Research Article

Characterization of Ag@Fe$_3$O$_4$core-shell nanocomposites for biomedical applications

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ABSTRACT

The core-shell nanocomposites Ag@Fe$_3$O$_4$withamagnetitecoreanda silver shell were synthesized by modified chemical co-precipitation. The physical-chemical properties of synthesized nanoparticles have been characterized using UV-vis absorption spectroscopy, X-ray diffraction, scanning electron microscopy. X-ray analyses has confirmed the phase purity and homogeneity of the nanocomposites. The particles are almost monodisperse with the average size <d> ~ 23 nm. The silver nanoparticles are in a form of islands (20-100 atoms) on the surface of magnetite.

Keywords: Magnetite nanoparticles, Silver, Core-shell, Optical methods, Surface Plasmon Resonance
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INTRODUCTION

Magneticnanotechnology is one of the most important research and development frontiers in modern pharmaceutical science [1-5]. Magnetite nanoparticles (Fe$_3$O$_4$) are the most used magnetic material for biomedical applications [6-9]. This material has a high magnetization value to allow its manipulation with an external field, superparamagnetic behavior, stability and biocompatibility. Surface modification of the magnetite particles can be used to prevent aggregation, improve stability, exhibit many interesting properties that can be exploited in a variety of biomedical applications such as drug delivery, magnetic resonance imaging, magnetic hyperthermia, cell separation and many others [6, 8, 10, 11].

For systems such as core-shell is a very important issue for determining the structure of the surface. One of the modern methods used to study the surface is an optical spectrometry – surface plasmon resonance spectroscopy (SPR). SPR is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold or silver) surfaces or onto the surface of metalnanoparticles. It is the fundamental principle behind many color-based biosensor applications and different lab-on-a-chipsensors [12, 13]. Silver nanoparticles have unique properties for biomedical application and plasmonic properties of silver nanoparticles have been studied for their extraordinarily efficient at absorbing and scattering light [8, 12, 14].

Silver nanoparticles have unique properties for biomedical application and plasmonic properties of silver nanoparticles have been studied, and they are extraordinarily efficient at absorbing and scattering light [12, 13,15].Such properties make the silver nanoparticles ideal for numerous technologies, including biomedical, materials, optical, and antimicrobial applications.

Therefore, to get more information about silver nanoparticles and to improve their applications or develop new ones, careful study related to their stability, functionality, particle sizes and also their materials and physical behaviors are essential. This paperreportscharacterizationofAg@Fe$_3$O$_4$ core-shell nanoparticles with a magnetite core and a silver shell, which have special attention because of their magnetic and optical properties for biomedical applications.

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EXPERIMENTAL SECTION

Materials

The chemicals used, $FeSO_4 \times 7 H_2O$, $FeCl_3 \times 6H_2O$, $NH_3 \times H_2O$ were purchased from Beijing Chemical Company (Beijing, China). Silver nitrate $AgNO_3$ and D (+)-glucose anhydrous were purchased from Merck co., Ltd. of Germany. All reagents were of analytical grade used without further purification.

Synthesis of Ag@Fe₃O₄ nanoparticles

At first the magnetite nanoparticles have been prepared by using the method of chemical co-precipitation from the solution. 13.89 g (0.05 mol) of $FeSO_4 \times 7 H_2O$ and 26.90 g (0.1 mol) of $FeCl_3 \times 6H_2O$ were dissolve in 1 L of distilled water at heating (60-70°C).25% aqueous ammonia solution was added drop-wise with continuous stirring until complete precipitation of the black ferrite was achieved (pH 9–11).

To apply the silver coating, in 10 – 15 min add successively 0.1 % $AgNO_3$ solutions and 10% glucose solution. Keep the reaction mixture for 40 min with continuous stirring. The change of a black color of the precipitate to light brown indicates completion of the reaction. Keep the resulting solution in a constant magnetic field for 24 h, wash with distilled water to pH = 9 – 10, filter on a Buchner funnel and dry in the air of a room temperature.

Characterization

The specular reflectance measurements of the nanoparticles were measured using a UV-visible spectrophotometer (Lambda Bio 40, Perkin Elmer, USA). X-ray diffraction analysis (XRD) was used to study structure of nanocomposites. The XRD analysis was carried out on the DRON-4-07 diffractometer using filtered radiation of the cobalt anode lamp (λ = 17.9021 nm) with standard Bragg-Brentano focusing geometry. Scanning Electron Microscopy (SEM) model Mira III LMU, Tescan (Czech Republic) was used to determine the approximate particle size.ThespecificsurfaceareaofthepowderswasmeasuredbytheBrunauer–Emmett–Teller (BET) method and the pore size distribution of the powders by the adsorption-desorption isotherm utilizing nitrogen as the adsorbate, Sorptometer Kelvin-1042 (Coztech Instruments) by BET method using nitrogen gas as an adsorbate.

