

Electronic Supplementary Information (ESI)

**Hollow titanosilicate nanospheres encapsulating PdAu alloy
nanoparticles as reusable high-performance catalysts for
H₂O₂-mediated one-pot oxidation reaction**

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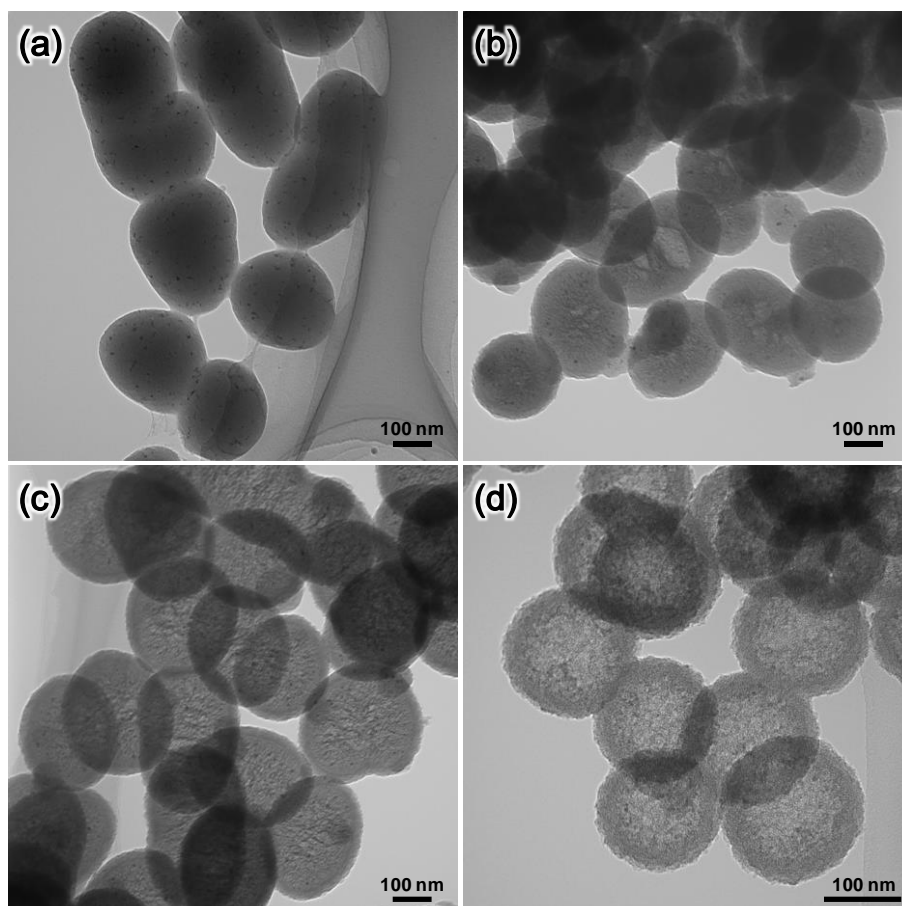


Figure S1. TEM images of the solids collected after (a) 0 h, (b) 10 min, (c) 30 min and (d) 2 h of BTME (1,2-bis(trimethoxysilyl)ethane) addition during the synthesis of Pd@Ti-HMSS.

