Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Reductive Dissolution of $Fe_3O_4$ Facilitated by the Au Domain of a $Fe_3O_4$/Au Hybrid Nanocrystal: Formation of a Nanorattle Structure Composed of a Hollow Porous Silica Nanoshell and Entrapped Au Nanocrystal

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***General consideration***. Any reagent including $FeCl_3$ (Acros), Sodium Oleate (TCI), Oleic acid, Igepal® CO-520 (Aldrich), $HAuCl_4$ (STREM), Cyclohexane, $NH_4OH$ (Samchun chem.), TEOS (Acros), $NaBH_4$ (Aldrich), $AgNO_3$ (Samchun chem.), and Hydrazine ($N_2H_4$, JUNSEI) was used as purchased without any purification. Analyses of transmission electron microscopy (TEM) were conducted with JEOL JEM-2010. Scanning tunneling microscopy (SEM) was carried out with LEO SUPRA 55 (Carl Zeiss, Germany). X-ray Photoelectron Spectroscopy (XPS) was obtained using K-Alpha (Thermo Electron, U.K.). X-ray diffraction patterns were obtained by using X-Ray Diffractometer (18kW) (Mac Science, Japan). UV absorption and fluorescence were observed by using V670 UV-Visible-NIR spectrophotometer (JASCO). The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 gas adsorption analyzer.

***Synthesis of silica nanospheres containing $Fe_3O_4$/Au hybrid nanocrystal ($Fe_3O_4$/Au@$SiO_2$).*** $Fe_3O_4$ nanocrystals having 8 nm of average core size were prepared through the previously reported procedure in Ref. S1. The encapsulation of $Fe_3O_4$ nanocrystals and Au complexes with the silica shell was conducted by the modification of a reverse microemulsion technique. Polyoxyethylene(5)nonylphenyl ether (7.68 g, 18.0 mmol, Igepal CO-520, containing 50 mol% hydrophilic group, Aldrich) was dispersed in a round bottom flask containing cyclohexane (170 ml) by stirring. Next, 8.0 mg of $Fe_3O_4$ nanocrystals dispersed in cyclohexane were added to the reaction solution. The resulting mixture was vortexed until the mixture became transparent. An aqueous solution of $HAuCl_4$ (24 mM, 0.5 ml) and ammonium hydroxide solution (30 %, 1.3 ml) were successfully added to the reaction mixture to form a transparent suspension. Lastly, tetraethylorthosilicate (1.5 ml, TEOS) was added, and stirred for 12 hr. The resulting silica nanospheres, $Fe_3O_4$/Au@$SiO_2$, containing $Fe_3O_4$/Au hybrid nanocrystal were collected by magnetic decantation. The collected nanospheres of $Fe_3O_4$/Au@$SiO_2$ were redispersed in EtOH and recovered by using a magnet. The dispersion of $Fe_3O_4$/Au@$SiO_2$ into EtOH suspension and magnetic separation was repeated three times for the purification. The control reaction to synthesize silica nanosphere containing Au nanocrystal (Au@$SiO_2$) was carried out in the same condition except for the absence of $Fe_3O_4$ nanocrystal.

***Reductive etching of $Fe_3O_4$ from $Fe_3O_4$/Au@$SiO_2$ and the synthesis of nanorattle having Au nanocrystal encapsulated by hollow and porous silica (Au@h-$SiO_2$).*** An aqueous solution of $NaBH_4$ (0.2 M, 1.0 ml) was added to an 2.0 ml of aqueous suspension containing 1.0 mg of $Fe_3O_4$/Au@$SiO_2$ and stirred for 30 min at room temperature. The pH of the reaction suspension was at around 13. The dark brown color of the suspension gradually faded with the evolution of $H_2$ gas. The resulting solids, Au@h-$SiO_2$, containing Au nanocrystal and hollow and porous

silica shell were collected by the centrifugation. The dispersion of Au@h-$SiO_2$ into an aqueous suspension and centrifugation was repeated three times for the purification.

