Supporting Information

for "Size-Controlled Pd Nanoparticle Catalysts Prepared by Galvanic Displacement into a Porous Si-Iron Oxide Nanoparticle Host."

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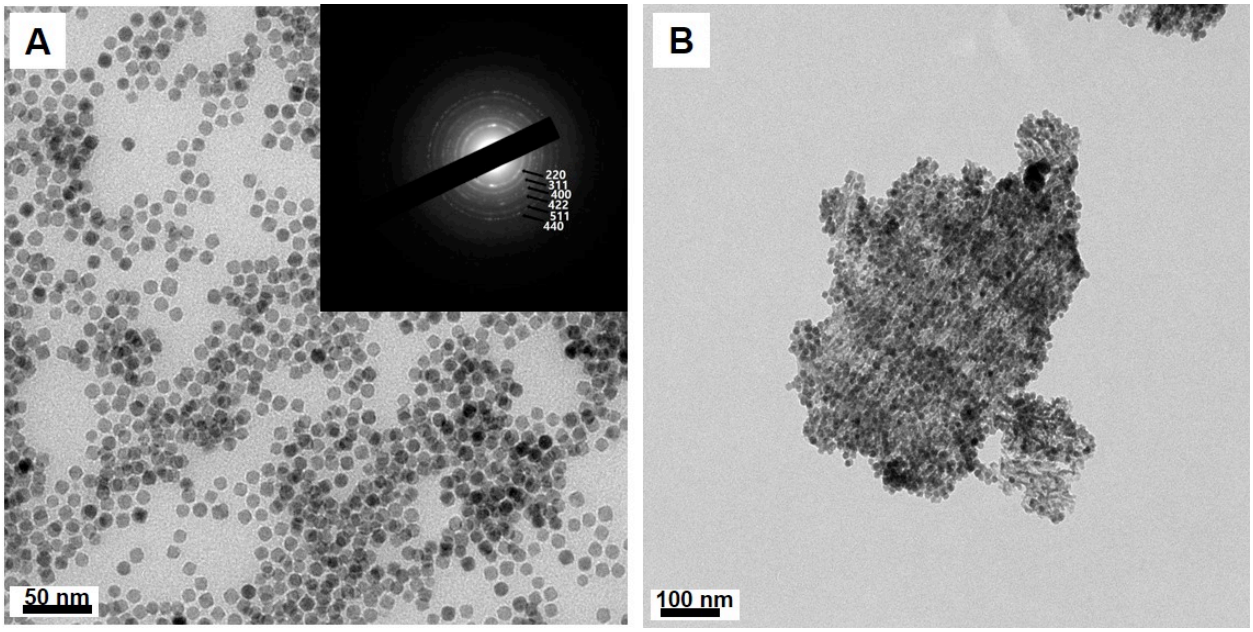

Figure S1. Transmission electron microscope (TEM) images of isolated γ-Fe_2O_3 nanoparticles (A) and composite nanoparticles consisting of γ-Fe_2O_3 nanoparticles trapped within a porous Si nanoparticle matrix (B). The γ-Fe_2O_3 nanoparticles in (A) show an average particle size (by DLS) of 7 nm. Inset of this (A) shows the selected area electron diffraction (SAED) pattern indexed with the cubic structure of the maghemite phase (JCPDS No. 39-1346) of iron oxide nanoparticles. The result of infiltration of γ-Fe_2O_3 nanoparticles into porous Si nanoparticles is referred to in this work as magnetic porous Si nanoparticles (MpSiNPs).

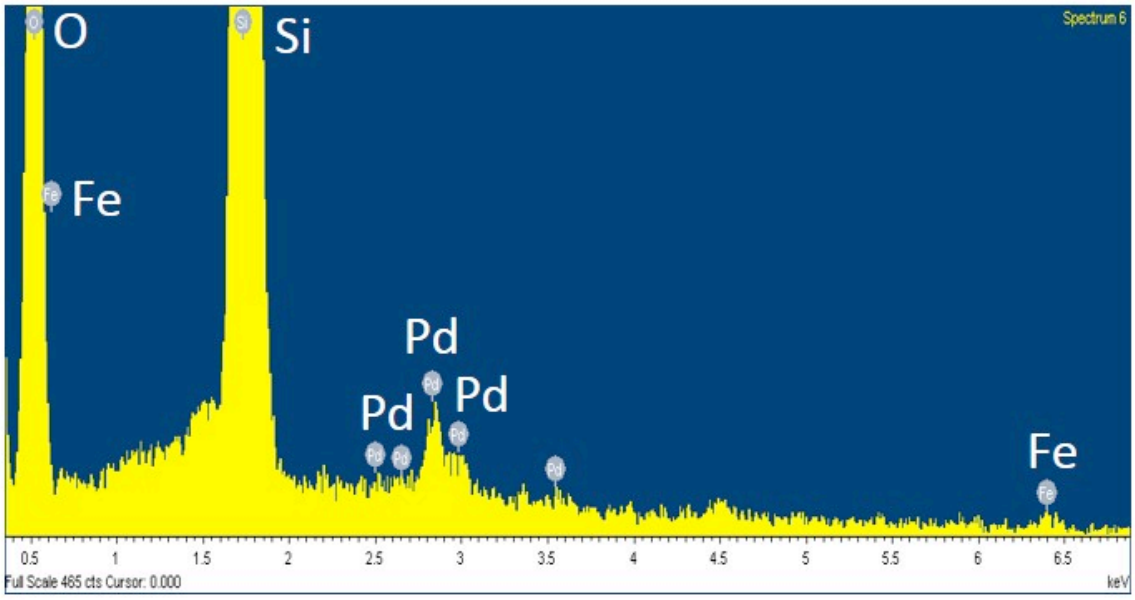

Figure S2. Energy-dispersed X-ray spectrum (EDS) of magnetic Pd-loaded porous Si nanoparticles (MpSi-PdNPs) prepared by sequential infiltration of γ-Fe_2O_3 nanoparticles and electroless deposition of Pd within a porous Si nanoparticle host. The coordination complex $[Pd(NH_3)_4]^{2+}$ was used as the palladium source.