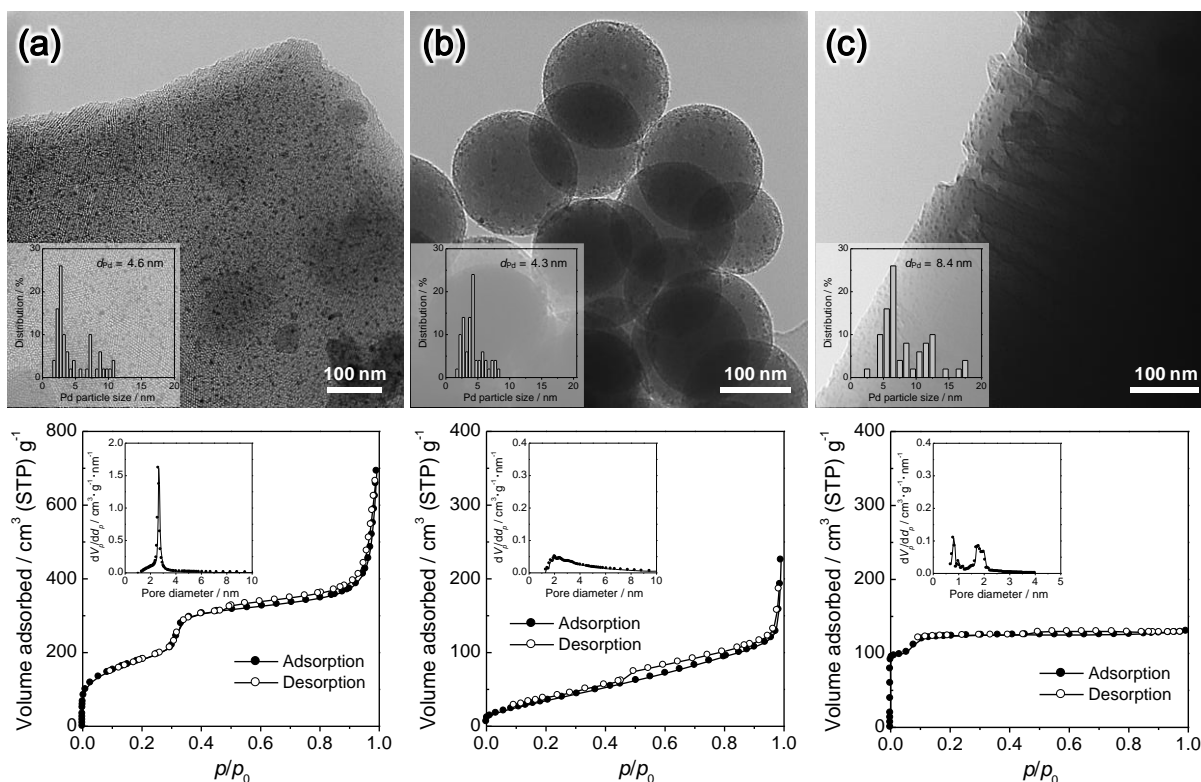


Figure S2. (Above) TEM images (insets show distribution diagrams for Pd NPs) and (Below) N_2 adsorption-desorption isotherms (insets show pore distribution curves) for (a) Pd/Ti-MCM-41, (b) Pd/Ti-SiO₂ sphere and (c) Pd/TS-1 catalysts. Pore distribution curves for Pd/Ti-MCM-41 and Pd/Ti-SiO₂ sphere were determined by BJH (Barrett–Joyner–Halenda) method, and that for Pd/TS-1 was determined by SF (Saito–Foley) method.