***Synthesis of Ag@$SiO_2$ nanosphere consisting of Ag nanocrystal encapsulated by a porous silica shell.*** An aqueous solution of $AgNO_3$ (0.3 M, 1.0 ml) was added to an 0.2 ml of aqueous suspension containing 1.0 mg of Au@*h*-$SiO_2$ and stirred for 6 hrs at room temperature without light exposure. Then a hydrazine solution ($N_2H_4$, 0.2 M, 0.02 ml) was added dropwise to the reaction suspension and stirred for 12 hrs. The dark brown color appeared from the reaction suspension immediately after the addition of hydrazine. The resulting solids, Ag@$SiO_2$ were collected by the centrifugation. The dispersion of Ag@$SiO_2$ into an aqueous suspension and centrifugation was repeated three times for the purification.

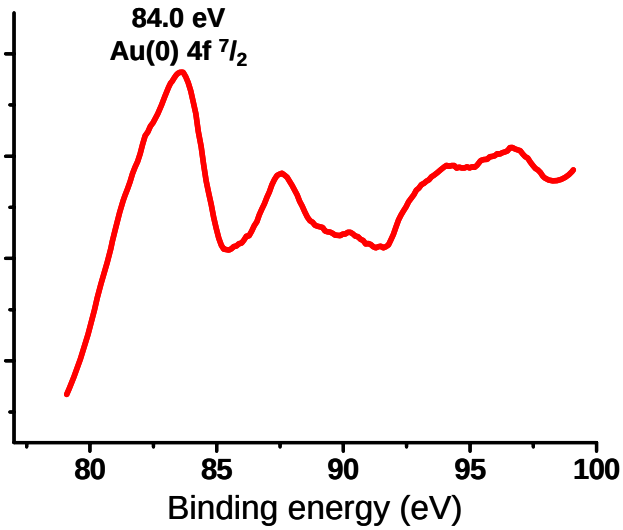


**Figure S1**. X-ray Photoelectron Spectroscopy (XPS) of $Fe_3O_4$/Au@$SiO_2$, showing the zero oxidation state of Au species in the nanosphere.

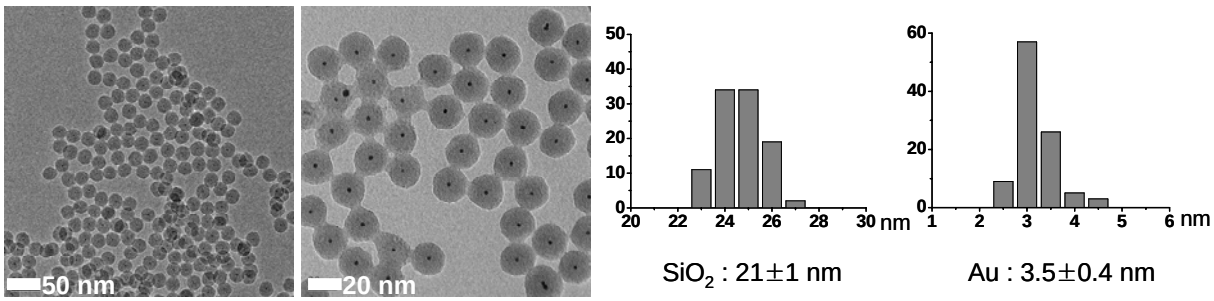


**Figure S2**. TEM images and histograms showing the size distribution of the silica nanosphere and Au nanocrystal of Au@$SiO_2$.

