Supporting info

Preparation of plasmonic magnetic nanoparticles and their light scattering properties

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Experimental details

Preparation of MNP@SiO₂ NPs¹

A dispersion of MNPs (18 nm in average diameter, oleate-stabilized in toluene) was purchased from Ocean Nanotech, Korea. A dispersion of oleate-stabilized MNPs in toluene (0.2 mL) was transferred into a 15 mL vial and diluted with 5 mL of DMF–DCM (1:1). To this, 60 mg of PVP was added and the mixture refluxed at 100 °C for

12 h (or overnight). The NPs were washed with EtOH and centrifuged at 4500 rpm for 5 min. The NPs were dispersed with 6.5 mL of EtOH to yield a stable dispersion of the PVP-stabilized MNPs. A 0.28 mL of ammonium hydroxide (30 wt.% in water) was added to the solution containing the MNPs, then 0.065 mL of TEOS in EtOH (10 vol. %) was added. The vial was stirred for 15 h at room temperature and the silica-coated NPs were isolated by centrifugation at 9000 rpm for 1 h. After washing with EtOH, the silica coated NPs were dispersed in distilled water. Then, 4 mL of TEOS in EtOH (3 vol. %) was added by means of a syringe pump at a rate of 0.4 mL/h. After stirring for one day, the resulting silica coated MNPs were dispersed in EtOH.

Surface modification and Au NPs immobilization onto the silica coated MNP

Thiolated $Fe_3O_4@SiO_2$ was prepared by treating the silica-coated MNP with a solution of MPTS in EtOH (2 % v/v) for 12 h at 25 °C. The particles were washed with EtOH three times by repeating the steps of rinsing and isolation using centrifugation.

An aqueous solution of Au NPs was prepared using a martin method. A chloroauric acid solution in HCl was reduced using NaBH₄ and NaOH in the presence of sodium citrate to produce gold seeds.²

The gold solution was then slowly added to a 100 μ L ethanol solution of functionalized SiO₂ spheres.

Theoretical simulation for scattering efficiency of the Au NPs

The theoretical scattering spectra of the Au NPs were calculated using a discrete dipole approximation package (DDSCAT 7.1).³ The diameters of each Au NPs were 5.5 nm based on the size estimation from TEM measurements. The interdipole

distance was set as 0.125 nm and numbers of dipoles were 43507 for the Au NP monomer and 87014 for the Au NP dimer. The dielectric constant was obtained from Johnson and Christy.⁴ The medium was set as water with a refractive index of 1.33 + 0i. The wavelength was set at 400–700 nm and the discretion of the wavelength was set as 10 nm.



Supporting Figure 1. TEM images of the Fe₃O₄@SiO₂@Au NPs (a) 5.5 nm Au NPs immobilized Fe₃O₄@SiO₂ (b) 10 nm Au NPs immobilized Fe₃O₄@SiO₂ (c) 25 nm Au NPs immobilized Fe₃O₄@SiO₂.



Supporting Figure 2. UV absorbance for different ratios of Au NPs to thiol-modified silicacoated MNPs.



Supporting Figure 3. UV absorbance at 530 nm as a function of the ratio of Au NPs to thiolmodified silica-coated MNPs.



Supporting Figure 4. High-resolution TEM image of the fabricated Fe₃O₄@SiO₂@Au NPs.



Supporting Figure 5. Absorption spectra of hybrid NPs in various solvents.



Supporting Figure 6. Light-scattering spectra of Fe₃O₄@SiO₂@Au NPs

The scattering of hybrid NPs was obtained by combining the scattering of silica and metal. Structures and theoretically calculated scattering spectra are shown in Cover Figure 2. In order to simplify the theoretical calculations, the diameters of the silica core and Au NPs were set to 40 and 5 nm, respectively, for a meaningful comparison of the scattering intensity when the number of Au NPs was increased on the surface of the silica core.



Supporting Figure 7. The enhancement of the scattering intensities of silica-coated MNP by plasmonic interactions between Au NPs on top of the silica coated MNP. a. Structures and light conditions used for the theoretical calculations. b. Scattering intensity of each structure.

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