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ORIGINAL ARTICLE

Template free solvothermal synthesis of single crystal magnetic Fe_3O_4 hollow spheres, their interaction with bovine serum albumin and antibacterial activities

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Abstract Uniform sized single crystal magnetic Fe_3O_4 hollow spheres (MFHS) have been synthesized through simple solvothermal method using ferric chloride hexahydrate and 1,3-propanediamine. The reaction time and the amount of 1,3-propanediamine play major roles in the formation of magnetic Fe_3O_4 hollow spheres. The synthesized products are characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy and vibrating sample magnetometry techniques. The crystalline Fe_3O_4 materials are composed of well-aligned hollow sphere magnetite nanoparticles and exhibit high saturation magnetization of 57.9 emu/g and a remnant magnetization of 17.6 emu/g at room temperature. MFHS interact strongly with bovine serum albumin (BSA) and brings out considerable conformational changes in BSA as evident from the UV–vis absorption, fluorescence and circular dichroism (CD) spectroscopic studies pertaining to the interaction of synthesized MFHS and BSA. The prepared MFHS effectively inhibit the growth of *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

1. Introduction

Over the past two decades, it has been reported that among different types of nanoparticles, magnetic nanoparticles have been widely utilised in the field of biotechnology and biomedicine preparation due to their strong magnetic behaviour, biocompatibility, chemical stability and low toxicity [1]. Applications of magnetic nanoparticles in the medical fields include, the immobilization of proteins, peptides, and enzymes [2], bioseparation [3,4], gene delivery [5] and magnetic resonance imaging (MRI) [6]. Magnetic nanoparticles are being used for delivery of drugs to targeted tissues by the application of external magnetic field, which in turn increases the stability of drugs against enzymatic or metabolic degradation by using pathways other than gastrointestinal [7,8]. The drug loaded magnetic nanoparticles helps in the controlled release of drug

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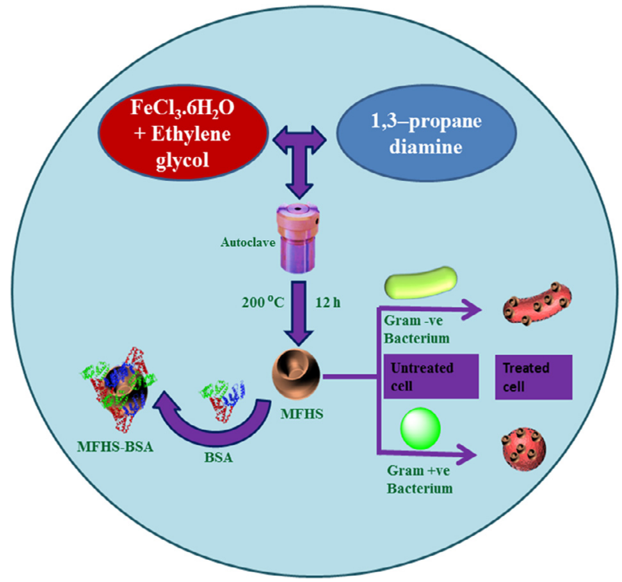
which reduce side effects due to their lower dosage. Magnetic iron oxide nanoparticles, mainly magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), have gained great attention owing to their biocompatibility and use in MRI contrast enhancement [9,10], tissue repair [11], immunoassay [12], detoxification of biological fluids [13], hyperthermia [14], targeted drug delivery [7,15] and cell separation [16]. Moreover, the magnetic iron oxide nanoparticles have intrinsic antibacterial and antifungal properties, thereby finding many applications [17,18]. Uniform-sized magnetite hollow spheres with a diameter of 200–300 nm exhibiting saturation magnetization of 68 emu/g have been reported [19]. Hierarchical hollow Fe_3O_4 microspheres reported to show high specific capacity for lithium storage [20]. Hollow sphere nanoparticles with high magnetic saturation and large surface area are being used as drug delivery carriers in biological fields.