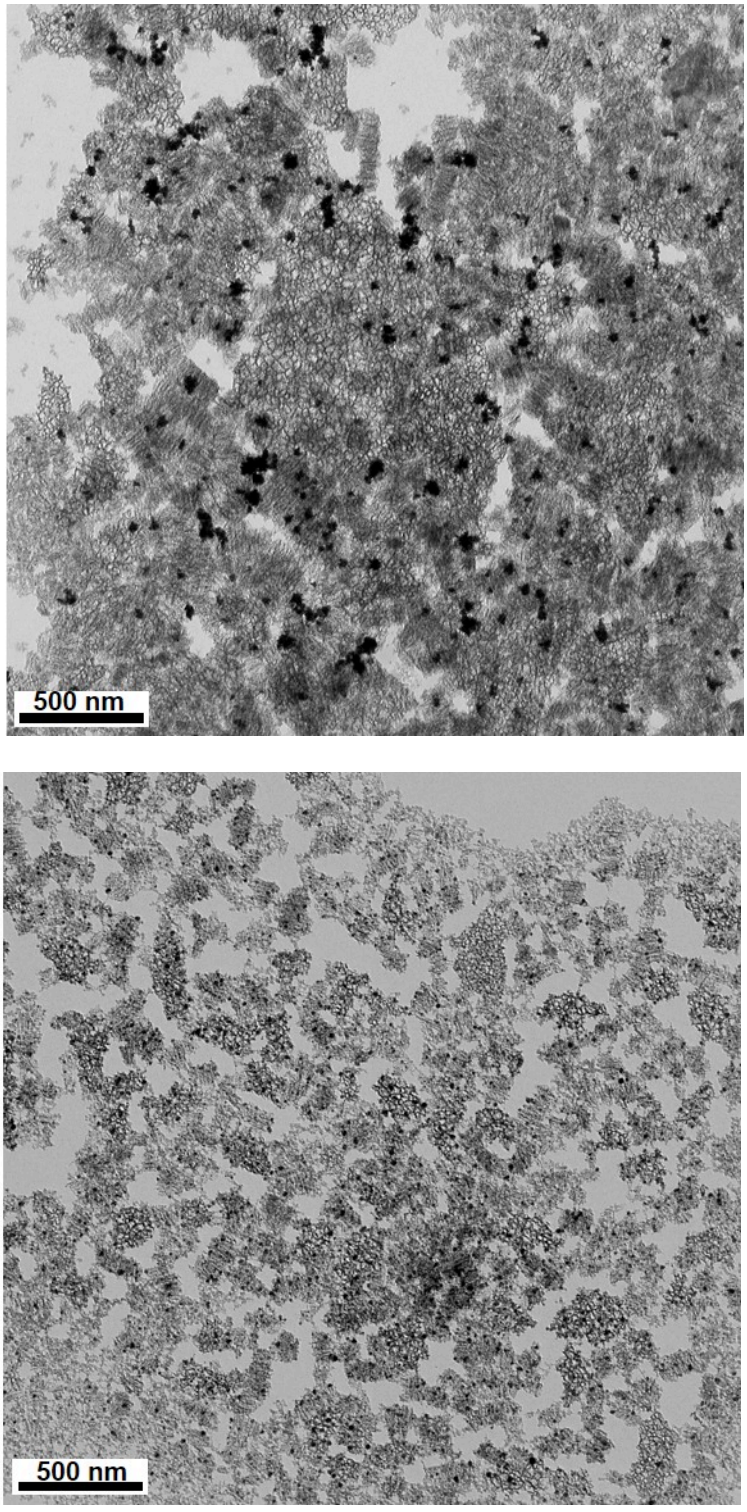

Figure S3. Low magnification TEM images of the result of Pd deposition within porous Si nanoparticles using aqueous $PdCl_2$ (top image) or $[Pd(NH_3)_4]^{2+}$ (bottom image) as the palladium source.

