

Supporting Information

Post-synthetic Functionalization of a Hollow Silica Nanoreactor with Manganese Oxide-Immobilized Metal Nanocrystals inside the Cavity

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General consideration. Any reagent including $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Kanto), Sodium Oleate (TCI), 1-Octadecene (Aldrich), Igepal CO-520 (Aldrich), Tetraethyl Orthosilicate (Acros), NH_4OH (Samchun chem.), Hydroxylamine (Aldrich), Hydrochloric acid (Samchun chem.), Pd on Carbon (Aldrich), Pd on Alumina (Aldrich), Pd on CaCO_3 (Aldrich), $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ (Strem), $\text{Na}_2\text{PtCl}_4 \cdot x\text{H}_2\text{O}$ (Strem), $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (Strem) and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (Strem) were used as purchased without any purification. Analyses of transmission electron microscopy (TEM) were conducted with JEOL JEM-2100. EDS mapping were performed using JEOL JEM-2100F with Cs corrected STEM at National Institute for Nanomaterials Technology (Dr. Nam-Suk Lee). Scanning electron microscopy (SEM) images were captured with a XL30S FEG field-emission scanning electron microscope (Philips electron optics, Netherlands). The contents of the metal elements in the nanoparticle were measured by inductive coupling plasma atomic emission spectrometry (ICP-AES) using Direct Reading Echelle ICP (LEEMAN). The adsorption-desorption isotherm for N_2 (77K) was recorded by using Micromeritics ASAP 2020 at Korea Basic Science Institute (Dr. Sang Moon Lee). The original DFT method for the slit pore geometry was used to extract the pore size distribution from the adsorption branch using the Micromeritics software.^{S1-S4}.

Preparation of CSNP@SiO₂. MnO nanoparticles were prepared by following the reported method.^{S5} The **CSNP@SiO₂** nanospheres were prepared through modifying the previously reported reverse microemulsion technique.^{S6} In the procedure, polyoxyethylene(5)nonylphenylether (1.4 mL, Igepal CO-520) was dispersed in a round bottom flask containing cyclohexane solvent (22 mL). Next, MnO nanoparticles (10 mg) dispersed in a cyclohexane and an ammonium hydroxide aqueous solution (30 %, 0.13 mL) was successively added with the vigorous stirring to form a translucent suspension. Tetraethylorthosilicate (0.34 mL, TEOS) was added to the microemulsion suspension and stirred for 3 h ~ 15 h (3 h, 6 h, 9 h, 12 h, and 15 h). The resulting **CSNP@SiO₂** nanospheres were precipitated out of the reaction suspension by the addition of methanol and then retrieved by the centrifugation. The crude **CSNP@SiO₂** was purified by repeating the dispersion in EtOH and distilled water and the centrifugation for several times. **CSNP@SiO₂** nanospheres synthesized with varying the time period of the silica encapsulation reaction were each used to prepare synthesize **HMON@h-SiO₂** having different silica shell thicknesses.

Preparation of HMION@h-SiO₂. The **HMON@h-SiO₂** was prepared through modifying the previously reported procedure.^{S6} 1 mg/mL of **CSNP@SiO₂** nanoparticles were immersed in a 0.5 M NH_2OH solution and stirred at room temperature for 15 h. The resulting

HMON@h-SiO₂ nanoparticles were isolated from the reaction dispersion by the centrifugation and then purified by repeating the dispersion in water and the centrifugation. The use of **CSNP@SiO₂** nanospheres prepared through silica encapsulation for 3 h, 6 h, 9 h, 12 h, and 15 h gave the **HMON@h-SiO₂** having 7.5 nm, 8.5 nm, 10.3 nm, 11.7 nm, and 12.5 nm of silica shell thicknesses, respectively.

Deposition of metal nanocrystals on the Mn₃O₄ layer of HMION@h-SiO₂; Preparation of HMION/Ms@h-SiO₂ (M = Pd, Pt, Ir, Rh, and Pd/Pt and Pd/Pt/Ir/Rh alloys). In the procedure to prepare **HMON/Pds@h-SiO₂**, 0.5 mg of **HMON@h-SiO₂** was immersed into a 2 mL of Na₂PdCl₄·3H₂O (1.5 mg/mL) aqueous solution, whose pH was adjusted to 2.4 by the addition of diluted HCl solution, at 70 °C and stirred for 30 min. After cooling to room temperature, the resulted **HMON/Pds@h-SiO₂** nanoparticles, which contain 2.5 wt% of Pd and 5.1 wt% of Mn contents, were collected by the centrifugation and purified by repeating the dispersion in an aqueous suspension and the centrifugation three times. The control experiment without Mn₃O₄ layer inside the silica shell was carried out by using hollow silica nanoparticles, which were prepared by treating the **HMON@h-SiO₂** (30 mg) in an aqua regia (12 mL) at room temperature for 12 h, instead of the **HMON@h-SiO₂**.

