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Morphology and Magnetic Properties of Fe_3O_4 and $Au@Fe_3O_4$ Nanoparticles Synthesized by Pulsed Plasma in Liquid

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***Abstract*—**Spherical shaped magnetite (Fe_3O_4) and $Au@Fe_3O_4$ nanoparticles were successfully synthesized from Fe electrodes immersed in water with CTAB surfactant and $HAuCl_4$ solution using simple method-pulsed plasma in liquid, without the use of dopants or special conditions for stabilization. Vibrating sample magnetometer indicated ferromagnetic behavior of particles at room temperature with coercivity and saturation magnetization of (Hc=105 Oe, Ms=6.83 emu/g) for Fe_3O_4 and (Hc=175, Ms=3.56emu/g) for $Au@Fe_3O_4$ nanoparticles. Structure and morphology of nanoparticles were characterized by X-ray Diffraction analysis and HR-TEM measurements. The cytotoxicity of nanoparticles was indicated using a XTT assay to be very low (cell viability: 98-89% with Fe_3O_4 and 99-91% for $Au@Fe_3O_4$ NPs).

***Keywords*—**Magnetite, Gold coated magnetite, Nanoparticles, Pulsed Plasma in Liquid, Cytotoxicity.

I. Introduction

RESENT studies suggest that magnetic nanoparticles can bind to bacteria [1], protein [2], and enzyme [3] and could be directed to an organ, tissue, or cancer tumor by using an external magnetic field [4]. There are several types of iron oxide nanoparticles, namely maghemite, magnetite and haematite, among which magnetite is very promising because of its proven biocompatibility [5]. Encapsulation at nanometric level of iron oxide particles with noble metals, like gold or silver, allow for biocompatibility because of the good tolerance of the human body to these noble metals [6]. Also, iron oxide alone in physiological media is unstable, resulting in oxidation, aggregation and precipitation. A coating layer is needed to improve their biocompatibility, functionality and stability [7]. By using both iron oxide and gold as a single drug delivery vehicle, a multifaceted system can be developed which exploits the surface chemistry of the gold whilst retaining the magnetic character of the iron oxide, allowing for biologically sound drug delivery and imaging.

Here we report the synthesis of magnetite (Fe_3O_4) and $Au@Fe_3O_4$ nanoparticles using pulsed plasma in liquid method and their physicochemical properties. Pulsed plasma in liquid (PPL) combines physical (spark discharge) and chemical (surrounding liquid) processes, which provide us a number of advantages (simple, one-step, low-energy and versatile) for the synthesis of various kinds of nanomaterials [8]. The main challenge in this method is obtaining well-defined chemical compositions in the bulk and at the surface of the nanoparticles.

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II. Experimental

A. Sample Preparation

The PPL experimental set-up (Fig.1) consists of two parts: a low voltage alternating current (AC) electric power supply and a glove box comprising electrodes submerged in liquid. For the experiments, rod shaped Fe electrodes with purity of 99.9% (Rare Metallic Co., Ltd) were immersed in a 200ml Pyrex beaker filled with a liquid. The liquid was water mixed with 1.0mM of 1n-Hexdecylpyridinium Bromide monohydrate «CTAB» ($C_{21}H_{40}BrNO$) (Cica-Reagent) for the Fe_3O_4 samples preparation; and water with $HAuCl_4$ (Cica-Reagent) for the preparation of $Au@Fe_3O_4$ samples. The gap between electrodes was about 1mm; duration of a single discharge was about 10μs and peak current about 100A. The AC electric power (200V, 6A) was applied for 1h in each experiment, and then reactor was cooled to room temperature. Samples were separated from the liquid with aid of centrifuge IEC61010-2-020, KUBOTA with 40×10^2rpm speed for 20min, and then dried. The resulting Fe_3O_4 powder was dark in color; the $Au@Fe_3O_4$ nanopowder was also dark but sparkled due to the presence of gold.

B. Sample Characterization

Obtained samples were characterized by classical techniques: X-ray diffraction (XRD: Rigaku RINT-2500HV, Cu-Kα, λ=1.5406Å) operated at 40kV and 200mA for structural analysis, vibrating sample magnetometer (VSM: Riken Denshi Co., Ltd) for studying magnetic properties. Morphology and dispersity of nanomaterials were analyzed using high resolution transmission electron microscopy (HR-TEM: Philips Tecnai F20 S-Twin, at 200keV). Cytotoxicity of Fe_3O_4 and $Au@Fe_3O_4$ nanoparticles was evaluated using a mammalian endothelial cell line, HeLa cells.