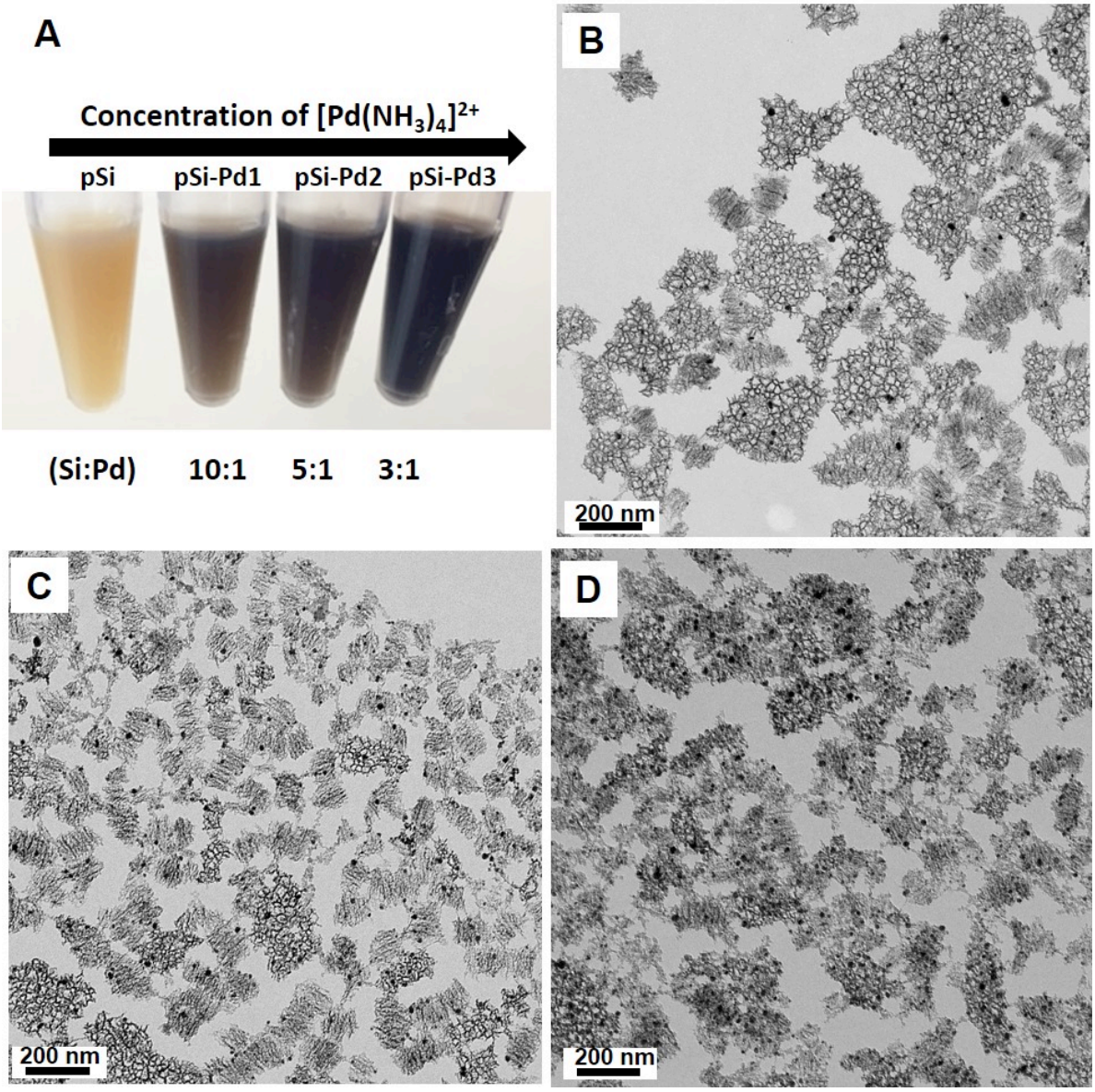

Figure S4. Photograph and TEM images of porous Si-Pd nanoparticles (pSi-PdNPs) prepared by introducing a given concentration of $[Pd(NH_3)_4]^{2+}$ solution to a set concentration of empty porous Si nanoparticles. (A) Photograph of pSi-PdNP suspensions prepared with increasing concentration of $[Pd(NH_3)_4]^{2+}$: 0, 1, 2, 4 μL of 0.1 M $[Pd(NH_3)_4]^{2+}$ solution, added to 0.2 mL of pSiNP (1 mg/mL) in deionized water. The Si to Pd mass ratio of the starting materials for the reaction is given below each vial. The vial on the far left is a control containing no Pd. The color of the nanoparticle solutions changes from yellow to dark brown to black with increasing Pd content. (B) TEM image of pSi-PdNPs with Si:Pd mass ratio of 10:1 (pSi-Pd1). (C) TEM image of pSi-PdNPs with Si:Pd mass ratio of 5:1 (pSi-Pd2). (D) TEM image of pSi-PdNPs with Si:Pd mass ratio of 3:1 (pSi-Pd3). Increasing the concentration of $[Pd(NH_3)_4]^{2+}$ solution increases the number density of Pd nanoparticles in the pSi matrix without substantially changing Pd nanoparticle size.