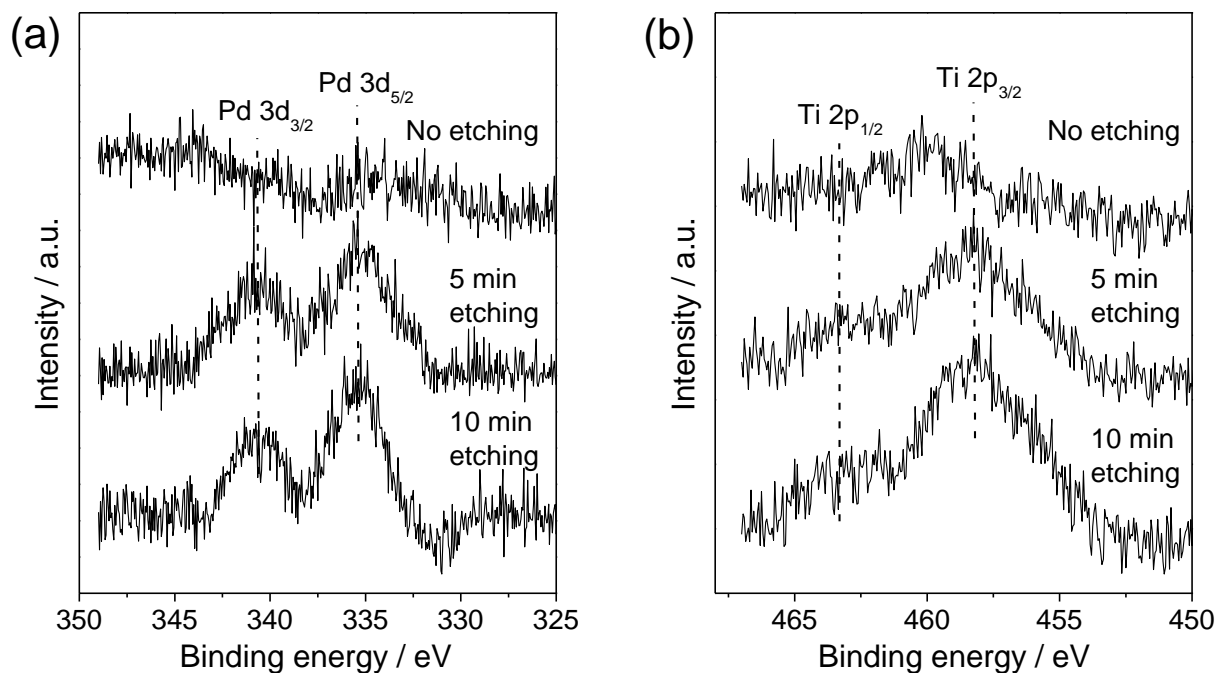


Figure S3. (a) Pd 3d XPS spectra and (b) Ti 2p XPS spectra for Pd@Ti-HMSS catalyst without Ar etching and after Ar etching for 5 min and 10 min.

The peaks seen at around 341 and 335 eV in Figure S3(a) are assignable to Pd 3d_{3/2} and Pd 3d_{5/2} core levels of Pd⁰ species, respectively. These peaks emerged after Ar etching treatment, while they could not be observed without Ar etching, indicating that Pd species are present inside the hollow silica spheres. Similarly, the peaks seen at around 463 and 458 eV in Figure S3(b) are assignable to Ti 2p_{1/2} and Ti 2p_{3/2} core levels of Ti⁴⁺ oxide species, respectively. The intensity of these peaks increased after Ar etching treatment, indicating that Ti species are mostly present in the silica matrices of the shell.

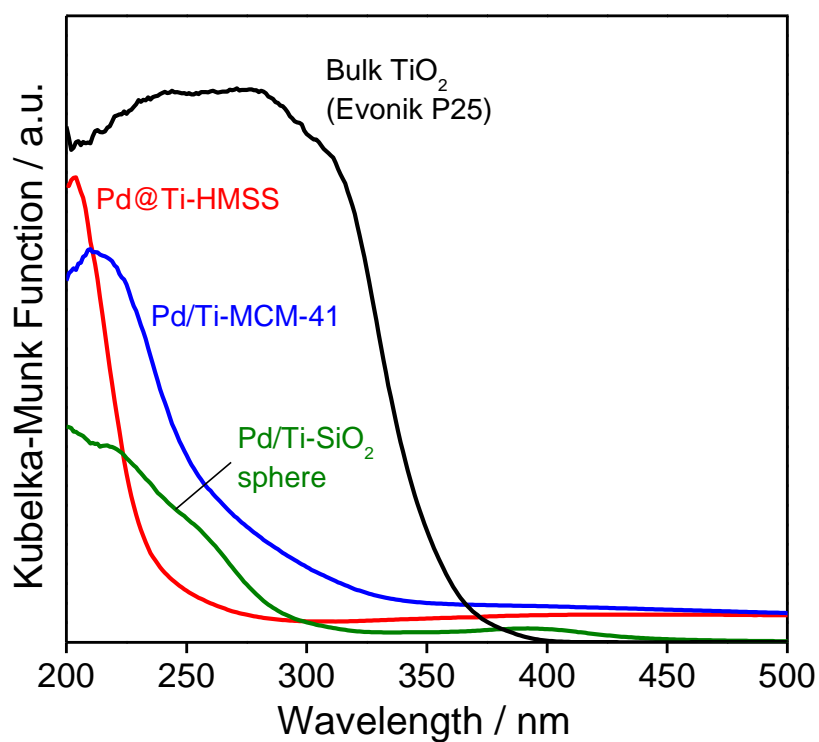


Figure S4. Diffuse reflectance UV-vis spectra of Pd@Ti-HMSS, Pd/Ti-MCM-41, Pd/Ti-SiO₂ sphere and bulk TiO₂ powder (Evonik P25).