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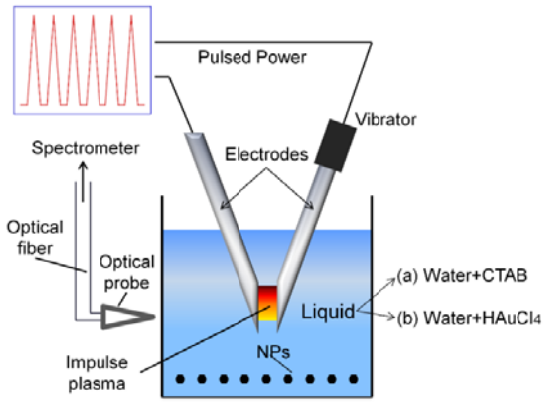


Fig. 1 Experimental set-up of pulsed plasma in liquid (PPL)

III. Results and Discussion

Phase composition and crystal structure of samples were examined by XRD, and effective tool to determine the phase, crystallinity and purity of samples prepared under various conditions. Fig. 2 shows XRD pattern of (a) Fe_3O_4 sample and (b) Au@Fe_3O_4 samples synthesized by pulsed plasma in liquid. In Fig.2a intensive characteristic reflections can be indexed as the face centered cubic structured Fe_3O_4 with Fd-3m space group which is in accordance with the JCPDS card no 19-0629. No obvious impurity can be detected in pattern indicating the pure phase of samples. The diffraction peaks (Fig. 2b) at 38.2˚, 44.4˚, 64.5˚, and 77.6˚ are attributed to gold, which can be indexed to 111, 200, 220 and 311 lattice planes of gold in a cubic phase (JCPDS card no 65-2870) and reflections at 35.42˚, 43.05˚, 53.49˚, 57.03˚, 62.74˚ and 74.24˚ corresponded to magnetite, indicating the presence of both Fe_3O_4 and gold in the sample.

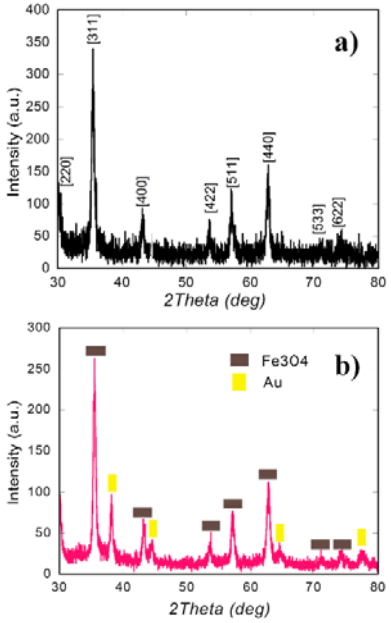


Fig. 2 XRD patterns of Fe_3O_4 (a) and Au@Fe_3O_4 (b) nanoparticles synthesized by pulsed plasma in liquid

Fig. 3 represents a surface view of Fe_3O_4 nanoparticles measured by HR-TEM. As shown in image, nanoparticles have an average diameter of ≈18 nm and majority of particles are nearly spherical in shape.

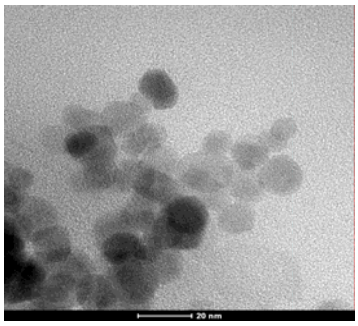


Fig. 3 Surface view of Fe_3O_4 nanoparticles synthesized by pulsed plasma in liquid, taken by HR-TEM

Fig. 4 shows HR-TEM micrograph (a) of Au@Fe_3O_4 nanoparticles with the line profile (b and c) of the image contrast. The Au nanoparticles appear black and Fe_3O_4 are light colored in the image, because Au has a higher electron density and allows fewer electrons to transmit. The interplanar d-spacings of the Au@Fe_3O_4 nanoparticles were calculated to be 3.48nm (d=2.9670Å) for Fe_3O_4 part and 2.34nm (d=2.3548Å) for Au part, in a good agreement with the (220) and (111) planes of face centered cubic structured Fe_3O_4 and Au (Fm-3m: 225), respectively.