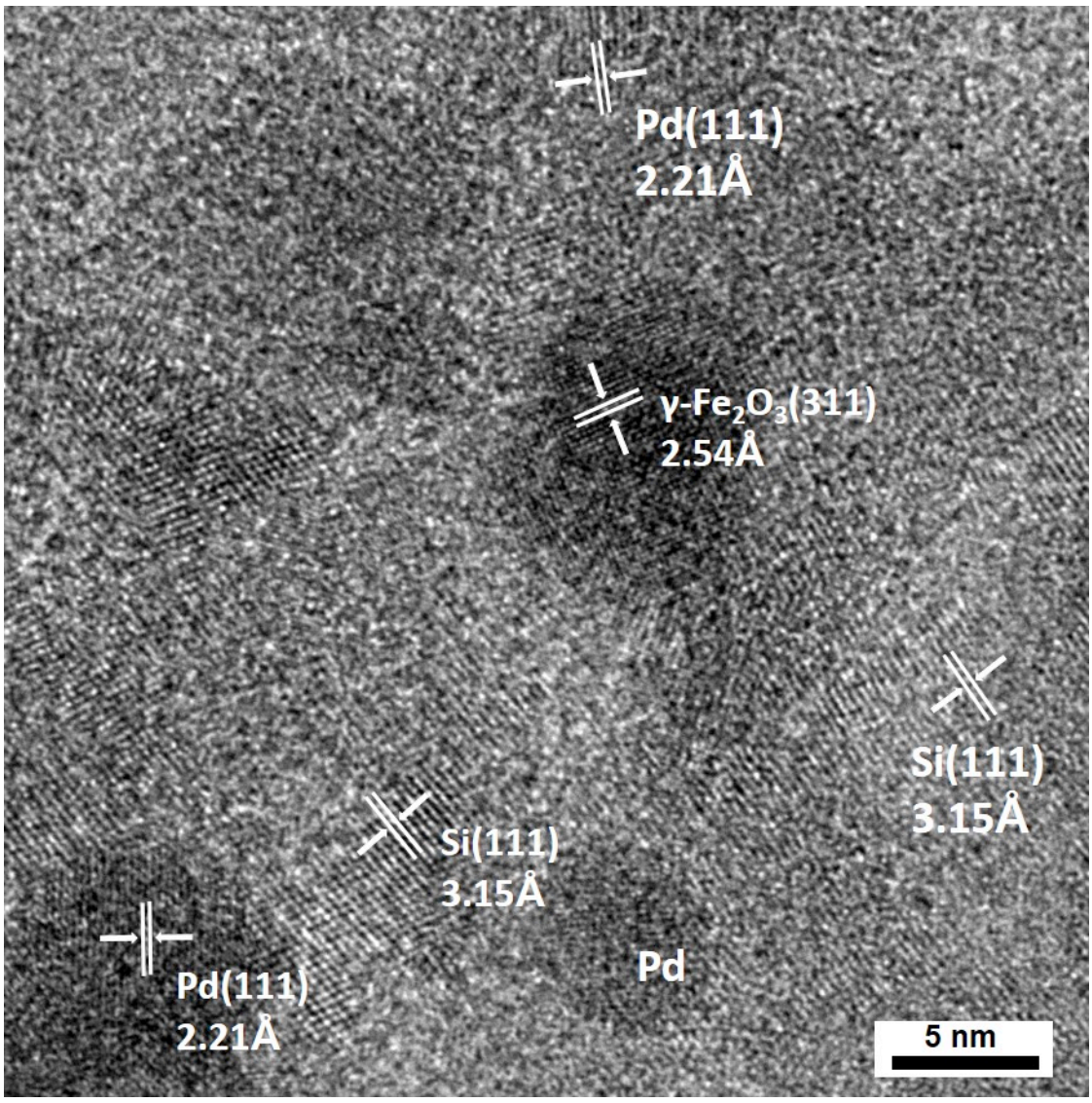

Figure S5. High-resolution TEM images of a single MpSi-Pd composite nanoparticle. All three nanoparticles are distinguishable, and the measured lattice spacings are: 3.15Å, assigned to the (111) plane of Si; 2.54Å, assigned to the (311) plane of γ-Fe_2O_3; and 2.21Å, assigned to the (111) plane of Pd.

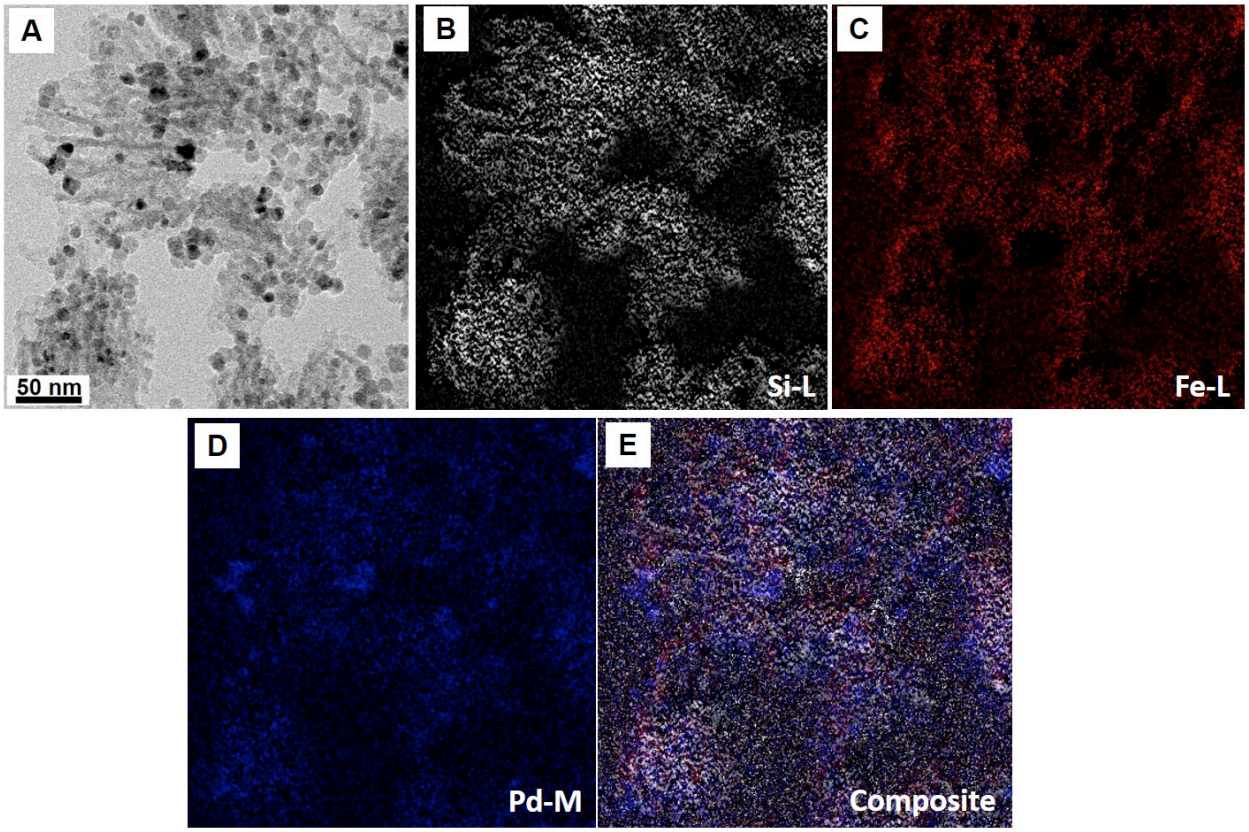

Figure S6. (A) TEM image of MpSi-Pd composite nanoparticles. (B)-(D) corresponding elemental maps of Si, Fe, and Pd derived from 2-dimensional energy-dispersive X-ray spectroscopy (EDS) maps. (E) overlay of images (B), (C), and (D).