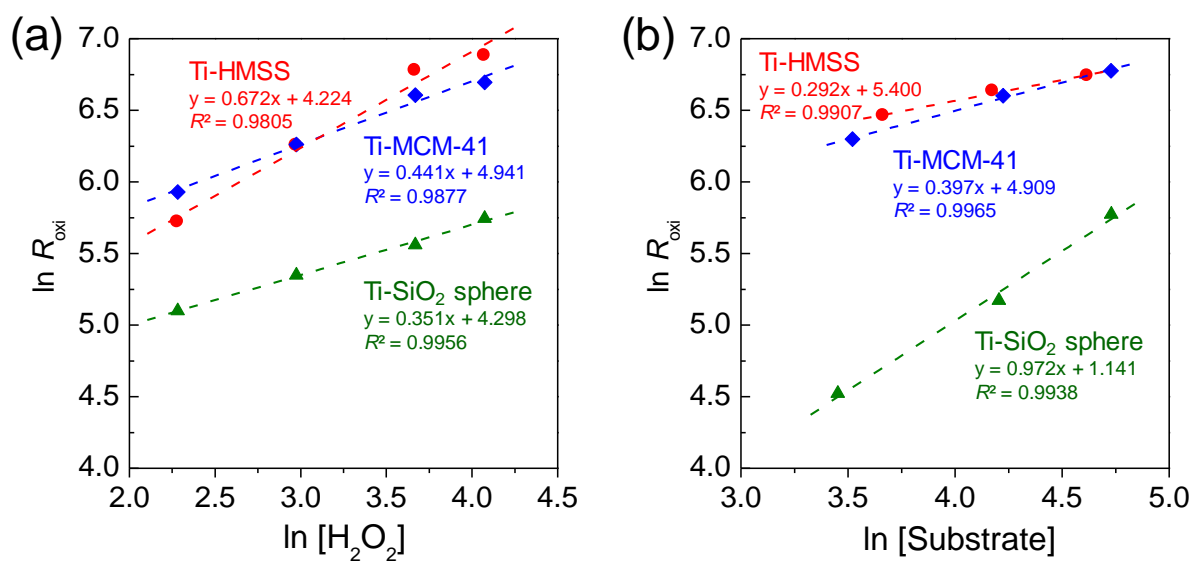


Figure S5. (a) Double logarithm plots of the H_2O_2 concentration ($[\text{H}_2\text{O}_2]$) and the initial reaction rates in the oxidation of methyl phenyl sulfide (R_{oxi}). *Reaction conditions:* catalyst (50 mg), methyl phenyl sulfide (0.3 mmol), H_2O_2 (0.1-0.6 mmol), acetonitrile (10 mL), 30 °C, $t = 15$ min. (B) Double logarithm plots of the substrate concentration ($[\text{Substrate}]$) and the initial reaction rates in the oxidation of methyl phenyl sulfide (R_{oxi}) over Ti-HMSS, Ti-MCM-41 and Ti-SiO₂ sphere catalysts. *Reaction conditions:* catalyst (50 mg), methyl phenyl sulfide (0.3-1.0 mmol), H_2O_2 (0.2 mmol), acetonitrile (10 mL), 30 °C, $t = 15$ min.