The preparation of the **HMON/Pts@h-SiO₂** (12 wt% of Pt and 4.4 wt% of Mn), **HMON/Irs@h-SiO₂** (12 wt% of Ir and 11 wt% Mn), and **HMON/Rhs@h-SiO₂** (6.4 wt% of Rh and 4.3 wt% Mn) were conducted by immersing 1 mg of **HMON@h-SiO₂** in Na₂PtCl₄·xH₂O (1 mL, 1 mg/mL), IrCl₃·xH₂O (1 mL, 3 mg/mL), and RhCl₃·xH₂O (1 mL, 3 mg/mL) solutions, at pH 2.4 and stirred for 30 min, 1 h, and 2 h, respectively, at 70 °C. **HMON/(Pd/Pt)@h-SiO₂** (0.5 wt% of Pd, 1.3 wt% of Pt, and 4.5 wt% of Mn) was prepared by adding 3 mg of **HMON@h-SiO₂** in a 3 mL of aqueous suspension containing 1 mg of Na₂PdCl₄·3H₂O and 2 mg of Na₂PtCl₄·xH₂O at pH 2.4 and stirred at 70 °C for 30 min. For the preparation of **HMON/(Pd/Pt/Ir/Rh)@h-SiO₂** (0.7 wt% of Pd, 1.5 wt% of Pt, 2.5 wt% of Ir, 5.5 wt% of Rh, 1.9 wt% of Mn exist), 3 mg of **HMON@h-SiO₂** was added to an aqueous solution of RhCl₃·xH₂O (1 mL, 1 mg/mL) at pH 2.4 and stirred at 100 °C for 20 min. After cooling down to 70 °C, IrCl₃·xH₂O (1 mL, 1 mg/mL, at pH 2.4), Na₂PtCl₄·xH₂O (1 mL, 1 mg/mL, at pH 2.4), Na₂PdCl₄·3H₂O (0.5 mL, 1 mg/mL, at pH 2.4) solutions were sequentially added to the reaction suspension at the interval of 20 min and then stirred for additional 30 min.

Deposition of various metal nanocrystals on Sf-MON. Sf-MON was in advance prepared through the previously reported procedure.^{S7} For the metal deposition of Ir, Rh, and Pd/Pt and Pd/Pt/Ir/Rh alloys, IrCl₃·xH₂O (2 mL, 7.5 mg/mL), RhCl₃·xH₂O (2 mL, 7.5 mg/mL),

and mixtures of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ (1 mL, 3 mg/mL) and $\text{Na}_2\text{PtCl}_4 \cdot x\text{H}_2\text{O}$ (1 mL, 3 mg/mL) and of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ (1 mL, 10 mg/mL), $\text{Na}_2\text{PtCl}_4 \cdot x\text{H}_2\text{O}$ (4 mL, 5 mg/mL), $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (5 mL, 2 mg/mL) and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (10 mL, 5 mg/mL) solutions were, respectively, mixed with 10 mL of an aqueous suspension containing **Sf-MON** (3 mg/mL) and gently stirred at 70 °C. After the reaction for 2 h, the isolated nanoparticles by the centrifugation were further purified by repeating the dispersion in distilled water and the centrifugation three times.

Evaluation of catalytic activities of **HMON/Pds@h-SiO₂** in the oxidation reaction of hydrosilanes.

General procedure for oxidation of hydrosilanes. 0.5 mmol of hydrosilanes, 1.5 mmol of water and 1.5 mL of acetone were mixed in a 10 mL round bottom flask and then 21 mg of **HMON/Pds@h-SiO₂** (1 mol% in Pd basis) was added to the solution. The mixture was stirred at room temperature until hydrosilanes were completely disappeared (as checked by TLC). For the investigation of the recyclability of the catalyst, the nanoparticles were retrieved after the catalytic reaction by the centrifugation, washed with acetone three times, and used for tenth consecutive reactions.