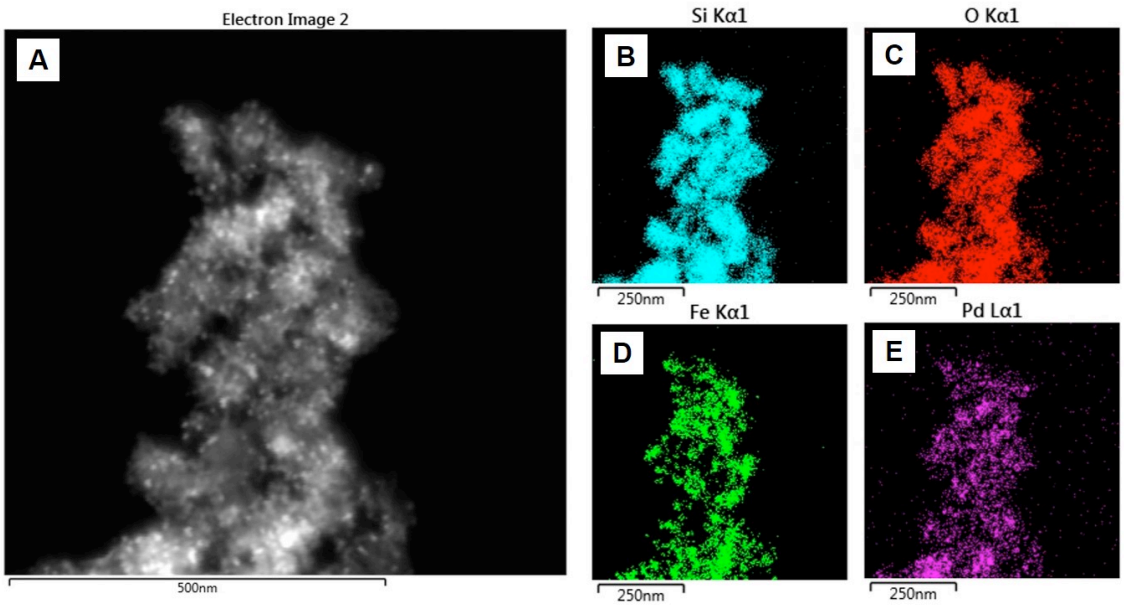

Figure S7. (A) High-angle annular dark-field (HAADF) STEM image of MpSi-Pd nanoparticles. (B)-(E) EDS elemental maps of the Si, O, Fe, and Pd signals as indicated.

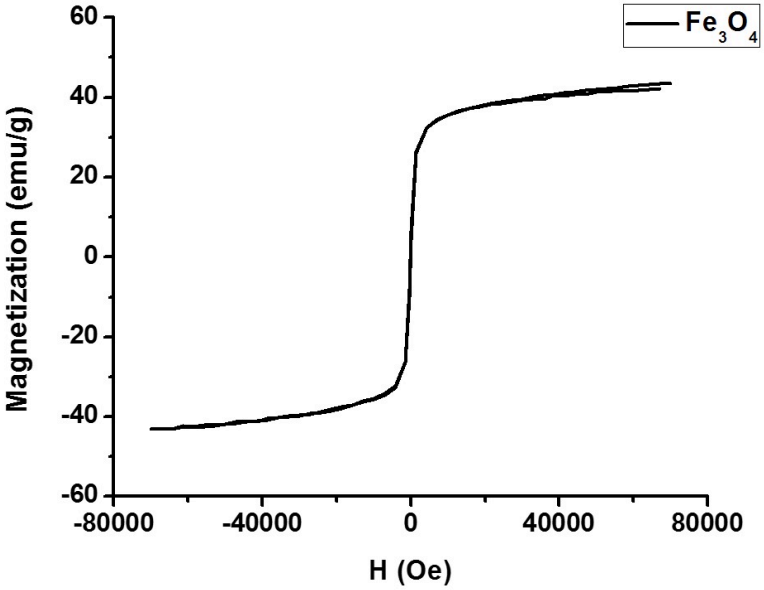

Figure S8. Magnetization curve (298 K) of γ-Fe_2O_3 nanoparticles used in this study. Saturation magnetization is 48 emu/g.

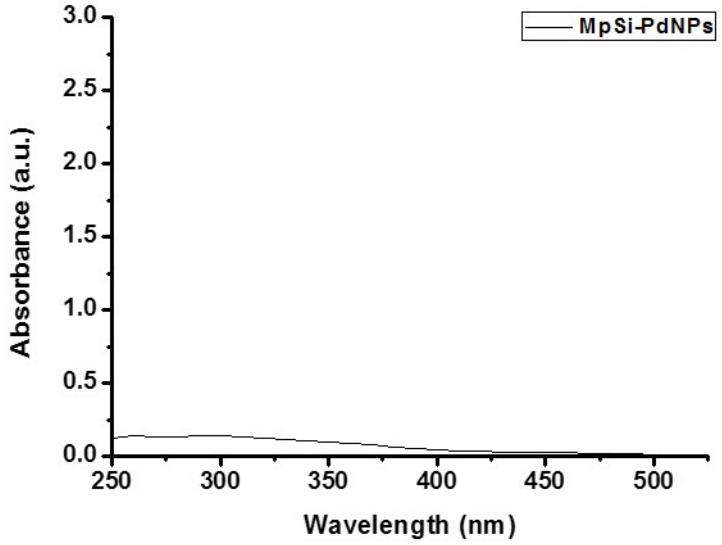

Figure S9. UV-Vis absorbance spectrum of the magnetic Pd-loaded porous Si nanoparticles (MpSi-PdNPs) used in this work, dispersed in deionized water. Nanoparticle concentration is comparable to that used in the catalytic reactions (see Figure 4 in the main text). The data show that at the concentrations used in the catalysis study, there is little spectral interference from nanoparticle absorbance.

