Selective Heating of Multiple Nanoparticles

Andy Wijaya[1], Katherine A. Brown[2], Joshua D. Alper[3], and Kimberly Hamad-Schifferli[2,3]
[1]Chemical Engineering; [3]Biological Engineering Division, and [3]Mechanical Engineering;
Massachusetts Institute of Technology, Cambridge, MA 02139 U.S.A.

ABSTRACT

A method for heating multiple types of magnetic nanoparticles independently is described. This technique exploits tuning of the size and material dependent properties of magnetic field heating of nanoparticles to allow independent heating by application of the field at different frequencies. Magnetic field heating experiments as a function of field frequency show that there is potential for this technique in vitro.

INTRODUCTION

Magnetic nanoparticles have been utilized for numerous biological applications, such as sensing, [1, 2], separation[3], drug delivery[4]. In particular, magnetic nanoparticles have found clinical application in hyperthermia for cancer treatment[5]. In this process, magnetic nanoparticles are injected near the site of a tumor or targeted via antibodies. Application of external magnetic fields heat the nanoparticles, raising the temperature of the tumor, burning it. Typically this has been achieved by using one type of nanoparticle, usually iron oxide. We explore here the possibility of using different types of nanoparticles that can differ in size or material, which can be heated independently at different magnetic field frequencies. This would enable greater flexibility in magnetic field heating applications.

EXPERIMENTAL DETAILS

Iron oxide nanoparticles were synthesized by literature methods [6, 7] or purchased (FerroTec, USA). Fe doped Au nanoparticles were synthesized according to a modification of literature Au nanoparticle synthesis [8] and functionalized with the ligand bis (p-sulphonatophenyl) phenylphosphine dihydrate, dipotassium salt (BPS). Nanoparticles were concentrated to high concentrations in water by salt precipitation in combination with lyophilization. Fe doped Au nanoparticles were at a final concentration of 3.7μM. Fe_3O_4 nanoparticles were at 3.9% volume fraction as received.

Approximately 100 μL of the nanoparticle solutions were placed in a coil of 25 turns. Alternating magnetic fields were generated by supplying a current from a signal generator and amplified by a 100W amplifier. The temperature of the solution was measured by a thermocouple placed in the solution. Custom built software was used to control data acquisition.

DISCUSSION

Magnetic field heating of superparamagnetic nanoparticles is described by the power loss equation[9, 10]

$$P = \frac{\left(mH\omega\tau_{eff}\right)^2}{2\tau_{eff} k_B T V\left(1+\omega^2\tau_{eff}^2\right)} \qquad (1)$$

where m is the magnetic moment per particle, ω the field frequency, V the nanoparticle volume, and teff the effective relaxation time. τ_{eff} depends on both Néel (τ_N)and Brownian (τ_B) relaxation losses by

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B} \tag{2}$$

where the timescale of Brownian relaxation losses is

$$\tau_B = \frac{8\pi\eta R_H^3}{k_B T} \tag{3}$$

and η is the sample viscosity and R_H the particle hydrodynamic radius. Néel relaxation losses are described by

$$\tau_N = \tau_0 \exp\frac{KV}{k_B T} \tag{4}$$

where τ_0 is the gyromagnetic ratio, K the anisotropy constant, and V the nanoparticle volume. The power loss equation shows that magnetic field heating is a function of the material, nanoparticle size, and the field characteristics. We illustrate that tuning of all of these parameters is necessary to find conditions under which multiple types of nanoparticles can be heated independently.

In order to investigate this possibility, the dependence of the power loss equation on these parameters is explored. The material dependence of power losses is reflected by the parameter m and K in equation (1) and (4) respectively. For the spinel ferrite MFe_2O_4 (M = Fe, Co, Mn) nanoparticles [7], the magnetic moment per particle, m strongly depends on the type of transition metal ion, M^{2+} occupying the tetrahedral and octahedral positions. The anisotropy constant, K highly depends on the type of crystal structure and the degree of crystallinity of the nanoparticles. Both m and K also have a strong dependence on nanoparticle size. Therefore the material and size dependence of the power losses are intertwined. Figure 1 shows a plot of equation (1) as a function of nanoparticle size for a given field of 0.01 T and frequency of 3 MHz for $CoFe_2O_4$, Fe_3O_4, and γ-Fe_2O_3, and $MnFe_2O_4$. The heating shows a strong size dependence for each of the materials, which has been observed experimentally[11].

