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Research Paper

Prolonged heating of Fe_3O_4–Au hybrid nanoparticles in a radiofrequency solenoid coil

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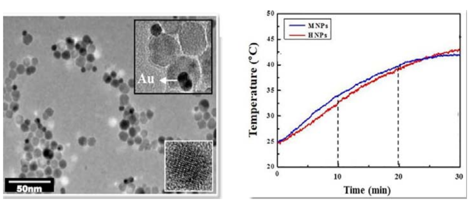
GRAPHICAL ABSTRACT



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ABSTRACT

We report the hyperthermia properties of Fe_3O_4–Au hybrid nanoparticles (HNPs) under a biocompatible alternating magnetic field (AMF) of 1.5 kA m^{-1} and 200 kHz. The HNPs were prepared by growing Au nanoparticles (AuNPs) with an average diameter of 3 nm on the surface of Fe_3O_4 magnetic nanoparticles (MNPs) with an average diameter of 10 nm. The structural properties were determined by transmission electron microscopy (TEM), dynamic light scattering (DLS), and X-ray diffraction (XRD). Under the AMF, the initial heating rate of the HNPs solution was lower than that of the MNPs solution because HNPs have a reduced saturation magnetization (*Ms*) value compared to MNPs. The continued AMF application increased the temperature of the HNPs solution steadily while the MNPs solution reached a thermal equilibrium. The heating effect of AuNPs conjugated to diamagnetic and non-conductive SiO_2 nanoparticles (SiO_2-AuNPs) was demonstrated under the same AMF condition, which suggests that the prolonged heating of HNPs can be attributed to the additional heating of AuNPs in the radiofrequency (RF) solenoid coil.

1. Introduction

Magnetic fluid hyperthermia (MFH) is a medical therapy based on the conversion of magnetic energy to thermal energy via magnetic nanoparticles (MNPs) under an external alternating magnetic field (AMF). Because the heat generation can be controlled remotely, MFH has advantages over traditional hyperthermia that requires physical operation or insertion of an electrode at the position of the targeted area. The region and the degree of therapy for the disease can also be selected with minimum influence on the neighboring normal cells since the local temperature can be controlled by the accumulation of MNPs into tumor cells, and the frequency and amplitude of the AMF. Both Fe_3O_4 (magnetite) and γ-Fe_2O_3 (maghemite) are the preferred materials for MFH because of their stability, biocompatibility, and suitable magnetization [1].

The heat generation of MFH is known to be originated from magnetic friction (Néel relaxation) and viscous friction (Brownian relaxation) [2–4]. Although the effective relaxation is a combination of both relaxation mechanisms, Néel relaxation is dominant for particles less than 10–20 nm while Brownian relaxation is dominant for larger particles [4,5]. The main parameters for magnetic hyperthermia are the size and magnetic property of MNPs, the frequency and amplitude of

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AMF, and the viscosity of the solution [2–4]. Magnetic heating efficiency is also dependent on the colloid concentration since the dipolar interaction between magnetic nanoparticles affects magnetic energy barrier or causes particle clustering [6,7].

Gold nanoparticles (AuNPs) have been investigated as a biocompatible material for clinical thermal therapy [8–11] and immunosorbent assay [12]. The strong optical absorbance of AuNPs from the visible to the near-infrared (NIR) and subsequent nonradiative energy dissipation result in an increase in temperature of the surrounding medium. Recently, radiofrequency (RF) electric field with deep penetration depth has been used for the study of AuNPs hyperthermia [13–15]. Hamad-Schifferli *et al.* reported that the induction heating of AuNPs with 1.4 nm diameter in solution was generated by a RF magnetic field with a frequency of 1 GHz and could be utilized for dehybridization of DNA [13]. The effective heating of AuNPs with diameters of less than 50 nm in water under capacitively coupled shortwave RF (13.56 MHz) electric field was reported by Moran *et al.* [14]. Chen *et al.* demonstrated the heating of AuNPs with diameters of 15–20 nm in the electromagnetic field of 64 kA m^{-1} and 200 kHz [15].

The conjugation of AuNPs to MNPs has provided an attractive approach to create nanoscale systems with diverse optical and magnetic characteristics [16–18] such as multimodal contrast probes for magnetic resonance imaging (MRI) [19], laser-induced photothermal ablation of cancers [20,21], and drug carriers [22]. The formation of core-shell Fe_3O_4-Au nanostructure is advantageous due to enhanced chemical stability against oxidation and corrosion, good biocompatibility, and easy functionalization [23]. Heterodimer-shaped Fe_3O_4-Au nanoparticles played a critical role in improving MRI contrast [24]. The dumbbell-like Au-iron oxide particles were utilized to modify the nonlinear optical transient absorption of the surface plasmons [25]. Recently, Mohammad et al. reported that the increased *Ms* of core-shell type Fe_3O_4-Au contributed to the overall enhancement in the heat release behavior [26]. The novel optical, magnetic, and catalytic properties of nanoscale materials rely largely on the creation of the hetero-type nanostructures [27–31].