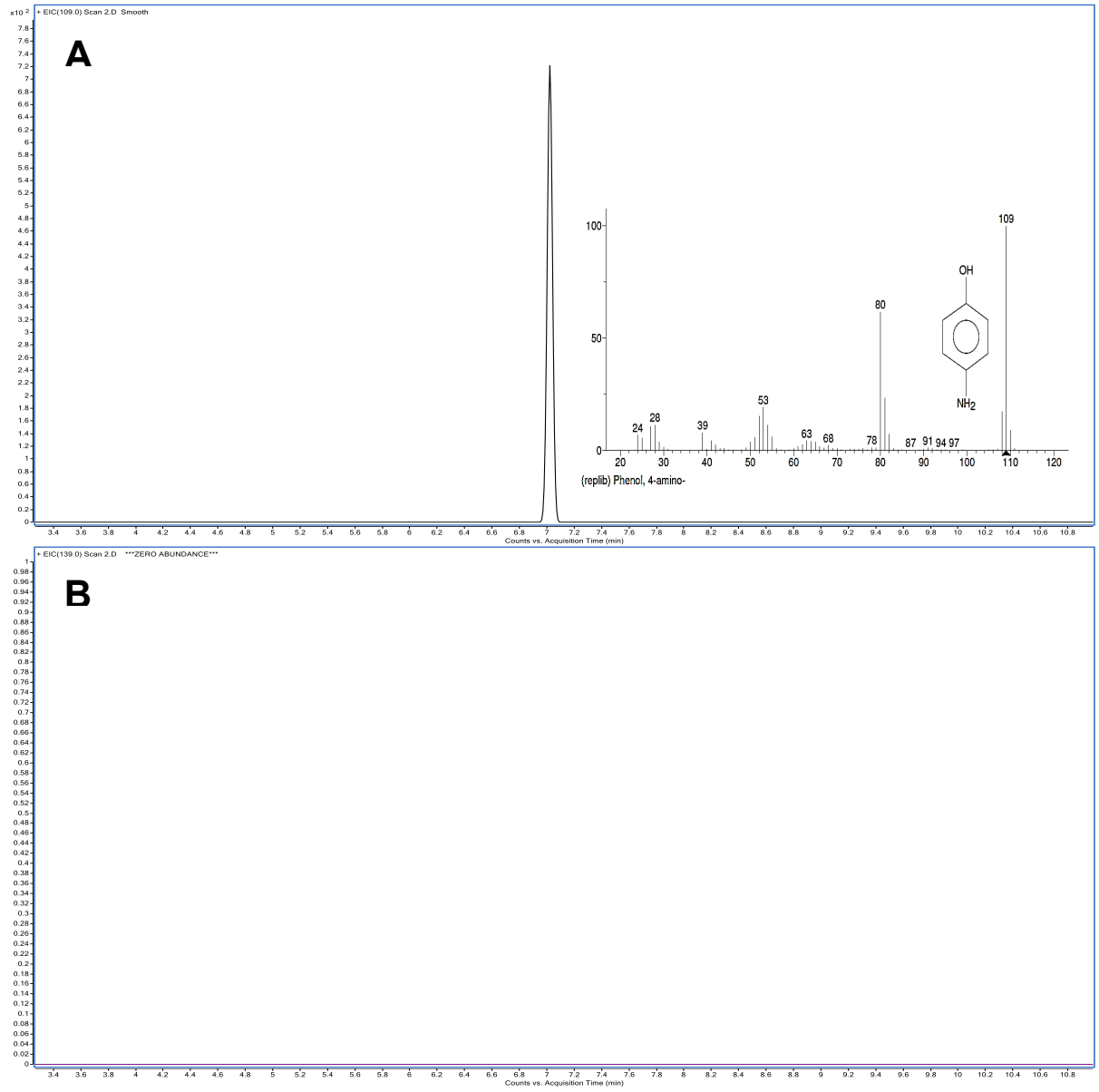

Figure S10. GC-MS analysis of catalytic reaction products. (A) The extracted ion chromatogram at m/z = 109. The M^+ peak is assigned to 4AP (C_6H_7NO). (B) The extracted ion chromatogram at m/z = 139. The M^+ peak is assigned to 4NP ($C_6H_5NO_3$). Inset of (A) shows the mass spectrum of the product.

