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Simulation and experimental results of optical and thermal modeling of gold nanoshells

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ABSTRACT

This paper proposes a generalized method for optical and thermal modeling of synthesized magneto-optical nanoshells (MNSs) for biomedical applications. Superparamagnetic magnetite nanoparticles with diameter of 9.5 ± 1.4 nm are fabricated using co-precipitation method and subsequently covered by a thin layer of gold to obtain 15.8 ± 3.5 nm MNSs. In this paper, simulations and detailed analysis are carried out for different nanoshell geometry to achieve a maximum heat power. Structural, magnetic and optical properties of MNSs are assessed using vibrating sample magnetometer (VSM), X-ray diffraction (XRD), UV–VIS spectrophotometer, dynamic light scattering (DLS), and transmission electron microscope (TEM). Magnetic saturation of synthesized magnetite nanoparticles are reduced from 46.94 to 11.98 emu/g after coating with gold. The performance of the proposed optical–thermal modeling technique is verified by simulation and experimental results.

1. Introduction

The increasing availability of nanostructures with highly controlled magnetic and optical properties has created widespread interest in the use of nanoshells for diagnostic and therapeutic applications. This is due to the unique properties exhibited by the nanoscale particles, which is not seen at bulk scale. The absorption property of nanoshells can be provided at specific wavelength and their movement can be controlled by an external magnetic field. Therefore, magneto-optical nanoshells (MNSs) can be guided to a specific tissue target [1].

Superparamagnetic magnetite has attracted increasing interest because of its outstanding properties especially in biotechnology and biomedicine applications [2–4]. In recent years, much effort has been devoted to the synthesis and characterization of MNSs such as gold coated iron-oxide nanoparticles (NPs) [1,5–7].

Generally, a nanoshell is a type of spherical nanoparticle which consists of dielectric core covered by a thin metallic shell, e.g. gold or silver. These nanoshells involve a plasmon which is a collective excitation or quantum plasma oscillation when excited by an electromagnetic field. This resonant interaction between the light field and the oscillating surface charges gives rise to a state known as surface plasmon. By different shapes and sizes of nanoshell, i.e. in core-shell ratio one can expect to achieve a tunable nanosystem ranging from visible (VIS) to the near infrared (NIR), based on the Mie theory [8].

When nanoshells are exposed to the appropriate wavelengths of a laser beam, they absorb energy and then heat up. These nanoshells mediate strong plasmon-induced surface heat flux upon absorption of light [2]. Therefore, the main application of nanoshells is for cancer treatment, known as nanoshell-based hyperthermia [9]. During hyperthermia, temperatures above 42 °C induce cell death in tumor tissues in the range of 41 °C to 47 °C [10–12]. So, nanoshell-based hyperthermia is noninvasive, safe, and efficient. It is readily shown that gold nanoshells can be an attractive alternative for both diagnostic and therapeutic applications such as medical imaging and skin wound soldering [13–15].

Recent studies in modeling attempt to analyze the optical and/or thermal effects of nanostructures [16–18]. Nevertheless, comprehensive evaluation of both optical and thermal characteristics of nanoshells (multiple-layer NPs) have been scarce. This paper presents a generalized and comprehensive technique which includes the optimal and thermal modeling to consider effects of nanoshell geometry and absorption cross section, irradiation source electric field, and concentration of nanoshells. The proposed optical–thermal modeling technique of synthesized MNSs is implemented in the MATLAB environment and verified by experimental results.

2. Materials and methods

All of analytic reagents are purchased from the indicated suppliers and used without further purification: ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (99%), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) (99%), sodium hydroxide (NaOH, 99%), hydrochloric acid (HCl, 37%), and absolute ethanol are purchased from Merck. 3-Aminopropyltriethoxysilane (APTS), tetrakis (hydroxymethyl) phosphonium chloride (THPC), chloroauric acid (H $AuCl_4$), potassium carbonate (K_2CO_3), and formaldehyde (37%) are obtained from Sigma-Aldrich (St. Louis, MO). Milli-Q

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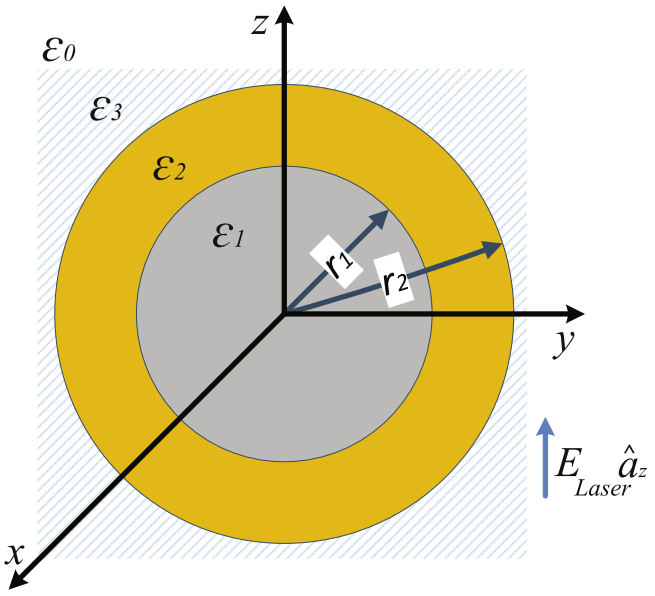

Fig. 1. Nanoshell geometry including the core, shell, and embedding regions.

water (specific conductance 0.1 μS/cm) is deoxygenated by bubbling N_2 gas for 1 h prior to the use. An Argon laser (514 nm) with power of 300 mW is used to illuminate the sample area.