Control catalytic reactions. Control experiments with **Mn₃O₄/Pds**, which was prepared through the previously reported procedure,^{S7} was conducted through the same procedure with that of the hydrosilane oxidation reaction with 1 mol% **HMON/Pds@h-SiO₂**. Another control experiment with **HMON@h-SiO₂** was conducted by adding 21 mg of **HMON@h-SiO₂** instead of **HMON/Pds@h-SiO₂** and stirring for 24 h. The product yields were determined by GC analysis.

References for the Supporting Information

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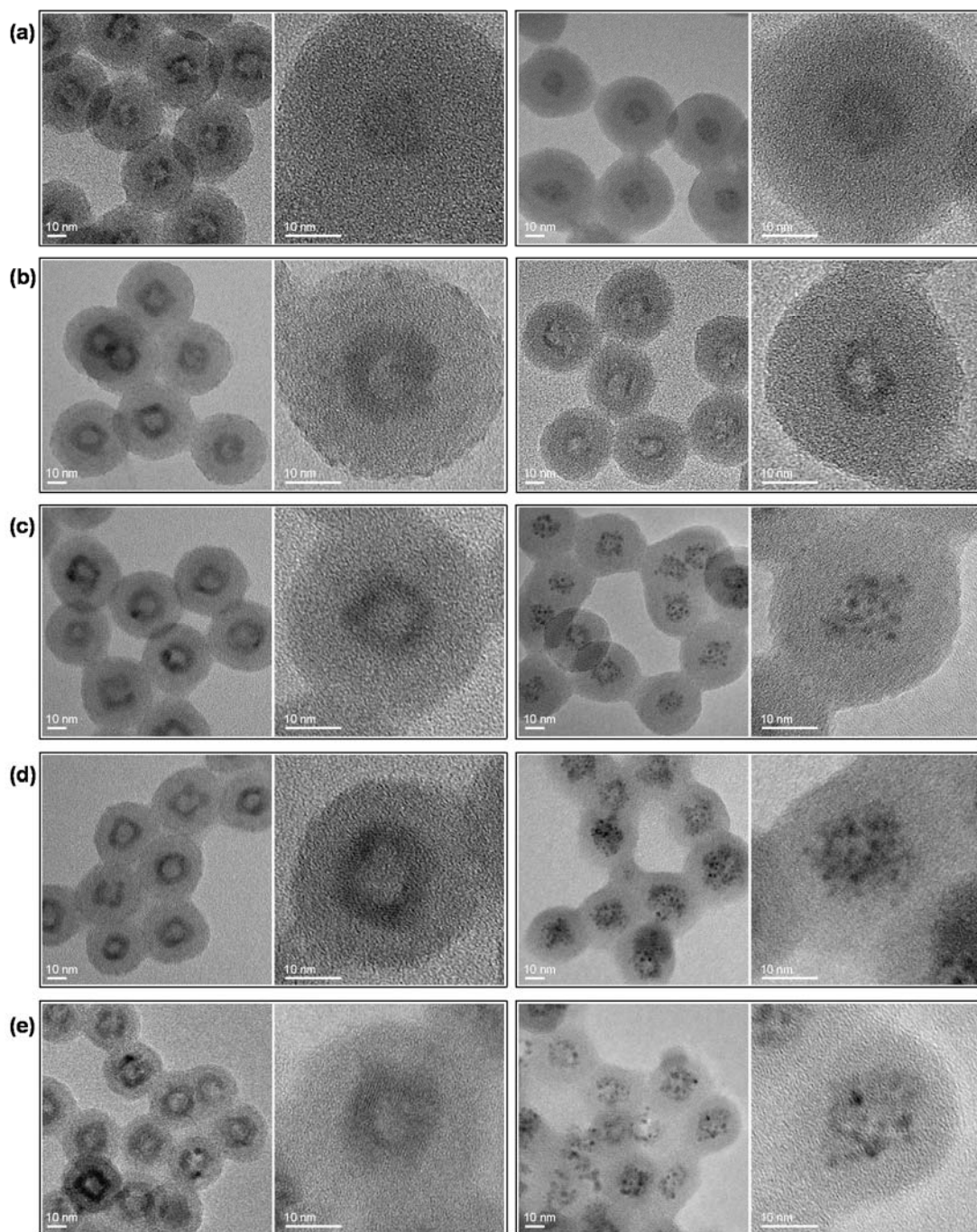


Figure S1. TEM and HRTEM images of **HMION@*h*-SiO₂** having shell thickness of (a) 12.5 nm, (b) 11.7 nm, (c) 10.3 nm, (d) 8.5 nm, and (e) 7.5 nm, which are prepared through silica encapsulation for 15 h, 12 h, 9 h, 6 h, and 3 h, respectively, before (left box) and after (right box) the treatment with Na₂PtCl₄ solution.