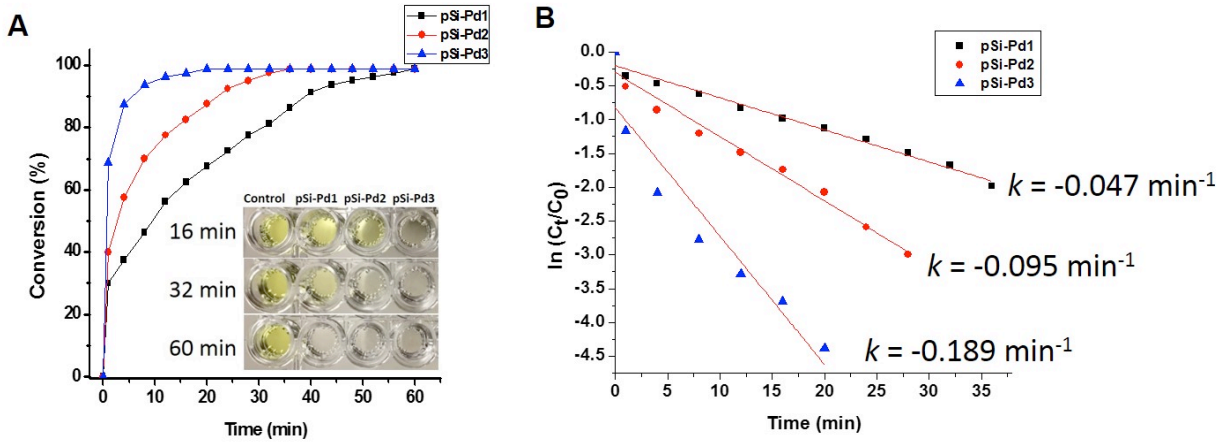

Figure S11. Effect of mass loading of Pd on the catalytic activity of Pd-loaded porous Si nanoparticles. The particles in this experiment were not loaded with γ-Fe_2O_3 nanoparticles and $[Pd(NH_3)_4]^{2+}$ was used as the Pd source. (A) Conversion of 4-nitrophenol (4NP) to 4-aminophenol (4AP) using the indicated Pd nanocomposite catalysts as a function of time: ■ pSi-Pd1 corresponds to Si:Pd mass ratio of 10:1; ● pSi-Pd2 corresponds to Si:Pd mass ratio of 5:1; ▲ pSi-Pd3 corresponds to Si:Pd mass ratio of 3:1. The inset shows photographs of the reaction at the indicated times after initiation. Control is empty porous Si nanoparticles (not loaded with Pd). (B) Plot of $\ln(C_t/C_0)$ *versus* time for the reduction of 4NP in the presence of the indicated Pd nanoparticle catalysts. The rate constant k is determined from the slope of the least-squares fit line. All experiments contained the same total mass of composite nanoparticle.

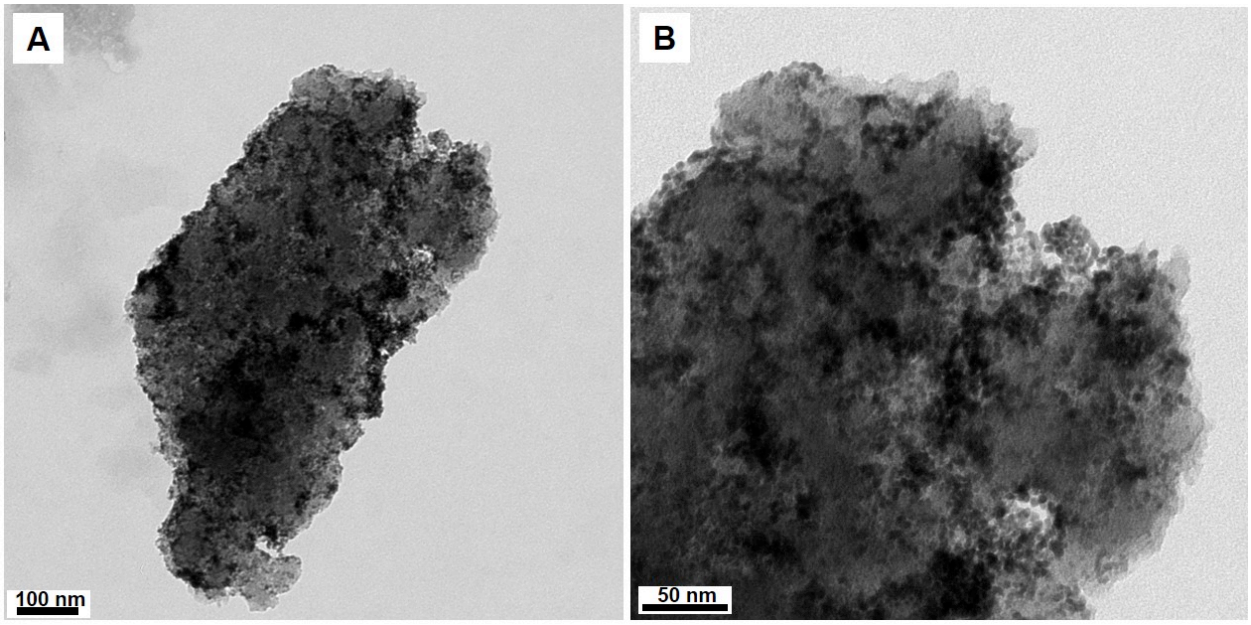

Figure S12. TEM images of commercial Pd/C catalyst used in this study. Sample obtained from Sigma Aldrich Chemicals (Atlanta, GA), Cat # 205699

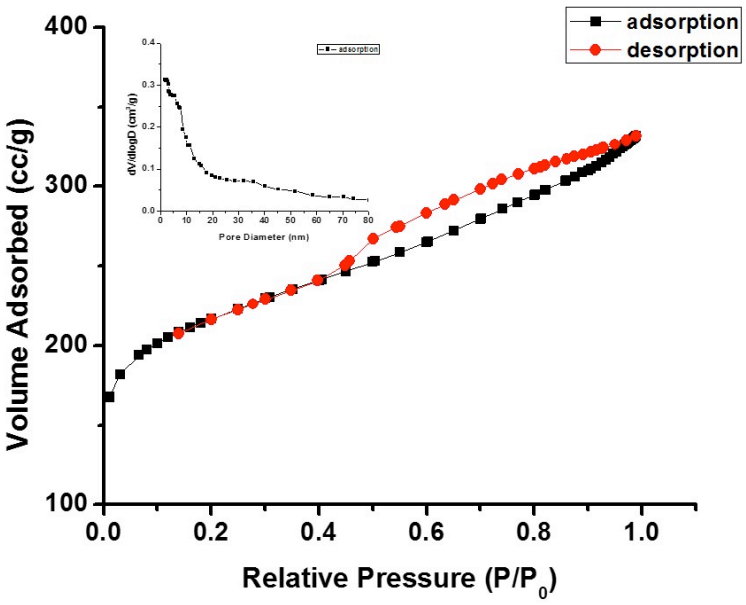

Figure S13. N_2 adsorption/desorption isotherm of commercial Pd/C catalyst. The inset shows the pore size distribution. The specific surface area (BET method) and pore volume (BJH method) were 762.2 m^2/g, 0.51 cm^3/g, and the average pore diameter was determined to be 2.6 nm.

