Supporting Information: Synthesis and Single Particle Optical Detection of Low Polydispersity Plasmonic-Superparamagnetic Nanoparticles

TEM images of iron oxide nanoparticles at difference stages of synthesis

A combination of two synthesis routes has been used to prepare ~20 nm iron oxide nanoparticles that are monodisperse, spherical and magnetically responsive. The Colvin method was used to make iron oxide particles roughly ~12 nm in diameter (Figure I.a.), which were used as nuclei for further growth by the Sun method. A TEM image of the final product shown in Figure I.c. The electron diffraction pattern of the final particles (Figure I.d.) also indicates that they are more crystalline than the particles made by the Colvin method alone (Figure I.b.) The SQUID measurement on these final particles reveal their specific magnetization and they’re superparamagnet at room temperature (Figure II).

Figure I. TEM images and electron diffraction micrographs, respectively, of iron oxide nanoparticles synthesized with (a) and (b) the Colvin method, and (c) and (d) after further coating to increase the particle size using the Sun method.
Figure II. Magnetization hysteresis loop for the final Colvin-Sun 18 nm iron oxide particles

**Observed color changes in different stages of gold seeding and shell completion**

Dense suspensions of iron oxide nanoparticles in water were dark brown in color but at high dilution (\(\sim 10^9\) particles/cc) the suspension appeared yellow. After the iron–oxide particles were seeded with small gold clusters the suspension turned pink, as shown in Figure III.b. Reducing more gold onto the seeded iron oxide-gold particles lead to the formation of completed core-shell structure, as illustrated in Figure 1 of the paper and the blue color seen in Fig. III.c.

Figure III. Observable color change from (a) iron oxide only suspension – yellow, (b) gold-seeded iron oxide particles – light red, followed by a color shift to (c) light blue due to the final completion of the gold shell by electroless deposition.
Extinction cross-section calculation for Core-shell particles

Figure IV. Schematic of the core-shell particles used in the Mie scattering calculation. The iron oxide core has radius $r_1$ and the overall particle radius is $r_2$. $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the complex dielectric functions of the iron oxide core, gold shell, and surrounding water, respectively.

Figure IV shows the geometry of the model particle used in the calculation of the extinction coefficient, with an inner sphere of radius $r_1$ that has a dielectric function $\varepsilon_1$, surrounded by a homogeneous shell that has a dielectric function $\varepsilon_2$, giving an overall particle radius of $r_2$. The particle is in a medium with dielectric function $\varepsilon_3$. The extinction cross-section is the sum of the scattering and absorption cross-sections, which are given by

\[
C_{\text{sc}} = \frac{128\pi^5 \varepsilon_1^2 r_2^6}{3\lambda^4} \left. \frac{\varepsilon_2 \varepsilon_a - \varepsilon_3 \varepsilon_b}{\varepsilon_2 \varepsilon_a + 2 \varepsilon_3 \varepsilon_b} \right|^2, \tag{1}
\]

and

\[
C_{\text{abs}} = \frac{8\pi^2 \sqrt{\varepsilon_1 r_2^3}}{\lambda} \text{Im} \left[ \frac{\varepsilon_2 \varepsilon_a - \varepsilon_3 \varepsilon_b}{\varepsilon_2 \varepsilon_a + 2 \varepsilon_3 \varepsilon_b} \right], \tag{2}
\]

respectively. $\varepsilon_a$ and $\varepsilon_b$ are defined by the relations...
\[ \varepsilon_a = \varepsilon_1 (3 - 2P) + 2\varepsilon_2 P, \quad \text{and} \]
\[ \varepsilon_b = \varepsilon_1 + \varepsilon_2 (3 - P), \quad \text{respectively.} \]

Here \( P \) is the ratio of the shell volume to the total particle volume, given by
\[ P = 1 - \left( \frac{r_1}{r_2} \right)^3, \]

The dielectric function for the Au shell depends on the dielectric function for bulk gold, but also on the shell thickness when it is less than the mean free path of the electrons.

For a gold shell of thickness \( a = r_2 - r_1 \), \( \varepsilon_2 (a, \omega) \) is given by:
\[ \varepsilon_2 (a, \omega) = \varepsilon(\omega)_{\text{exp}} + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{\text{bulk}}} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}, \]

where \( \varepsilon(\omega)_{\text{exp}} \) is the experimentally measured dielectric function for gold\(^{[44]}\), \( \omega_p \) is the bulk plasmon frequency of gold (1.36 \times 10^{16}\, \text{rad/s}) and \( \gamma_{\text{bulk}} \) is the bulk electron collision frequency (3.33 \times 10^{13}\, \text{s}^{-1})\(^{[45]}\)

The second term in Eq. 4 is the plasmon resonance associated with Drude scattering, and the width of this resonance depends on \( \gamma_{\text{bulk}} \). The last term describes modifications to this resonance width associated with damping. The collision frequency with damping \( \Gamma \) has previously been modeled as
\[ \Gamma = \gamma_{\text{bulk}} + \frac{A v_F}{a}, \]

where \( A \) is a theory-dependent parameter which is dependent on the details of the scattering process, which is taken to be one\(^{[45]}\), \( v_F \) is the electron velocity at the Fermi energy and \( a \) is the thickness of the gold shell\(^{[45]}\).

Using this calculation, we predict with a iron oxide core size of 18 nm and gold shell thickness of 4.5 nm yields the theoretical curve which fits the experimental data (Figure 4). Increasing the gold shell thickness to 15 nm would make these particles behave just like gold particles (Figure V) with resonance close to 530 nm.
Figure V. Theoretical predictions for plasmonic spectra of 18 nm iron oxide particles with different gold-shell thicknesses. The surface plasmon resonance undergoes a blue shift with the thickening of the gold shell.