Supporting Information

"Synthesis of Fe₃O₄/PdO Heterodimer Nanocrystals in a Silica Nanospheres and their Controllable Transformation into Fe₃O₄/Pd Heterodimers and FePd Nanocrystals"

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General consideration. Any reagent including FeCl₃, Sodium Oleate (TCI), Oleic acid, Igepal[®] CO-520 (Aldrich), Na₂PdCl₄ (STREM), Cyclohexane, NH₄OH (Samchun chem.), TEOS (Acros) were used as purchased without any purification. Analyses of transmission electron microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray Spectroscopy (EDX) were conducted with JEOL JEM-2010 and JEOL JEM 2100F. Scanning tunneling microscopy (SEM) was carried out with LEO SUPRA 55 (Carl Zeiss, Germany). Magnetic properties of nanoparticles were measured using superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5XL), which is equipped with a 5 T superconducting magnet. X-ray Photoelectron Spectroscopy (XPS) was obtained using K-Alpha (Thermo Electron, U.K.).

Synthesis of silica nanospheres containing Fe_3O_4 nanocore and Pd^{2+} complexes, 1, and its conversion into 2 and 3 via the thermal annealing. Iron oxide nanoparticles having 8 nm of average core size were prepared through the previously reported procedure in Ref. 1. Polyoxyethylene(5)nonylphenyl ether (1.54 mg, 3.49 mmol, Igepal CO-520, containing 50 mol% hydrophilic group, Aldrich) was dispersed in a round bottom flask containing cyclohexane (34 ml) by sonication. Next, 3.2 mg of Fe₃O₄ nanoparticles dispersed in cyclohexane were added to the reaction solution. The resulting mixture was vortexed until the mixture became transparent. An aqueous solution of Na₂PdCl₄ (0.285 M, 0.2 ml) and ammonium hydroxide solution (30 %, 0.26 ml) were successfully added to the reaction mixture to form a transparent suspension. Lastly, tetraethylorthosilicate (0.3 ml, TEOS) was added, and stirred for 12 hr. The resulting silica nanospheres, **1**, containing Fe₃O₄ nanocores and tiny aggregates of Pd²⁺ complexes were collected by magnetic decantation. The collected nanospheres of **1** were redispersed in EtOH and recovered by using a magnet. The dispersion of **1** into EtOH suspension and magnetic separation was repeated three times for the purification. The powder of **1** was heated up with 5 °C/min heating rate in a furnace and annealed in air condition for 5 hr at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C, generating the nanospheres of **2**. For the generation of **3**, the nanospheres of **2**(**700** °C) was annealed under a flow of Ar + 4% H₂ at 150 °C, 200 °C, 300 °C, and 500 °C for 2 hr.

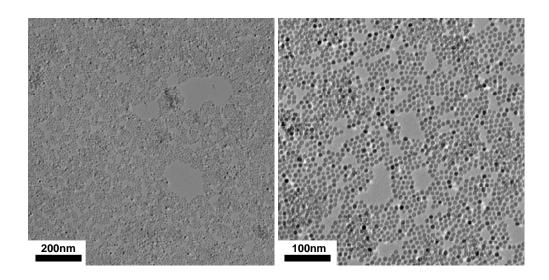


Figure S1. (a) TEM images of 8 nm sized Fe_3O_4 nanoparticles used in this work.

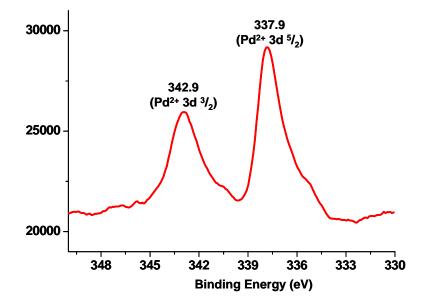


Figure S2. X-ray Photoelectron Spectroscopy (XPS) of **1**, showing the 2^+ oxidation state of Pd species encapsulated in the nanosphere.

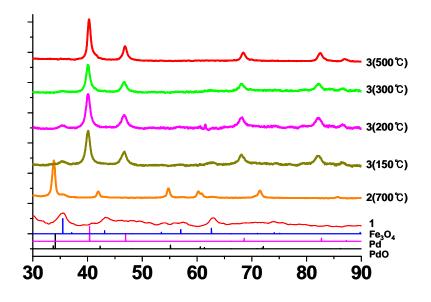


Figure S3. XRD patterns of the nanoshperes of 1, 2, and 3.

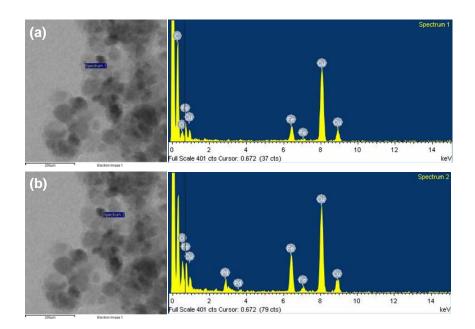


Figure S4. Energy dispersive spectroscopy (EDS) of heterodimer of Fe_3O_4 and Pd nanoparticles.

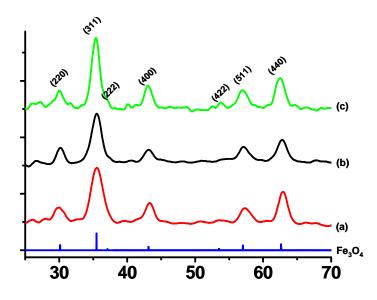


Figure S5. X-ray diffraction patterns of the silica nanospheres containing Fe_3O_4 nanoparticle, prepared without the addition of Pd^{2+} complex (a) before and after thermal annealing (b) in air at 500 °C and (c) in Ar + 4% H₂ at 700 °C.

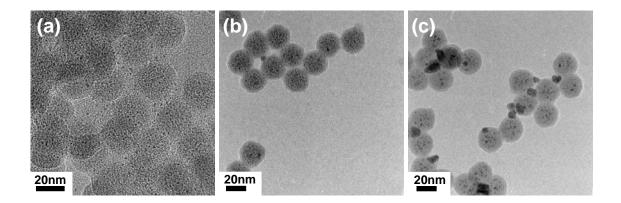


Figure S6. TEM images of silica nanospheres containing Pd^{2+} complexes prepared in the absence of Fe₃O₄ nanoparticles. (a) as-synthesized silica nanosphere and after thermal annealing in air (b) at 500 °C and (c) at 800 °C.

Reference

1. J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. Hyeon, *Nat. Mater.*, **2004**, *3*, 891.