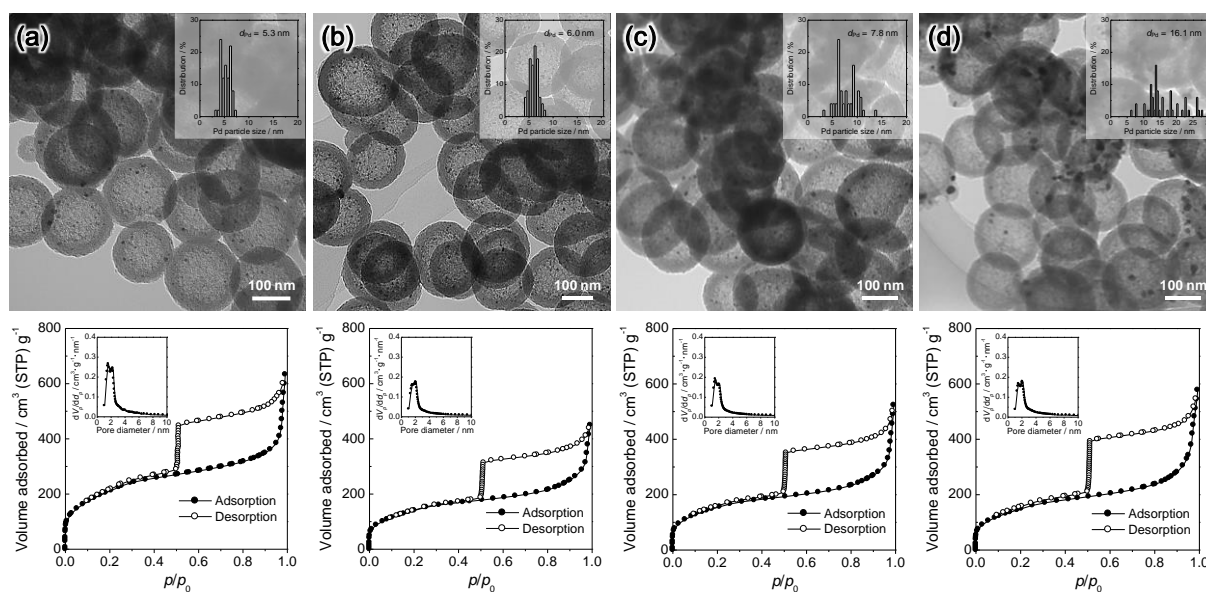


Figure S6. (Above) TEM images (insets show distribution diagrams for PdAu NPs) and (Below) N_2 adsorption-desorption isotherms (insets show pore distribution curves determined by BJH method) for PdAu@Ti-HMSS catalysts synthesized with varied Pd/Au ratios (Pd : Au = (a) 1 : 0.3, (b) 1 : 0.5, (c) 1 : 1, (d) 1 : 3).