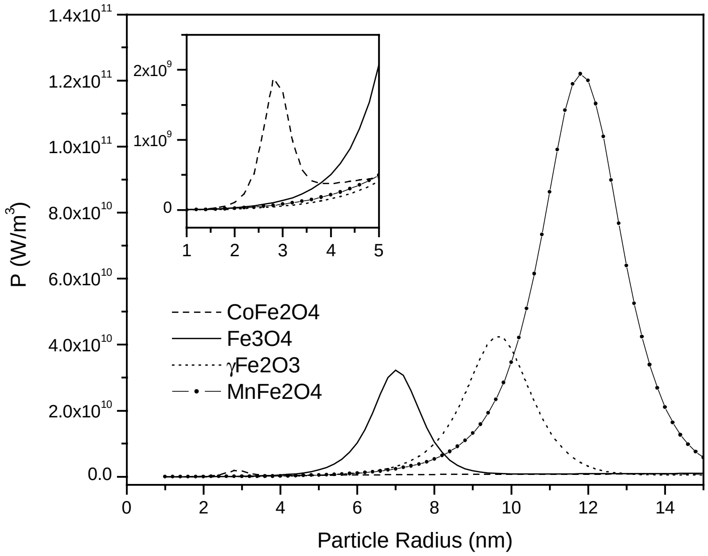

Figure 1. Power loss equation as a function of nanoparticle size for a field of 0.01 T and frequency of 3 MHz for $CoFe_2O_4$ (dashed line), Fe_3O_4, (solid line) and γ-Fe_2O_3 (dotted line) and $MnFe_2O_4$ (points and line).

The frequency dependence of the magnetic field heating based on the power loss equation is plotted in Figure 2 for 14nm $CoFe_2O_4$ (dashed line), 15nm Fe_3O_4 (solid line), 15nm γ-Fe_2O_3 (dotted line), and 12nm $MnFe_2O_4$ (points and line) with an applied field of 0.01T. The power dissipated by the nanoparticles increases with frequency and then plateaus at higher frequencies. This general shape has been observed experimentally in the literature [9, 12].

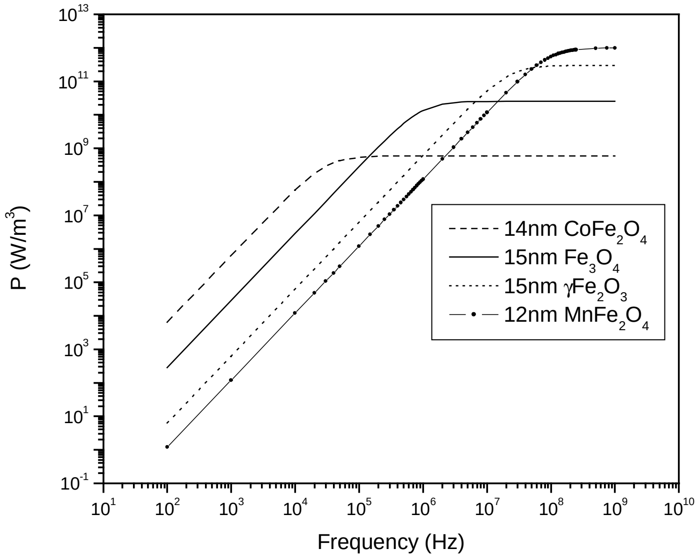

Figure 2. Power loss equation as a function of frequency at 0.01T for 14nm $CoFe_2O_4$ (dashed line), 15nm Fe_3O_4 (solid line), 15nm γ-Fe_2O_3 (dotted line), and 12nm $MnFe_2O_4$ (points and line).

