowmen, which were composed of magnetic core coated with ethylenediamine-modified chitosan/polyacrylic acid (Fe_3O_4 @ECS/PAA) NPs and Ag NPs. Successful preparation was evidenced by different techniques like Fourier Transform Infrared Spectra (FT-IR), Transmission Electron Microscope (TEM), X-Ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). We also investigated the biocidal activity and magnetic recyclable property of as-prepared samples. The resultant heterodimeric nanoparticles exhibited powerful and long term antimicrobial activity. After ten cycles of antibacterial trials, the biocidal efficiency still remained nearly 100% for model microbes *E. coli* and *S. aureus*.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$), ammonium hydroxide (25–28%), sodium citrate ($\geq 99\%$), acrylic acid (purified by distilling) and isopropyl alcohol (99.7%) were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. (China). Chitosan (degree of deacetylation 80–95%, Mw $\sim 20,000$) and poly (vinyl pyrrolidone) (PVP, Mw $\sim 40,000$) was obtained from Sinopharm. Chemical Reagent Co., Ltd. (China). Ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\geq 98\%$) was purchased from United Initiators Co., Ltd. (China). Silver nitrate (AgNO_3 , AR) was available from Shanghai Aladdin Chemistry Co. Ltd. (China).

2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 NPs were prepared through an improved chemical coprecipitation method [32,33]. Briefly, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.773 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.10 g) were dissolved in 160 mL of deionized water with 1:2 M ratio. Then, NH_3 aqueous solution (25 wt%) was added dropwise under vigorous mechanical stirring, and the final pH was maintained at about 10. Afterwards, the mixture was promptly heated to 80 °C and held for 30 min. After cooling to room temperature, the Fe_3O_4 NPs were separated by magnetic separation and washed with deionized water for three times.

2.3. Preparation of Fe_3O_4 @ECS/PAA nanoparticles

To deposit polymer coatings efficiently, Fe_3O_4 NPs were modified with sodium citrate [34]. Briefly, Fe_3O_4 nanoparticles (107 mg) were dispersed in 40 mL of distilled water by sonication for 10 min and 40 mL sodium citrate (108 mg) aqueous solution were added. The contents was stirred for 2 h at 40 °C. Then, water-based magnetic fluid was obtained. Subsequently, the CS (1.0 g) was dissolved in 100 mL acrylic acid (0.60 g) water solution, and then magnetic

fluid was added simultaneously. After N_2 bubbling for 30 min, approximately 30 mg of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as initiator was loaded in and polymerized at 80 °C for 8 h. The resulted Fe_3O_4 @CS/PAA NPs were recovered by placing on a permanent magnet and washed with deionized water for three times. In order to further improve the hydrophilia and adsorption capacity of nanocomposites, Fe_3O_4 @CS/PAA NPs were modified with ethylenediamine [35]. The Fe_3O_4 @CS/PAA NPs (181 mg) were suspended in 30 mL isopropyl alcohol, to which 2 mL epichlorohydrine (25 mmol) dissolved in 40 mL acetone/water mixture (1:1 v/v) was added. The mixture was stirred for 24 h at 60 °C. The solid was separated by a permanent magnet and washed several times with water and ethanol. The solid obtained were suspended in 50 mL ethanol/water mixture (1:1 v/v), then ethylenediamine (2 mL) was added. The contents were stirred at 60 °C for 12 h, then the solid products were separated by a permanent magnet again and washed with deionized water.

2.4. Preparation of Fe_3O_4 @ECS/PAA-Ag nanoparticles

50 mL dispersion of Fe_3O_4 @ECS/PAA NPs was mixed with 40 mL of PVP aqueous solution (3.75×10^{-4} M). Then, 10 mL of freshly prepared aqueous solution of $[\text{Ag}(\text{NH}_3)_2]^+$ (0.15 M) was quickly added into the dispersion, stirred at room temperature for 1 h. Subsequently, this mixture was held at 70 °C and stirred for 7 h [36]. The final products were collected by a permanent magnet and washed with deionized water several times.

2.5. Characterizations

Transmission Electron Microscope (TEM) images were obtained with a Tecna G2 20 S-Twin TEM at 200 kV. Fourier-Transform Infrared Spectra (FT-IR) were recorded on a Shimadzu IR Prestige-21 spectrometer with a diffuse reflectance attachment over a range from 500 to 4000 cm^{-1} . The X-Ray Diffraction (XRD) patterns of the samples were measured using a Bruker model D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ nm). Thermal characterization of samples was carried out with the aid of Mettler Tary Thermogravimetric Analysis (TGA) operated at the heating rate of 20 °C/min under N_2 . Magnetization curves as a function of magnetic field were measured at room temperature under magnetic field up to 10 kOe. The kinetics of silver ion release was monitored by PerkinElmer SCIEX ELAN DRCII Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.6. Silver ion release study

The 10 mL Fe_3O_4 @ECS/PAA-Ag nanoparticles (1 mg/mL) were added in a beaker containing 90 mL of PBS at 37 °C. At regular time intervals (4, 8, 12, 24, 36 and 48 h), 1 mL solution was taken and analyzed for the amount of Ag^+ by ICP-MS.

2.7. Antibacterial activity determination

Antibacterial testing was conducted against both *S. aureus* (ATCC 25923, Gram-positive) and Gram-negative *E. coli* (ATCC 25922). For the Inhibition Zone Test, a 0.1 mL of diluted bacterial suspension with 10^7 – 10^8 colony forming units per milliliter (CFU/mL) was taken to spread on the surface of the nutrient LB agar uniformly. Then three filter paper slices with the same size (1.5 cm) saturated with 40 μL of different nanoparticles (Fe_3O_4 , Fe_3O_4 @ECS/PAA, Fe_3O_4 @ECS/PAA-Ag) dispersions (10 mg/mL) were placed onto the Petri dish and incubated at 37 °C for 24 h. For the kinetic test, 10 mg of antibacterial NPs were placed in a sterile bottle with 10 mL of bacteria suspension (10^7 – 10^8 CFU/mL) in PBS. After contact time of

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