Electronic Supplementary Information
for
Multi-responsive Hybrid Particles: Thermo-, pH-, Photo-, and Magneto-responsive Magnetic Hydrogel Cores with Gold Nanorod Optical Triggers

Supparesk Rittikulsittichai,[1] Arati G. Kolhatkar,[1] Subhasis Sarangi,[2] Maria A. Vorontsova,[3] Peter G. Vekilov,[3] Audrius Brazdeikis,[2] and T. Randall Lee[*, 1]

[1]Department of Chemistry and the Texas Center for Superconductivity, [2]Department of Physics and the Texas Center for Superconductivity, [3]Department of Chemical and Biomolecular Engineering, University of Houston, 4800 Calhoun Road, Houston, TX 77204-5003

Synthesis of Multi-Responsive MNPs. The targeted hybrid magnetic nanoparticles (MNPs) were prepared by synthesizing hydrogel-encapsulated-silica-coated Fe_3O_4 MNPs and Au_{rods} separately, and then assembling the Au_{rods} on the outermost hydrogel surface.

Synthesis of Fe_3O_4 MNPs. A round-bottomed flask was charged with $FeCl_3 \cdot 6H_2O$ (2.0 g), which was then dissolved in 15 mL of ethylene glycol, followed by the addition of sodium acetate (5.4 g). The addition of the latter led to a rapid change in the color of the solution from orange to brown. The solution was stirred for an additional 30 min and then injected at once into a round-bottomed flask containing a vigorously stirred solution of polyvinylpyrrolidone (0.60 g) in 60 mL of ethylene glycol at 180 °C. The mixture was then vigorously stirred for 8 h. After cooling the solution to rt, the resulting black precipitate was collected using a bar magnet. The particles were purified by repeated cycles of washing and redispersing in ethanol and Milli-Q water. *By adjusting the amount of the iron precursor, the diameters of these magnetic Fe_3O_4 particles can be tuned from less than 10 nm to several hundred nanometers.*

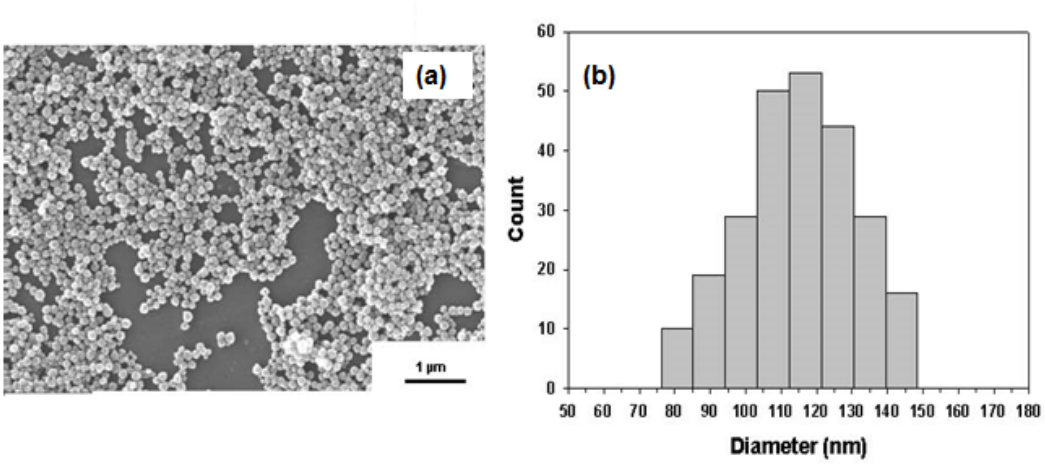

Figure S1: (a) SEM image of the Fe_3O_4 MNPs and (b) the associated size distribution (evaluated by measuring the diameters of 250 particles in the SEM image)

Corresponding author: trlee@uh.edu

Synthesis of SiO_2 Shell@Fe_3O_4 Core (SiO_2@Fe_3O_4). In this procedure, 0.025 g of the magnetic particles described above were redispersed into a mixture of ammonia (1.0 mL) and ethanol (40 mL). The resulting solution was mechanically stirred for 5 min, after which tetraethylortho-silicate (TEOS, 0.10 mL) was added to initiate the coating reaction. The mixture was then stirred for 40 min at rt to afford silica-coated magnetic particles, which could be isolated using a bar magnet and were further purified by washing with copious amounts of ethanol. *Importantly, using this procedure, the thicknesses of the silica shell can be tuned from 5 nm to more than 100 nm simply by adjusting the amount of TEOS added to the solution.*

Preparation of Gold Nanorods (Au_{rods}). Briefly, a seed solution was prepared by mixing equal portions of an aqueous solution of 0.2 M CTAB solution (2.5 mL) and 0.5 mM $HAuCl_4$ (2.5 mL) at rt in a clean glass vial. A cold solution of 1 mM $NaBH_4$ (0.3 mL) was then injected into the mixture. The color of the solution immediately changed from golden yellow to brownish yellow. Vigorous stirring of the seed solution was continued for 2 min prior to being added to a growth solution (*vide infra*).