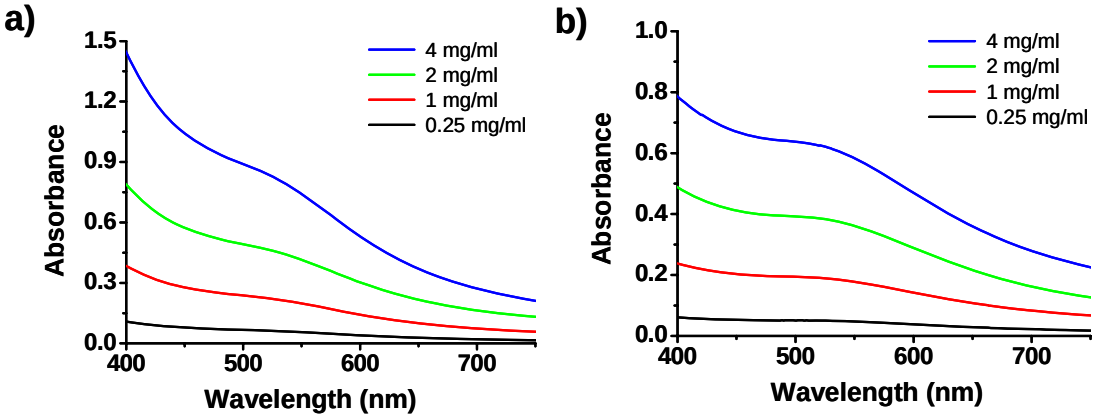


**Figure S3**. UV-Vis absorption spectra of aqueous suspension containing various concentration of Au@*h*-$SiO_2$, synthesized from (a) 8 nm and (b) 5 nm sized $Fe_3O_4$ nanocrystals.

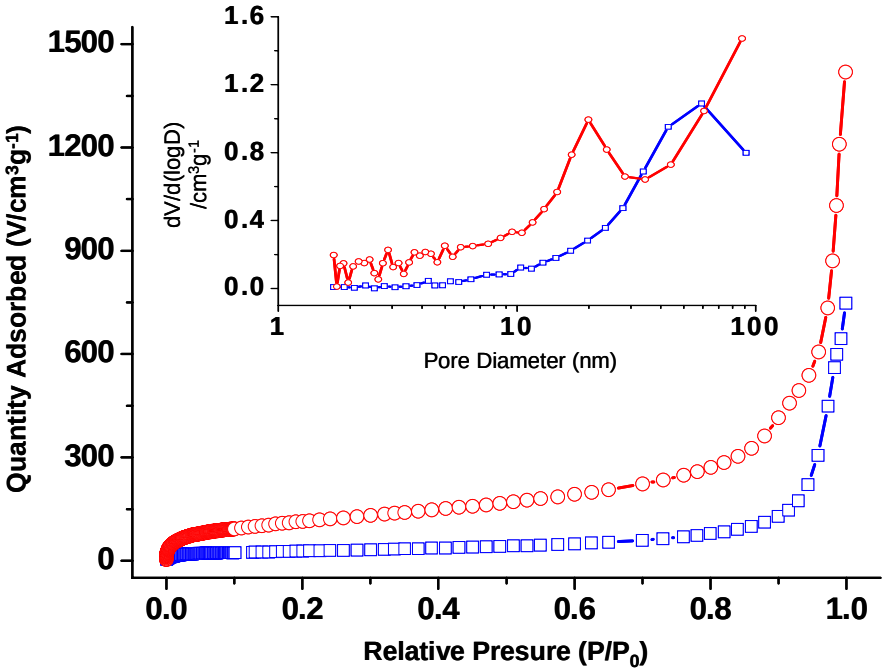


**Figure S4**. $N_2$ sorption isotherms of $Fe_3O_4$/Au@$SiO_2$ (blue line) and Au@*h*-$SiO_2$ (red line). Insect shows the corresponding pore size distributions derived by using BJH (Barret-Joyner-Halenda) model.