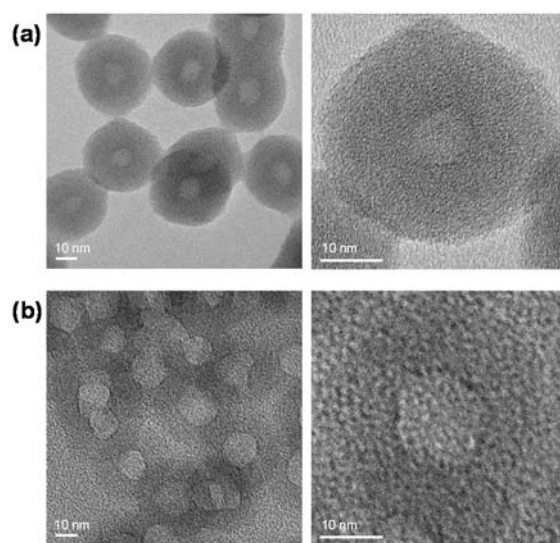


Figure S2. TEM and HRTEM images of a hollow silica nanoparticles, which were prepared from **HMON@*h*-SiO₂** by dissolving Mn₃O₄, (a) before and (b) after the treatment with Na₂PdCl₄ solution.

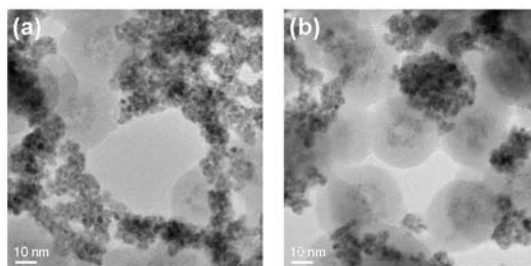


Figure S3. TEM images of the adducts obtained from the reaction of **HMON@*h*-SiO₂** having as a shell thickness of 8.5 nm in Na₂PtCl₄ solutions at (a) pH 3.4 and (b) pH 2.8.

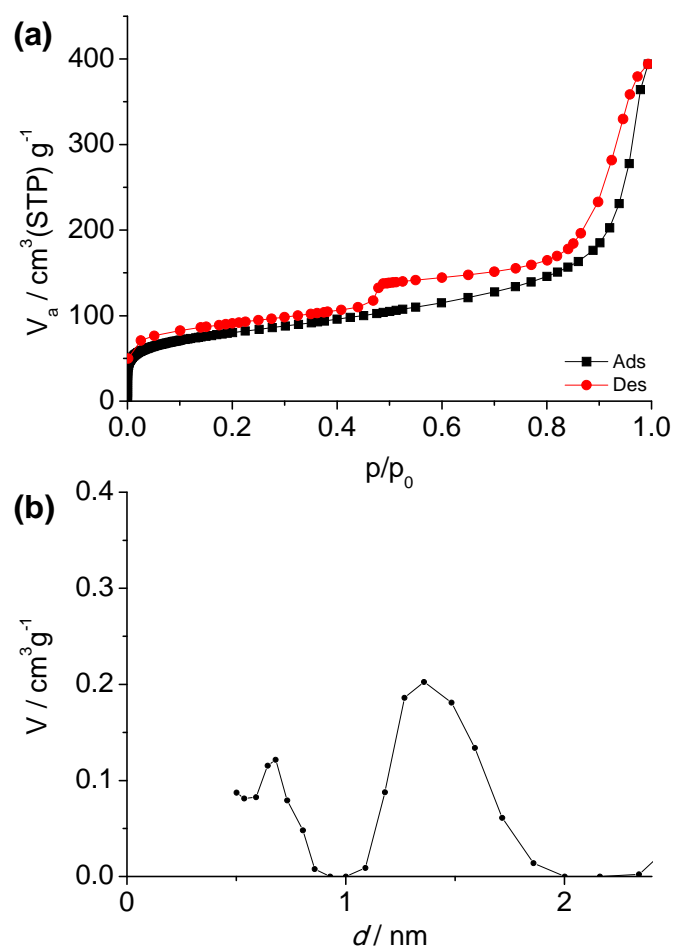


Figure S4. (a) Nitrogen adsorption/desorption isotherm at 77K of the **HMON/Pds@*h*-SiO₂** powder. (b) pore size distribution diagrams by using the DFT method based on the slit-pore geometry.