The growth solution was prepared by sequentially mixing an aqueous solution of 0.2 M CTAB (12.5 mL), 4 mM $AgNO_3$ (0.70 mL), 1 mM $HAuCl_4$ (12.5 mL), and 78.8 mM ascorbic acid (0.175 mL) in a 50-mL centrifuge tube. After adding ascorbic acid, the color of the solution gradually changed from dark yellow to colorless. The seed solution (30 µL) was then rapidly injected into the growth solution and mixed gently for 10 s. The solution was allowed to sit at rt without agitation. The color of the solution evolved slowly from colorless to pale blue and finally a dark blue color within 15 min, suggesting the formation of the Au_{rods}. To obtain a stable plasmon resonance, quenching of the Au_{rods} growth is necessary. The dark blue solution was transferred to an aqueous solution of 1 M Na_2S (40 mL).[43] The Au_{rods} were purified twice by decantation and centrifugation at 8000 rpm to remove excess CTAB, and finally redispersed in 10 mL of Milli-Q water. Using this standard procedure, Au_{rods} with a longitudinal plasmon band at ~775 nm were obtained. These particles were used throughout our studies (47 nm length and 15 nm diameter). It is worth noting that the longitudinal plasmon bands can be systematically controlled from 600 to 850 nm by varying the volumes of $AgNO_3$ solution (0.10 mL-1.0 mL) mixed with the growth solution.

Characterization of MNPs:

Selected Area Electron Diffraction and XRD: The crystallinity of the MNPs was characterized by recording the selected-area electron diffraction (SAED) pattern of an individual magnetic cluster and by collecting an X-ray powder diffraction pattern for a sample of the MNPs (Figure S2).

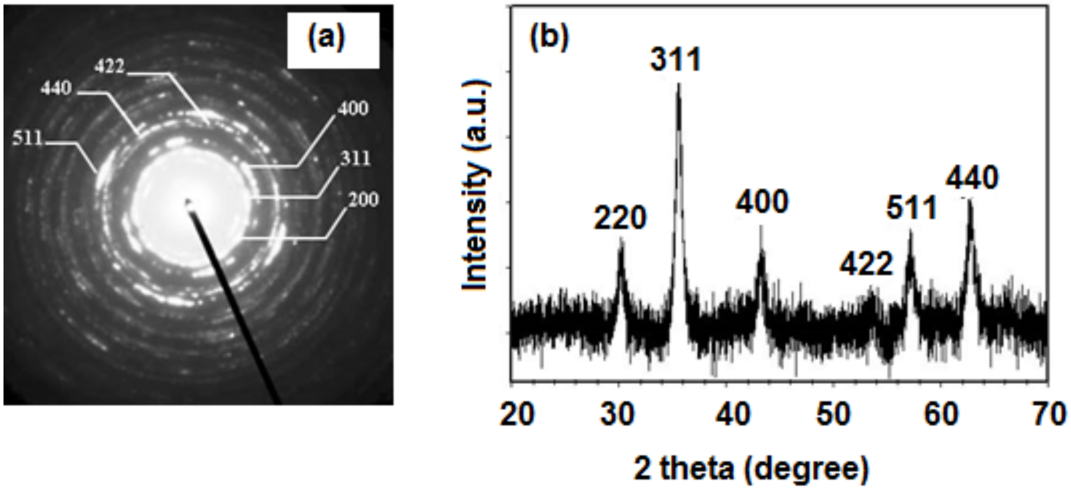

Figure S2: Characterization data for the Fe_3O_4 MNPs: (a) SAED pattern and (b) XRD pattern.

The X-ray powder diffraction pattern reveals peaks indexed to (220), (311), (400), (422), (511), and (440) lattice planes of Fe_3O_4 in a cubic phase. Both SAED (bright spots corresponding to Bragg reflections of many crystallites) and XRD (wider peaks indicating smaller grain size and hence multiple grains/MNP) confirmed the polycrystalline nature of the MNPs.

Magnetic Properties. The magnetization curves in Figure S3 were obtained using a vibrating sample magnetometer (VSM, LakeShore VSM 7300 Series with LakeShore 735 Controller and LakeShore 450 Gaussmeter Software Version 3.8.0). The saturation magnetizations obtained for Fe_3O_4 and $SiO_2@Fe_3O_4$ were 40 and 24 emu/g, respectively. The slightly low saturation magnetization of the Fe_3O_4 nanoparticles likely arises from the nanoparticles being polycrystalline because they were synthesized at relatively low temperature.

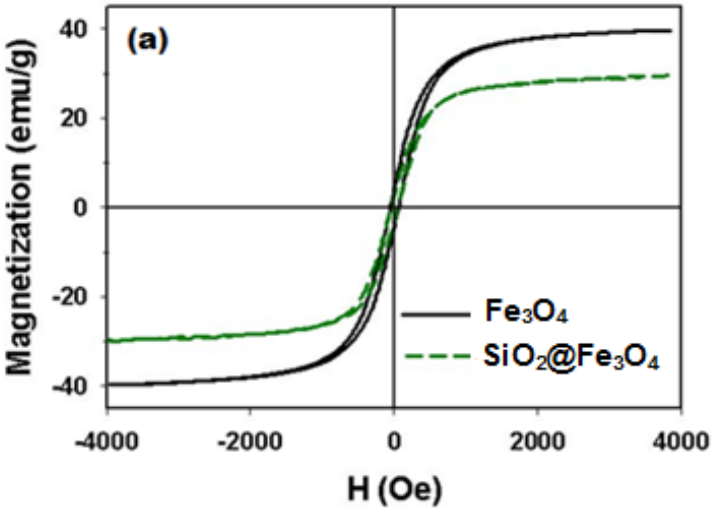

Figure S3. Room temperature magnetic hysteresis curves of Fe_3O_4 (black line) and $SiO_2@Fe_3O_4$ (dotted line) particles.