RESULTS AND DISCUSSION

The UV-Visible spectra of the samples measured in the range 100–1200 nm, using a double beam UV-Vis spectrophotometer. Figure1shows a strong broad reflection bands located between 250 and 710 nm for both samples with the minimum value~440 nm. This peak, assigned to a surface plasmon resonance typical of silver nanoparticles, is well-documented for various metal nanoparticles with sizes from 2 to 100 nm [12,13]. The magnetite nanoparticles band has the maximum ~720 nm (Fig. 1, curve 1), the band of sample of Ag@Fe₃O₄ has the maximum ~770 nm (Fig. 1, curve 2). Hyperchromic effect (an increase reflection intensity almost in two times)observed in the band of Ag@Fe₃O₄nanocomposites. Such effect in the case of continuous nanoshells is more significant [16]. It can be assumed, that the maximum shift caused by the influence of magnetite.
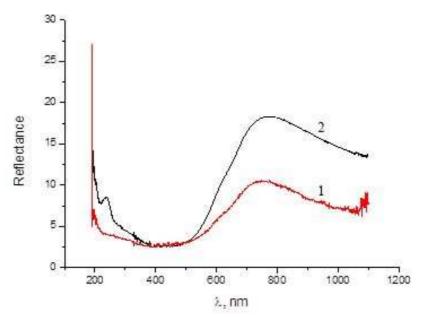

Fig. 1: Diffuse reflectance spectra of magnetite nanoparticles (1) and Ag@Fe₃O₄(2)

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Clusters of surface layer are sensitive to changes of the metal core, such as the oxidation state and the number of metal atoms in the cluster. The plasmon width increases with decreasing cluster size for typical cluster shape distributions [12, 13].The peak appears in the band of Ag@Fe_3O_4nanocomposites (Fig. 1, curve 2,) at ~265 nm, indicating the formation of sub-nanometer silver clusters(smaller than 1 nm). The peak at ~770 nm can be attributed to an increase in the thickness or/and surface area of silver clusters. The location of this resonant peak matches to a flat silver clusters [12].

The SEM micrograph of the as-synthesizedAg@Fe_3O_4 nanoparticles is given in Fig. 2 showing almost homogeneous and uniform (spherical).
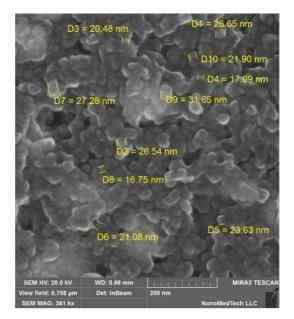

Fig. 2: SEM image of the sample Ag@Fe_3O_4

The particles are almost monodisperse with the average size <d> ~ 23 nm. The silver nanoparticles form of islands (20-100 atoms) on the surface of magnetite. Theoretical calculations have shown that the surface area of the silver-coated Fe_3O_4 less than 30-40%.
Surface-area values of the nanocomposites Ag@Fe_3O_4 and nanoparticles of magnetite were determined after the first stage of adsorption by the BET method (Table 1).

Table 1: Surface-area values of the samples

Sample	Mass (mg)	Specific surface area (m^2/g)
Fe_3O_4	217.8	110
Ag@Fe_3O_4	238.75	145

Among the samples it is apparent that there is a general increase in the measured surface area as the silver coat appears. This fact suggesting that the coverage of magnetite by silver is not complete. It can be assumed, that the silver atoms form "island-like" structures on the surface of magnetite. Such organization of surface layer will increase the contact area of the silver nanocomposite with bacteria or viruses, greatly improving its bactericidal effect. It is known that particles with a large specific surface area have a high chemical and biochemical activity [17].

The X-ray diffraction pattern of the as-synthesizedAg@Fe_3O_4 nanoparticles is presented in Fig. 3.

All the 2θ and indices corresponding to both the Fe_3O_4 and Ag pattern, which indicates that a thin coating of Fe_3O_4 by silver and some bare portion of magnetite particles remain. The silver coverage divided on the Ag islands. The same results were reported for the other system core-shell [18, 19]. In the case of complete coverage, the diffraction peaks from core are not observed in the XRD pattern [20].

As silver does not exhibit magnetic properties, and a continuous coating layer provides a low degree of magnetization of the samples [18, 19], creating Ag@Fe_3O_4nanocomposite with partially coated magnetite surface

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areas enables to preserve the magnetic properties of the sample and the silver–modifier, in its turn, imparts antimicrobial properties even with a minimal content.
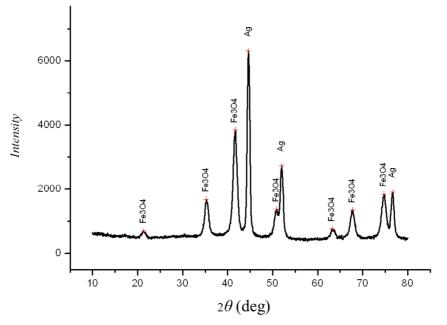

Fig. 3: X-ray diffraction pattern of the as-synthesizedAg@Fe₃O₄ nanoparticles

CONCLUSION

In summary, the modified chemical co-precipitation technique has been used to yield core-shell nanocomposites Ag@Fe$_3$O$_4$with a magnetite core and a silver shell. At first the magnetite nanoparticles have been prepared. Then silver shell was coated on the magnetite nanoparticles by using D (+)-glucose anhydrous as a reductant. Characterization of the particles by XRD, SEM, and SPR analyzed the particles and the coatings. SEM and XRD data reveal that the particles are almost monodispersed with the average size <d> ~ 23 nm. The silver nanoparticles form of islands (20-100 atoms) on the surface of magnetite. As-synthesized core-shell nanocomposites Ag@Fe$_3$O$_4$have good perspectives of applications, including chemical and biological sensing, due to the broad absorption in the optical region associated with localized surface plasmon resonance.

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