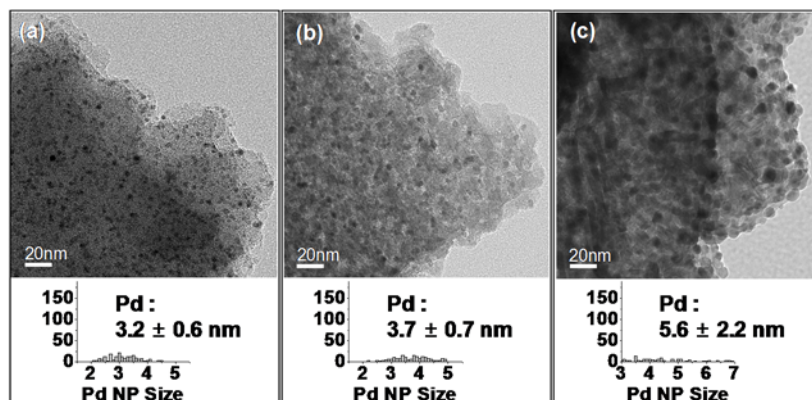


Figure S5. TEM images and Pd nanoparticle histograms of (a) Pd/C, (b) Pd/Al₂O₃, and (c) Pd/CaCO₃.

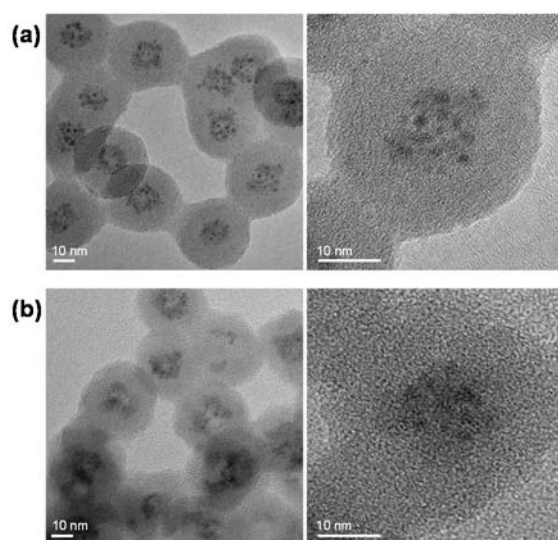


Figure S6. TEM (left) and HRTEM (right) images of **HMON/Pds@*h*-SiO₂** (a) before and (b) after annealing in vacuo at 200 °C for 12 hrs.

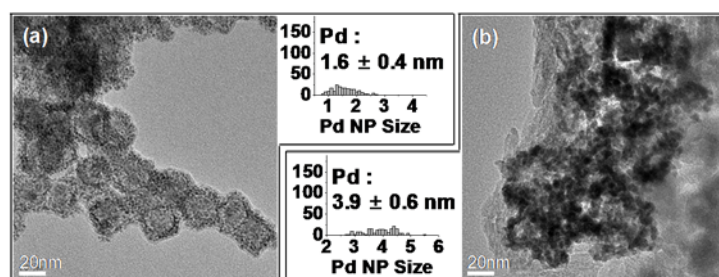


Figure S7. TEM images of $\text{Mn}_3\text{O}_4@\text{Pds}$ (a) before and (b) after the silane oxidation reaction by using 0.0005 mol% of the catalyst.

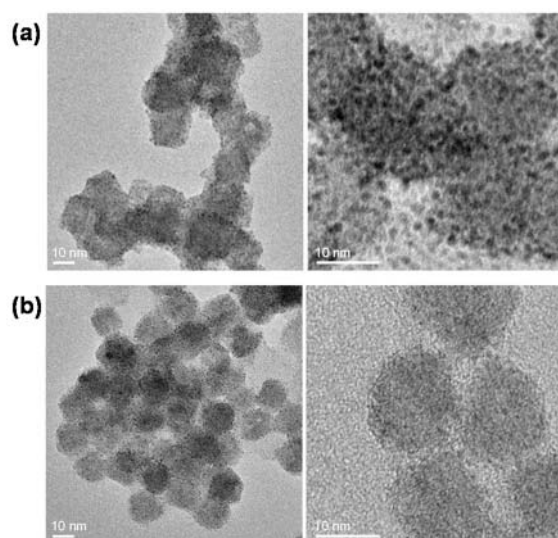


Figure S8. TEM (left) and HRTEM (right) images of **Sf-MON** after treatment in aqueous solutions of (a) IrCl_3 , (b) RhCl_3 .