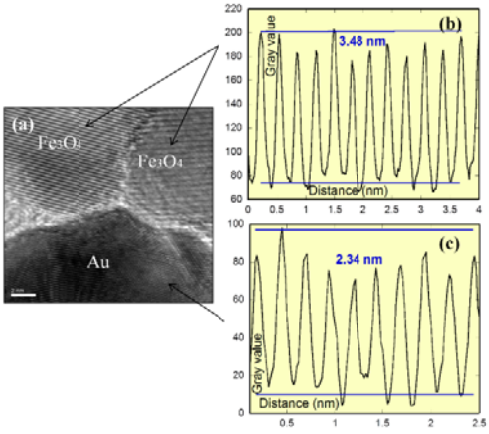


Fig. 4 HR-TEM results (a) high magnification view of Au@Fe_3O_4 nanoparticles (b) line profile image contrast for Fe_3O_4 and (c) for Au

HR-TEM was equipped with an Energy dispersive spectrum (EDS) detector for elemental analysis. Fig. 5 displays the elemental compositions of samples: a) Fe_3O_4 and b) Au@Fe_3O_4 nanoparticles. The composition of the magnetic phase (Fe_3O_4) is 43% of Fe and 57% of oxygen; copper and carbon peaks are due to the sample holder, made of cupper mesh coated with carbon. Thus, this confirms that, absent the presence C and Cu peaks due to the TEM micro-grid, the nanoparticles were composed solely of Fe and O. The presence of Au@Fe_3O_4 particles in the sample b) was confirmed indicating that besides C and Cu peaks only Fe, O and Au (b) were detected.

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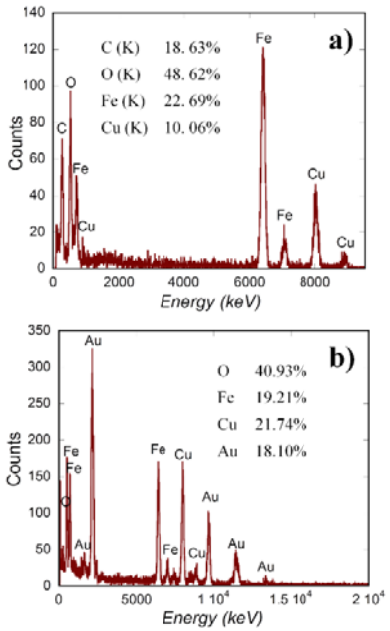


Fig. 5 EDS pattern of magnetite (a) and Au@Fe_3O_4 (b) nanoparticles

Magnetic properties of NPs are strongly influenced by many parameters, including crystallinity, size, shape and crystal defects. Fig. 6 represents ferromagnetic behavior of magnetite (green line) and Au@Fe_3O_4 (red line) NPs with low saturation magnetization measured by VSM at room temperature. Surprisingly, magnetic properties of magnetite remained in Au@Fe3O4 nanoparticles, even though Au is non magnetic material. As a matter of function, in many cases the protecting shells not only act to stabilize the magnetic iron oxide NPs, but also may be used for further functualization, in other words, gold can both provide stability for the magnetic NPs in solution as well as provide a good inert surface to assist in the binding of various biomolecules. Saturation magnetization (M_s) at room temperature decreases sharply with decreasing crystalline size D, which was first pointed out by Berkowitz and co-workers in the late sixties [9].

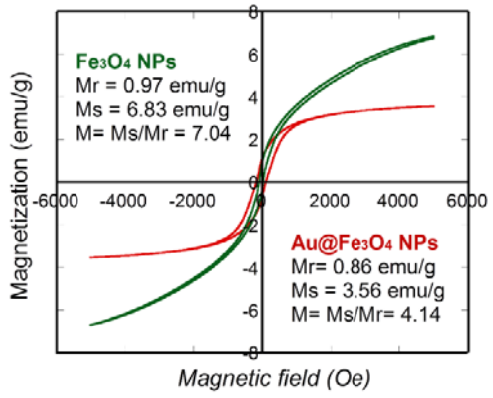


Fig. 6 Hysteresis loop of magnetization (M, emu g^{-1}) versus magnetic field (H, Oe) for magnetite (Fe_3O_4) and Au@Fe_3O_4 nanoparticles