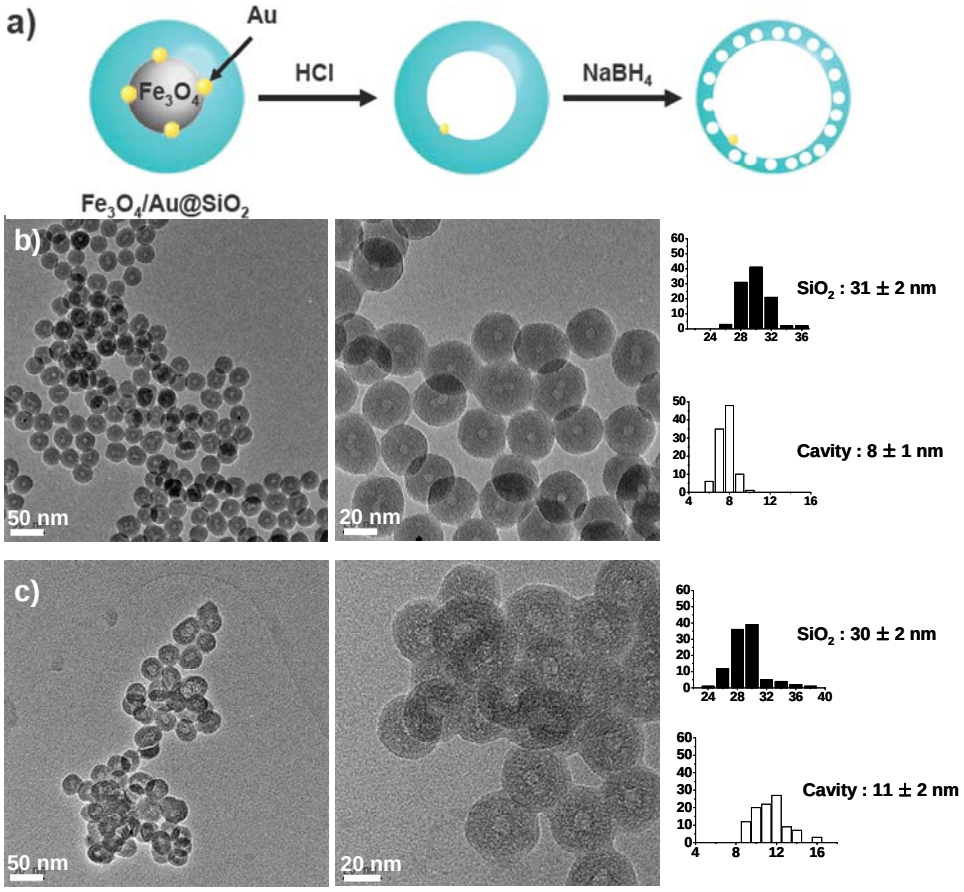


**Figure S5**. (a) Schematic representation illustrating the control experiment to prove the expansion of cavity, newly generated by $Fe_3O_4$ dissolution, during the $NaBH_4$ treatment. TEM images and histograms showing the size distribution of inner and outer diameter of hollow silica nanosphere, synthesized by etching $Fe_3O_4$/Au@$SiO_2$ with HCl solution, (b) before and (c) after $NaBH_4$ treatment.

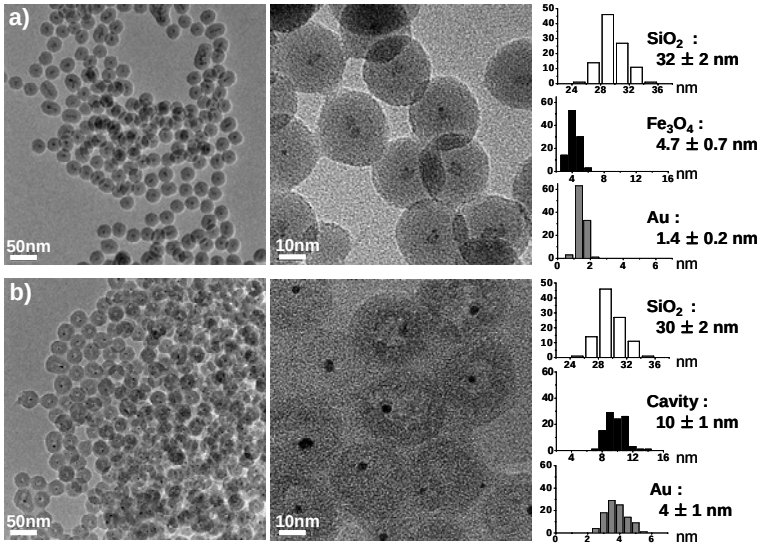


**Figure S6**. TEM images and histograms showing the size distribution of the silica nanosphere, hollow cavity, and $Fe_3O_4$ and Au grains of (a) $Fe_3O_4$/Au@$SiO_2$ and (b) Au@*h*-$SiO_2$ synthesized from 5 nm sized $Fe_3O_4$ nanocrystal.