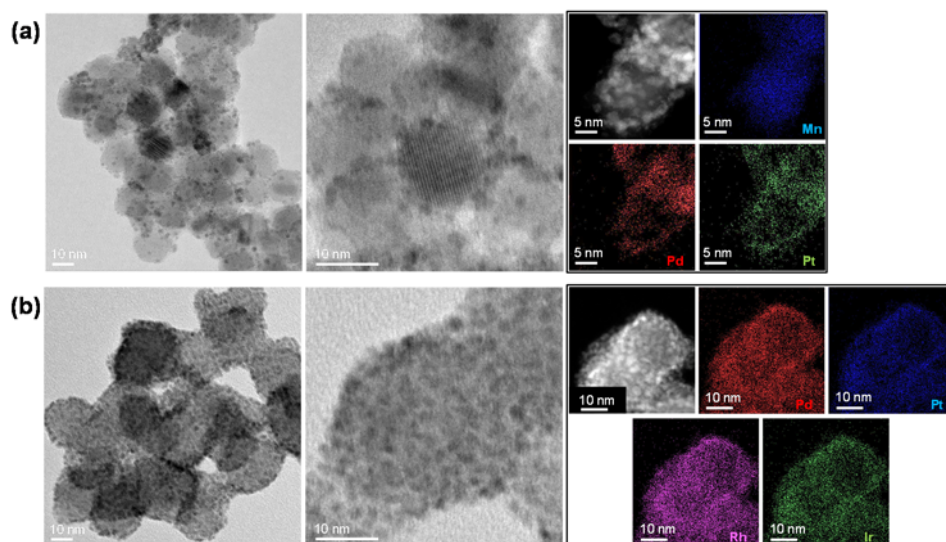


Figure S9. TEM (left), HRTEM (middle), and STEM-HAADF images and elementary maps (right) of the adducts obtained from the reaction of the **Sf-MON** in aqueous solutions of mixtures of (a) Na_2PdCl_4 and Na_2PtCl_4 and (b) Na_2PdCl_4 , Na_2PtCl_4 , IrCl_3 and RhCl_3 .

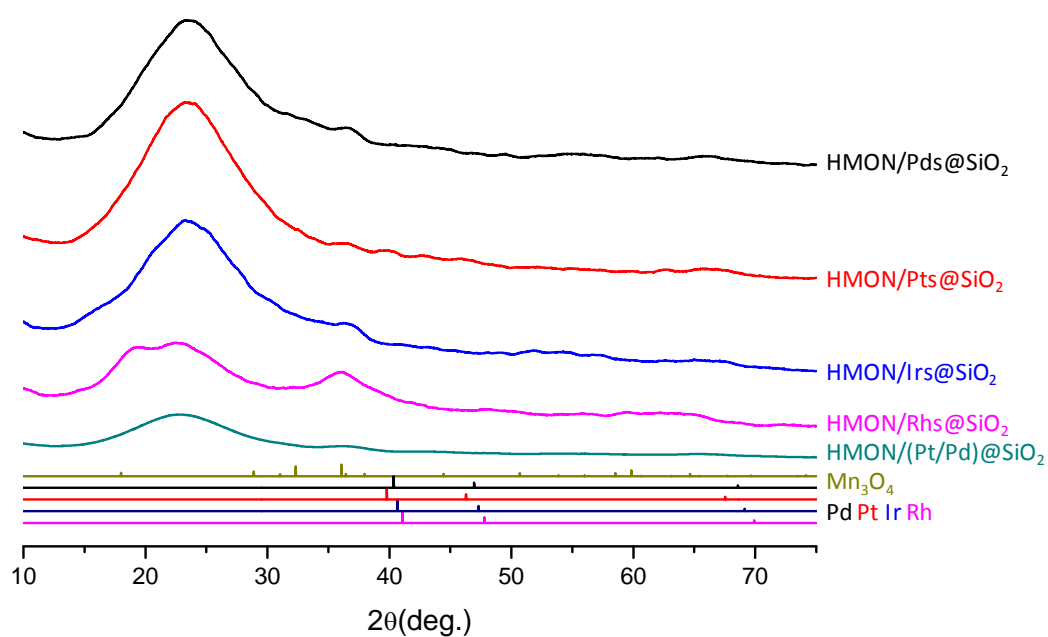


Figure S10. XRD patterns of **HMION/Pds@SiO₂**, **HMION/Irs@SiO₂**, **HMION/Rhs@SiO₂**, **HMION/Pts@SiO₂** and **HMION/(PdPt)@SiO₂**.