Magnetic nanoparticles have been of significant use for many different technological areas, especially in biomedical applications [10]. However, for use in biological system they should have among other properties biocompatibility with cells and tissues. Cytotoxicity of Fe_3O_4 and Au@Fe_3O_4 nanoparticles synthesized by PPL was evaluated by using a mammalian endothelial cell line, HeLa cells. HeLa cells are commonly used for testing the toxicity and trafficking of nanoparticles [11]. The Fig. 7 shows representative results obtained from the measurements. HeLa cells were exposed to magnetite (Fe_3O_4) and Au@Fe_3O_4 NPs for 24 h. Suspensions of nanoparticles with concentration of 25, 50, 100 and 200 μg ml^{-1} (Table I) were prepared by serial dilution. Cytotoxic effects were determined using a sodium 3'-] 1-(phenylaminocarbonyl)-3, 4-tetrazolium] bis (4-methoxy-6-nitro) benzenesulfonic acid hydrate (XTT; molecular fornula: $C_{22}H_{16}NaO_{13}S_2$) assay kit. The organics used in the XTT assay are more stable and give more accurate results. The cell viability (%) was calculated according to the following equation:

$$\text{Cell viability (\%)} = \text{OD (sample)}/\text{ OD (control)} \times 100$$

where OD (sample) represents the optical density of the wells treated with Fe_3O_4 and Au@Fe_3O_4 samples of various concentrations, OD (control) represents that of the wells treated with Dulbecco's modified eagle medium (D-MEM). The cytotoxicity assay results indicate that magnetite and Au@Fe_3O_4 nanoparticles have a negligible effect on cells; indeed, cell viability was slightly higher with Au@Fe_3O_4 nanoparticles than with Fe_3O_4 nanoparticles. This demonstrates their potential for nanomedicine and biotechnological applications.

TABLE I
CYTOTOXICITY OF MAGNETITE AND AU@FE_3O_4 NPS

Concentration (μg mL^{-1})	Cell viability (%)	
	Fe_3O_4	Au@Fe_3O_4
25	98	99
50	95	99
100	95	98
200	89	91

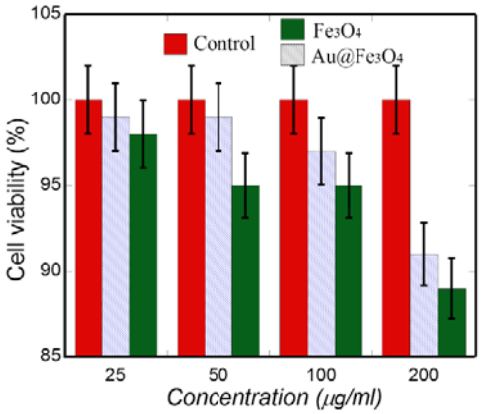


Fig. 7 Cytotoxicity of Fe_3O_4 (green) and Au@Fe_3O_4 (gray) nanoparticles prepared by pulsed plasma in liquid

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IV. Conclusion

Based on this study the following conclusions can be drawn:

1. Magnetite (Fe_3O_4) and Au@Fe_3O_4 NPs were synthesized by a simple, inexpensive method- pulsed plasma in liquid.
2. X-ray diffraction analysis indicated cubic structure of Fe_3O_4 with a=8.296Å (Fd-3m) for the sample (a); and a combination of cubic Fe_3O_4 with Au phase (Fm-3m; a=4.079Å) for the sample (b).
3. Nanoparticles of Fe_3O_4 have a spherical shape with average size of 19nm, and Au@Fe_3O_4 nanoparticles combine spherical shaped Au and Fe_3O_4 particles which proven by interplanar d-spacings calculated from HR-TEM image results.
4. VS-Magnetometer revealed weak ferromagnetic behavior of nanoparticles at room temperature.
5. Cytotoxicity assay results indicate that nanoparticles of Fe_3O_4 and Au@Fe_3O_4 synthesized by pulsed plasma in liquid have no effect on the cells, demonstrating their potentiality for biotechnological (-medical) applications.

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