Here, we report the prolonged hyperthermia of Fe_3O_4–Au hybrid nanoparticles (HNPs) where AuNPs with an average diameter of 3 nm were formed on the surface of Fe_3O_4 MNPs. The physical properties of the synthesized HNPs were characterized and the heat generation by the HNPs under biocompatible AMFs was monitored. The temperature increase profile of HNPs was clearly distinguished from that of MNPs, which is attributed to the additional heating of the AuNPs in the RF solenoid coil.

2. Material and methods

2.1. Synthesis and characterization

The MNPs and HNPs were synthesized according to previously reported procedures [32,33]. Briefly, iron pentacarbonyl (0.4 mL) was added to a mixture of octyl ether (20 mL) and oleic acid (1.92 mL) at 100 °C under an Ar atmosphere. The mixture was stirred at reflux for 1.5 h and cooled to room temperature. Oxygen gas was flowed through the reaction mixture for 0.5 h at 80 °C. The solution was treated with excess ethanol, centrifuged, and magnetically separated. To a mixture solution of MNPs (0.1 mg) and oleylamine (2 mmol) in chloroform (10 mL), a mixture of $HAuCl_4{\cdot}3H_2O$ (1.3 mmol) and oleylamine (0.5 mmol) in chloroform (5 mL) was added twice at intervals of 5 min with vigorous stirring. After 24 h, the dark purple precipitates were magnetically separated from the reaction solution after centrifugation and re-suspended in hexane.

The AuNPs were conjugated on diamagnetic and non-conductive SiO_2 nanoparticles (SiO_2-AuNPs) to investigate the heating effect under AMF. SiO_2 nanoparticles were treated with 3-aminopropyltriethoxysilane (APTES). The amine-modified SiO_2 nanoparticles were reacted with commercially available AuNPs with an average diameter of 3 nm for 3 h [34]. The resulting light purple SiO_2-AuNPs were dispersed in water.

Transmission electron microscopy (TEM, JEM-2100F) was used to investigate the morphology and the crystal structure of MNPs and HNPs. The size and size distribution of the hydrodynamic diameter were measured using a dynamic light scattering (DLS, Malvern Zetasizer Nano ZS). Energy dispersive spectroscopy (EDS) was taken to assess the wt% of Au in HNPs. The intrinsic magnetic properties of MNPs and HNPs were measured by generating a magnetic hysteresis loop using a vibrating sample magnetometer (VSM, Lakeshore 7300) in the magnetic field strength range of ± 10 kOe. The X-ray diffraction (XRD, Rigaku D/Max 2200PC) analysis was performed using copper Kα rays with a scan speed of 5 deg min^{-1}.

2.2. Hyperthermia measurements

A homemade hyperthermia system was constructed to monitor the temperature variation over time ($\Delta T/\Delta t$) of nanoparticle solutions under an AMF. Fig. 1(a) and (b) show the design and the assembled hyperthermia system used in this work, respectively. The system was composed of a power generator (AG1006, max. 14 kHz), a fluoroptic thermosensor (Luxtron Model 502), a circulation cooling system, a laminated Si-steel core with 20 turns of 3Φ copper coil, and a data recording system. The specimen area was surrounded by a polycarbonate frame (body and cap) to prevent any possible direct heat exchange by conduction and diffusion through the inductive coils. The water-cooling system was employed to remove the generated heat from the coil. A Si-steel alloy core was used to concentrate the induced magnetic flux and laminate-type plates were adopted for more efficient electrical insulation. This type of core structure can reduce the demagnetization factor by tailoring electric current flow on the surface of the core. A capacitor was added to the circuit to maximize the amplifier capability by tuning the resonance with the coil impedance (~ 4 Ω at 200 kHz).

The solutions of MNPs and HNPs in hexane (1 mg mL^{-1}, 10 mL) were placed at the center of the solenoid. The position of the sample

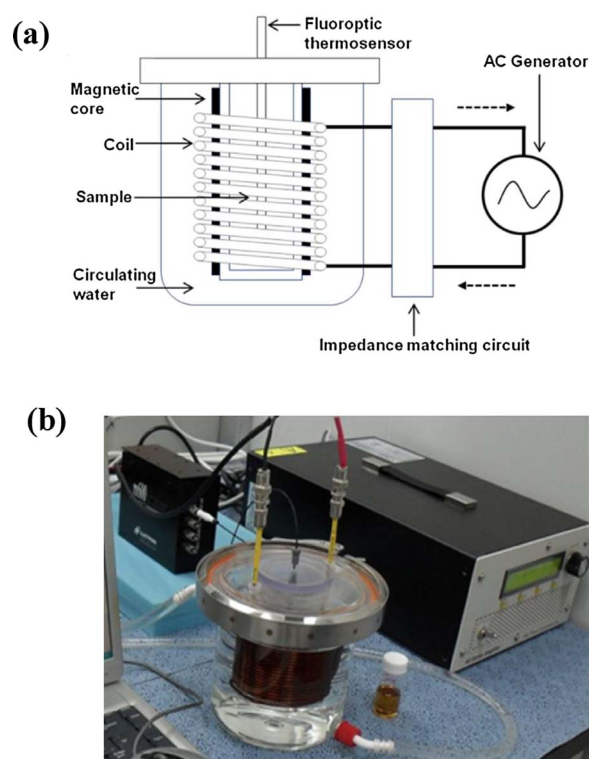

Fig. 1. (a) The design and (b) assembled heating system used in the hyperthermia experiment.