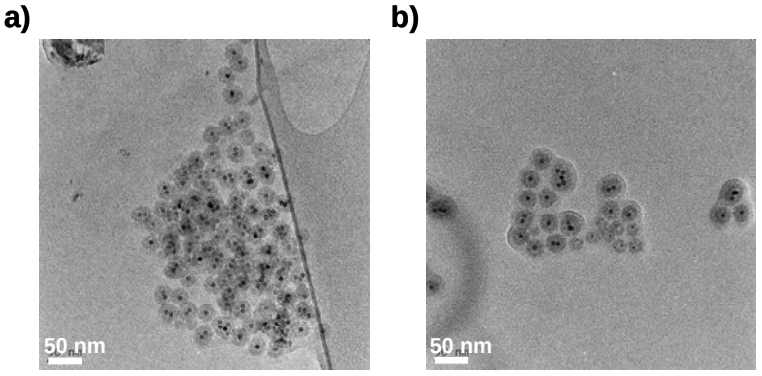


**Figure S7**. TEM images of the nanospheres obtained after the treatement of the (a) $Fe_3O_4$@$SiO_2$ and (b) their mixture with Au@$SiO_2$ with $NaBH_4$.

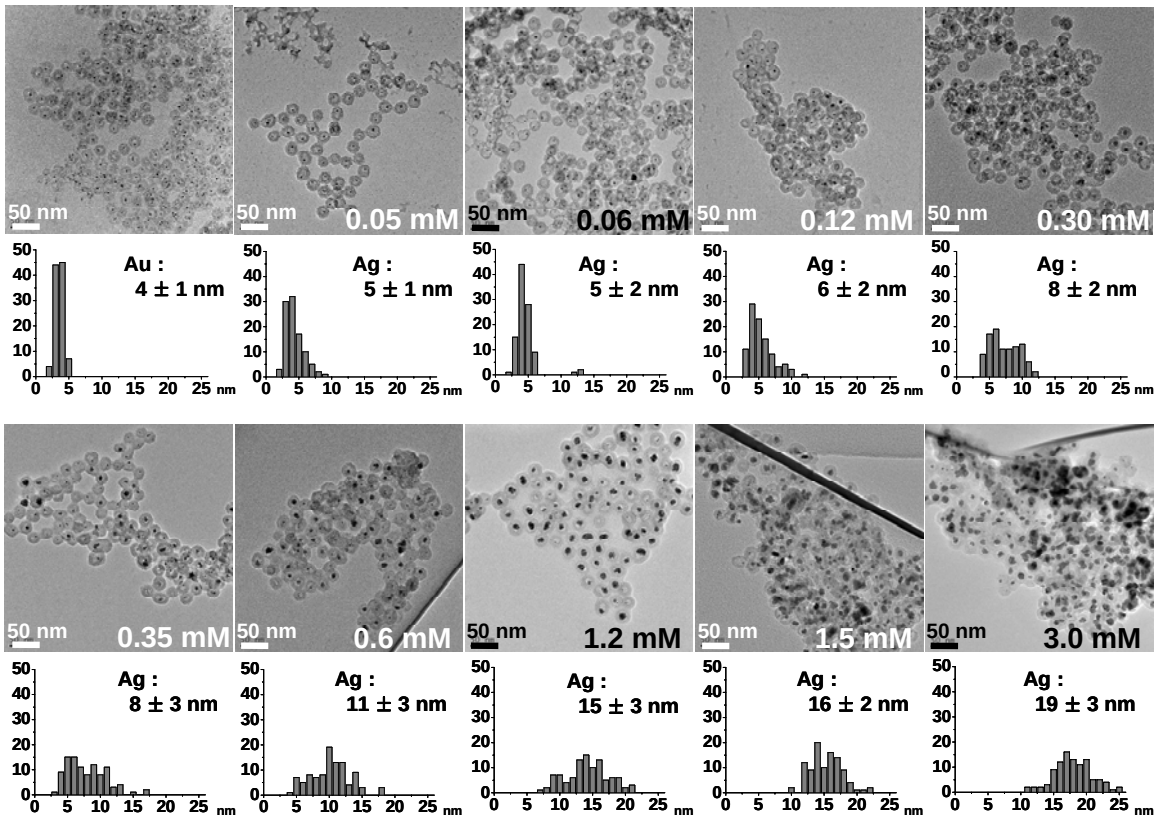


**Figure S8.** TEM images and histograms showing the size distribution of $Ag@SiO_2$ nanocrystals at various $AgNO_3$ concentrations.

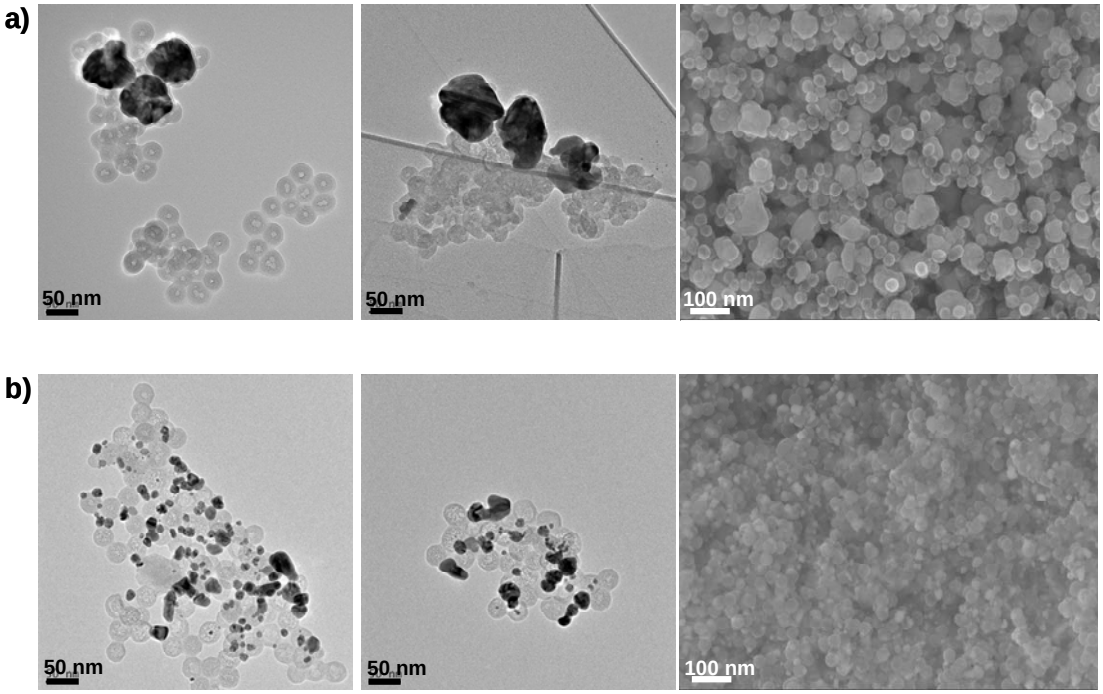


**Figure S9**. Photographs of aqueous suspensions and TEM and SEM images of the adducts obtained from the control reactions for Ag growth in the presence of (a) hollow and porous silica nanopsheres, prepared from $Fe_3O_4$@$SiO_2$ through the etching with HCl followed by the treatment with $NaBH_4$, and (b) Au encapsulating hollow silica nanospheres, synthesized by etching $Fe_3O_4$/Au@$SiO_2$ with HCl solution.

## References for the Supporting Information

[**S1**] Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T. *Nat. Mater*. **2004**, *3*, 891.