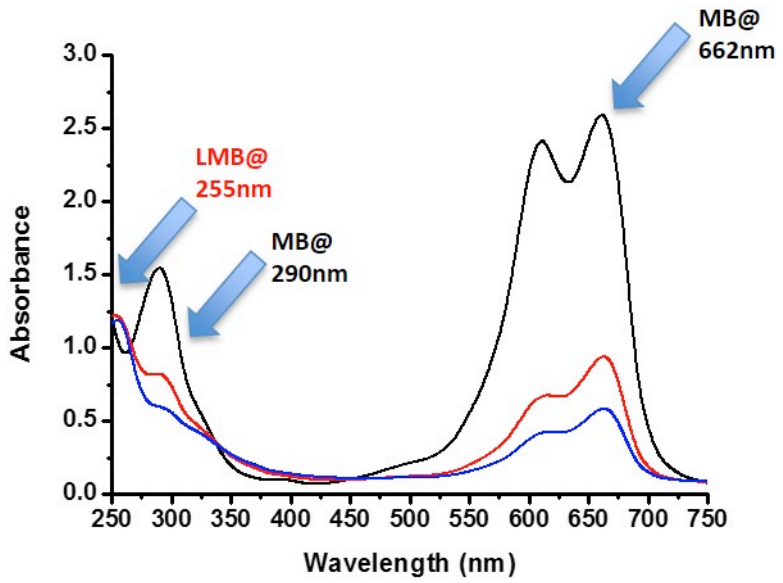

Figure S14. UV-visible absorbance spectra for the reduction of organic dye MB by $NaBH_4$. After the addition of MpSi-Pd nanoparticles, the absorption peaks for MB (290 nm and 650 nm) decreased and new band for Leuco-MB at 255nm appeared in the spectrum.

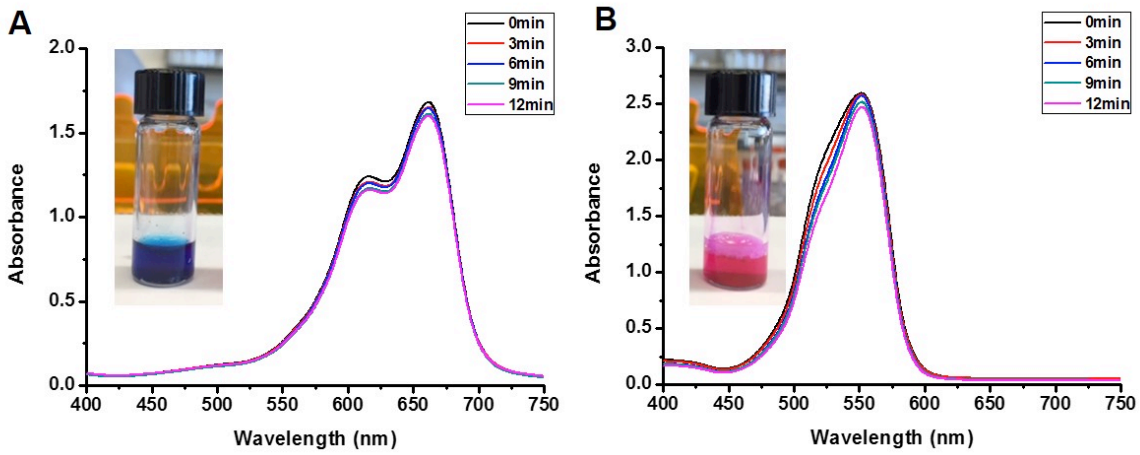

Figure S15. Time-dependent UV-visible absorbance spectra for the reduction of organic dyes by $NaBH_4$, after the addition of MpSi nanoparticles (1mg/mL). No absorbance changes were detected within 12 mins for (A) methylene blue (MB) aqueous solution (1 mM) and (B) Rhodamine B (RhoB) aqueous solution (1 mM). Insets show photographs of the reaction mixtures 12 mins after the addition of the MpSi nanoparticles to the dye + $NaBH_4$ solutions.

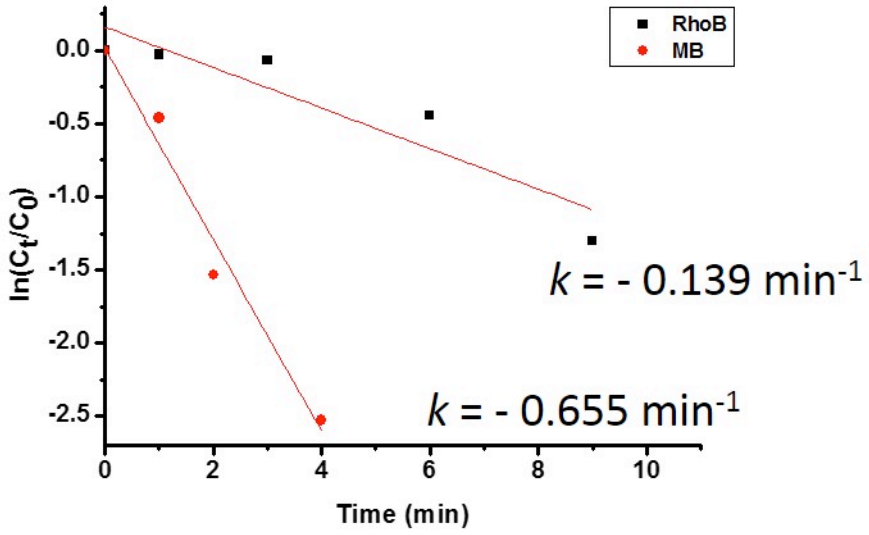

Figure S16. Plot of ln(C_t/C_0) *versus* time for reduction of the organic dyes methylene blue (MB) and rhodamine B (RhoB) by $NaBH_4$, catalyzed by MpSi-Pd nanocomposite; ■ RhoB (1 mM) ; ● MB (1 mM). The rate constant *k* is estimated from the slope of straight line of ln(C_t/C_0) *versus* reaction time.