Independent heating of these four types of nanoparticles is possible if field strength H is also tuned. Figure 3 shows the power loss equation where four different field strengths are applied at different frequency ranges. 14nm $CoFe_2O_4$ (dashed line) can be heated preferentially over the 15nm Fe_3O_4 (solid line), 15nm γ-Fe_2O_3 (dotted line), and 12nm $MnFe_2O_4$ (points and line) at any frequency below 20kHz and at any field strength. 15nm Fe_3O_4 can be heated over others if one applies field strengths of 1mT at a frequency of 1MHz. 15nm γ-Fe_2O_3 can be heated if one applies field strengths of 0.35mT at a frequency of 20MHz. Finally, 12nm $MnFe_2O_4$ can be heated preferentially at frequencies above 100MHz if the field strength is 0.13mT. This shows that according to the power loss equation, tuning the parameters of nanoparticle size, material, field strength and field frequency, one can preferentially heat one type of nanoparticle over others.

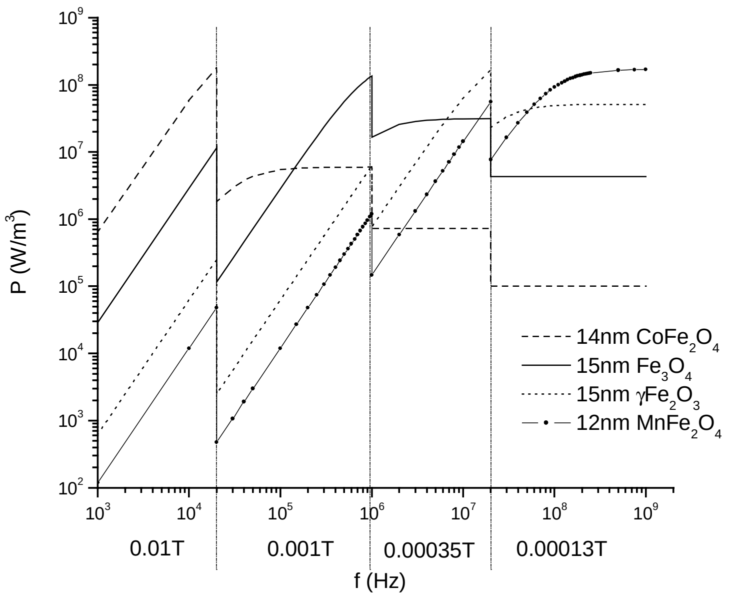

Figure 3. Power loss equation as a function of field frequency and field strength for 14nm $CoFe_2O_4$ (dashed line), 15nm Fe_3O_4 (solid line), 15nm γ-Fe_2O_3 (dotted line), and 12nm $MnFe_2O_4$ (points and line).

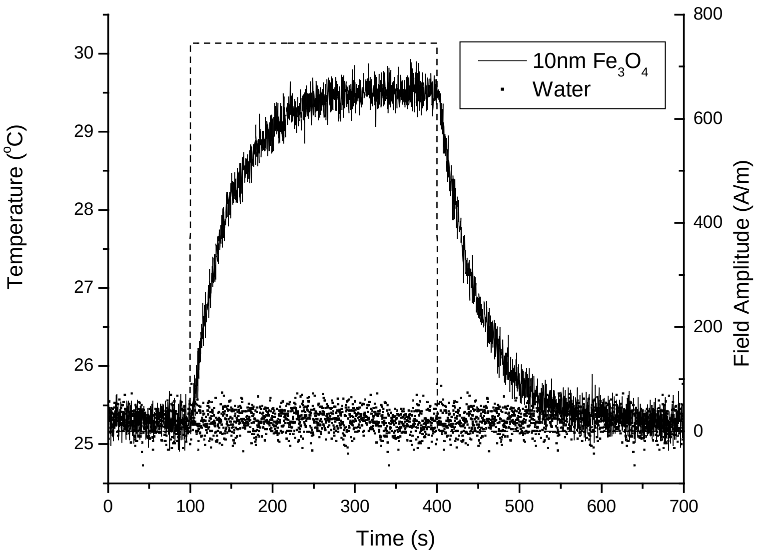

Figure 4. Experimental temperature curves for 10nm Fe_3O_4. Magnetic field of 1MHz (dashed line, right axis), temperature of an aqueous solution of nanoparticles (thick black line, left axis) and control solution of water (points, left axis).