Various nanostructured magnetite nanoparticles have been prepared by a variety of methods, like reverse-micelle transition, hydro- or solvothermal treatment, polyol-mediated processes, etc. [21–23]. Particularly, hollow sphere magnetic nanoparticles were prepared through conventional methods, utilising polymer latex spheres, emulsion droplets/micelles, etc. [23,24]. However, disadvantages related to high cost and tedious synthetic procedures limit the use of such templates and prevent them from being used in large-scale applications. Hence, a one-step template-free method for the controlled preparation of hollow structure nanoparticles will be preferred. Recently a number of one-pot template-free methods have been developed for generating hollow inorganic micro- and nanostructured particles using Kirkendall effect [25] and corrosion-based inside-out evacuation [26].

The nanoparticles change the protein structure and activity when they adsorbed on the surface of the protein and the extent of the change depends on both the nature of the protein as well as the surface properties of the nanoparticle [27]. Serum albumin is the most abundant protein; plays important roles in transport and distribution of reversibly bound endogenous and exogenous ligands including fatty acids, amino acids, steroids and a variety of drugs [28,29]. Therefore, it is necessary to understand the performance of magnetic nanomaterials on serum proteins. Bovine serum albumin (BSA), a heart-shaped globular protein, is generally employed as a model protein because of its low-cost and availability and it is structurally homologous with human serum albumin. In the present work, we focus on the preparation of hollow structured magnetic nanoparticles using simple reagents, namely, ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$) and 1,3-propanediamine. Herein, we report the synthesis and characterization of magnetic Fe_3O_4 hollow spheres (MFHS). The interaction of MFHS with BSA and the bactericidal effect of MFHS were investigated. The overall schematic representation is shown in Scheme 1.



Scheme 1 Synthesis, binding with BSA and bactericidal activity of MFHS.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$), 1,3-propanediamine, 1 M phosphate buffer solution (pH 7.4) and Bovine Serum Albumin (BSA) were purchased from Sigma–Aldrich. Ethylene glycol and propidium iodide were purchased from Merck and HiMedia respectively. The bacterial strains *Pseudomonas aeruginosa* (Gram-negative bacteria; Strain No. ATCC15442) and *Staphylococcus aureus* (Gram-positive bacteria; Strain No. MTCC1144) were collected from Bose lab, Madurai, India. Deionised water was used in all the experiments.

2.2. Synthesis of magnetic Fe_3O_4 hollow spheres (MFHS)

Magnetic Fe_3O_4 hollow spheres were synthesized through a template-free solvothermal method. In a typical experiment, 0.1 M $FeCl_3\cdot 6H_2O$ was prepared in ethylene glycol (EG) (30 mL) to form a clear solution. To this solution, 2.5 mL of 1,3-propanediamine (1,3-Pn) was added drop-wise with stirring. The mixture was stirred vigorously until it became homogeneous and then sealed in a Teflon-lined stainless steel autoclave. The autoclave was maintained at 200 °C for 12 h. After cooling the autoclave to room temperature, the black solid product was obtained by magnetic separation and washed with ethanol for several times and finally dried at 100 °C for 6 h.

2.3. Characterization methods

The XRD patterns were recorded using a PAN analytical X-Pert PRO X-ray diffractometer operated at a voltage of 40 kV and a current of 30 mA, with Cu Kα1 radiation. The morphological studies were carried out through field-emission scanning electron microscope (JEOL, JSM-6701F model) and transmission electron microscope (JEOL JEM 2100 model). UV–vis absorption spectra, in the wavelength range of 190–800 nm, were recorded in a Jasco spectrophotometer (V-630, Japan) by taking ~2 mL of test solutions in 1.0 cm quartz cells. The concentration of BSA was determined spectrophotometrically using an absorption coefficient (ε) of 43,800 M^{-1} cm^{-1} at 278 nm. A stock solution of BSA was prepared by dissolving it in 0.01 M Phosphate buffer solution (pH