2.1. Synthesis of superparamagnetic iron oxide nanoparticles (SPIONs)

SPIONs are fabricated following a previously reported procedure with some modification [19]. Briefly, $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ are added to 25 ml aqueous solution of 0.4 M HCl under vigorous stirring. Then the iron solution is added dropwise to 250 ml 1.5 M NaOH under magnetic stirring (1500 rpm) for 30 min at room temperature. The precipitated nanoparticles are separated by a magnet. The isolated precipitate is washed with water for 5 times and followed by washing twice using ethanol. The final precipitate is dried under vacuum at room temperature. All the synthesis steps are carried out under passing N_2 gas through the solution medium.

2.2. Functionalization of SPIONs

Amino groups are functionalized on the nanoparticle surface by silanization reaction. Magnetite nanoparticles (0.074 g) are dispersed in 25 ml ethanol by probe sonicator for 30 min. This suspension is diluted to 150 ml by ethanol and 1 ml H_2O. 35 μl APTES is added to the magnetic suspension under vigorous stirring [20]. One milliliter H_2O is introduced into the reaction medium to initiate the hydrolysis. The synthesis operation proceeds for 7 h at room temperature. After that, modified magnetite nanoparticles are isolated by magnet and washed for 5 times and dried under vacuum at room temperature.

2.3. Synthesis of SPION/gold nanoshells

SPION/gold nanoshells are fabricated by a multistep procedure through electroless plating of Au onto precursor nanoparticles (i.e. gold-seeded SPIONs) as reported previously by some modifications [15]. Briefly, a THPC gold solution composed of 2–3 nm gold colloids is produced according to Duff and Baker method [21] and aged for 2 weeks. Nanoshell precursor particles are synthesized by adding 1 ml of 0.0128 M amine-terminated magnetite nanoparticles in ethanol into 40 ml THPC gold solution and 4 ml 1 M NaCl and left at 4 °C. After 12 h the nanoparticles are washed and redispersed in 10 ml water. A plating solution is prepared by mixing 3 ml H $AuCl_4$ (1%) with 200 ml aqueous solution of K_2CO_3 (1.8 mM). A gold shell is grown around the SPIONs by adding 1 ml of precursor suspension to 9 ml of plating solution. 50 μl of H_2CO is quickly added into a 10 ml prepared suspension of precursor nanoparticles in plating solution in a glass vial and gently vortexed by hand for 10 s for reduction of Au^{3+}, and left for 15 min. UV–Vis absorption spectrum of the solution is recorded 20 min after reaction to verify the formation of gold nanoshell. The excess formaldehyde is removed by washing twice. The fabricated magnetite/gold nanoshells are collected by centrifuge at 6000 *g*.

2.4. Characterization methods

X-ray diffraction (XRD) measurements are performed at ambient temperature using a PHILIPS PW1800 X-ray diffractometer with Cu-Kα radiation. Transmission electron microscopy (TEM) is performed using a CM 200 FEG STEM Philips-M.E.R.C. operating at a voltage of 200 kV. Magnetization measurements are carried at 300 K in a magnetic field (H) of up to 20 kOe with a vibrating sample magnetometer (Meghnatis Daghigh Kavir Co. VSM/AGFM) that can measure magnetic moments as low as 10^{-3} emu. For the magnetization measurements, uncoated Fe_3O_4 NPs are in dry powder form obtained by evaporating the water from the solution. The samples are dried by freeze dryer (Pishtaz Engineering Co. Model: FD-4 or FD-10). Calculation of the absorption efficiency is performed using MieLab software. Each number presented in this paper is the average of at least three measurements and reported using SPSS 15.0.

3. Optical and thermal modeling

In order to investigate optical and thermal properties of nanoshells, the dynamic model of nanoshells in the embedding medium must be first derived. This model should consider both accuracy and simulation time to manifest the precise dynamic properties.

3.1. Nanoshell configuration

There are two distinct size regimes to be considered in the determination of the optical and thermal properties of metallic NPs and nanoshells [22]. In the extrinsic size regime, the optical properties can be fully described by specification of the nanoparticle radius and by the use of the bulk frequency dependent dielectric constant ($\varepsilon(\omega)$). Conversely, in the intrinsic regime ($2r < 50$ nm), dipole plasmon absorption is by far the dominant contributor to the extinction cross-section. Thus, size dependent effects must be accounted for by employment of a size dependent dielectric function as [23,24]:

$$\varepsilon(a,\omega) = \varepsilon_{\exp}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{bulk}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (1)$$

where $\varepsilon_{\exp}(\omega)$ is the experimental dielectric function and a is the shell thickness. ω_p and ω are the bulk plasma frequency and electromagnetic wave frequency, respectively. γ_{bulk} is the bulk collisional frequency which is expressed by:

$$\gamma_{bulk} = \frac{V_F}{l_0} \quad (2)$$

where V_F is the Fermi speed and l_0 is the gold electron mean free path at room temperature [25].

Dielectric function of the gold nanoshell becomes size-dependent when the nanoshell size is smaller than the gold electron mean-free