We have begun to test this hypothesis experimentally. Heating profiles of two different types of nanoparticles, 8 nm Fe doped Au nanoparticles (Fe % = 1.8 atomic%) and 10nm Fe_3O_4 nanoparticles were initially measured. Fields were applied as a function of time for a continuous block of time (Figure 4, dashed line) while the temperature of the entire nanoparticle solution was measured. An example of 10nm Fe_3O_4 is shown (solid black line). The temperature of the solution increases from room temperature (T=25°C) to 29.5°C with the application of the magnetic field of approximately 750 A/m at a frequency of 1 MHz. A control solution of water (points) shows no appreciable temperature rise with the field application (dotted line).

The data is extracted from the experimental curves as the specific absorption rate, or SAR, which is the rate of temperature rise:

$$SAR = c\frac{dT}{dt} \qquad (5)$$

c dT/dt is the initial slope of the time-temperature curves multiplied by the heat capacity of the sample, *c*. The heat capacity of the iron oxide nanoparticles utilizes literature values. For the Fe doped Au nanoparticles, *c* is approximated as a weighted average of bulk Au and water (approximately 4.07 J/g·K). The power is then normalized to the field strength H^2, as SAR is proportional to H^2[10]. The normalized power per nanoparticle is plotted as a function of field frequency (Figure 5). For lower frequencies (0-6MHz), the Fe_3O_4 nanoparticles heat more than the Fe doped Au. However, at higher frequencies (10-100MHz), the Fe doped Au nanoparticles heat more than the Fe_3O_4. This indicates that independent heating of multiple types of nanoparticles is possible.

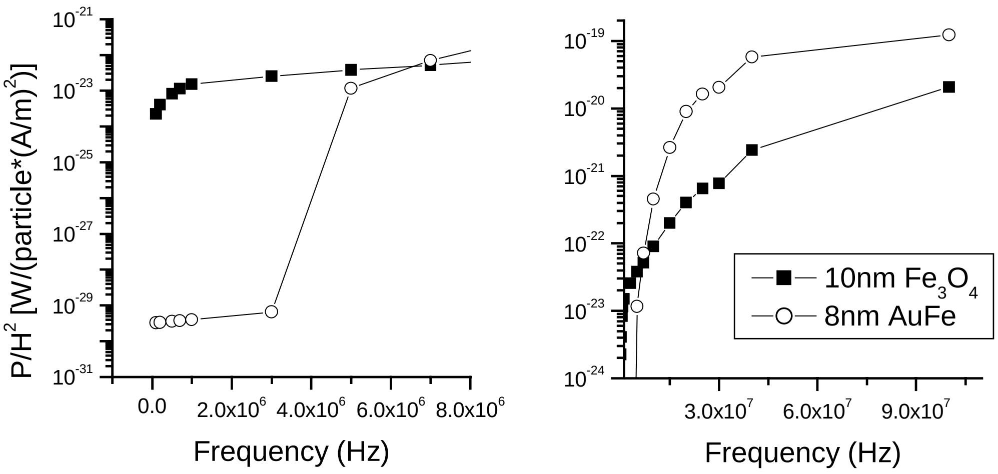

Figure 5. Experimental power per particle normalized by the field strength as a function of frequency. 8nm Fe doped Au nanoparticles (open circles) and 10nm Fe_3O_4 (filled squares).

CONCLUSIONS

In summary, we study the size and material dependence of magnetic field heating of nanoparticles. Independent heating of multiple types of nanoparticles is possible by exploiting the size and material dependence of the power loss equation. Preliminary results from experiments on two different types of nanoparticles show that independent heating has feasible experimental potential.

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