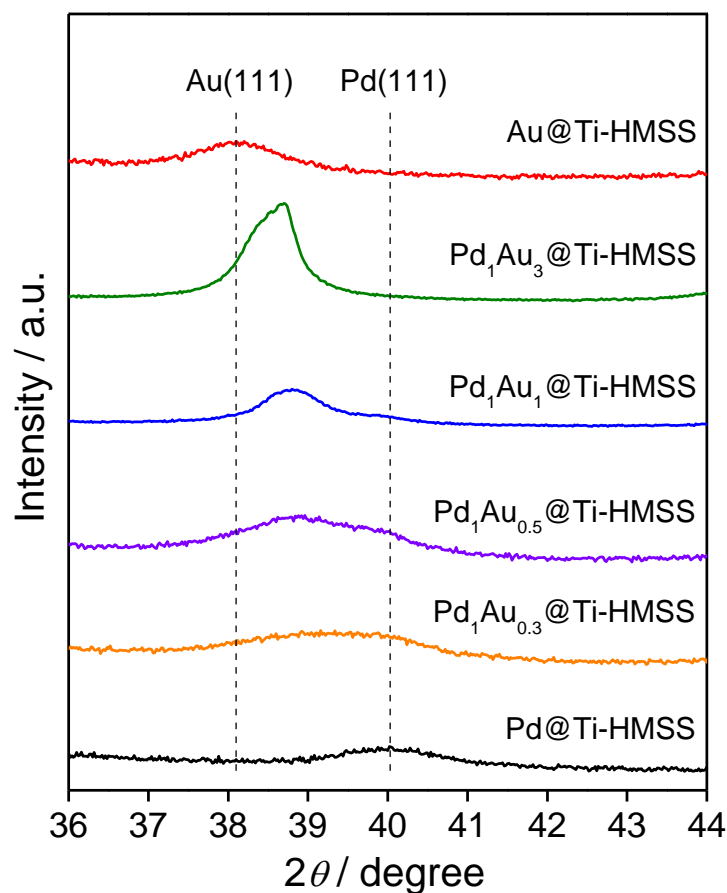


Figure S7. XRD patterns of PdAu@Ti-HMSS catalysts synthesized with varied Pd/Au ratios. The peaks seen at around $2\theta = 38.1^\circ$ and 40° are assigned to (111) plane of Au metal and Pd metal, respectively.

The gradual shift of the peak is due to the increased lattice constant which is caused by the incorporation of Au with larger atomic radius than that of Pd, evidencing the formation of randomly-mixed PdAu alloy NPs. The gradual increase of peak intensity is simply due to the increased content of Pd+Au in the samples (Pd content was fixed in all samples, and Au content was varied in this study. For Pd and Au contents of the samples, see Table 2 in the main text).

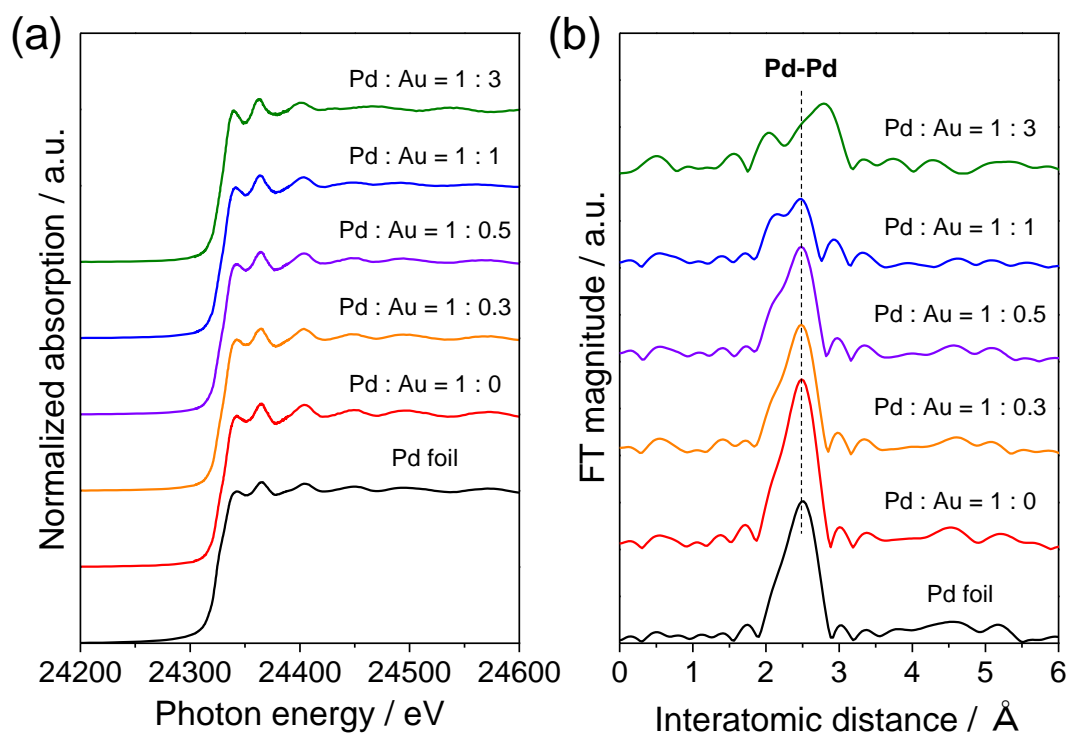


Figure S8. (a) Pd K-edge XANES spectra and (b) RDFs obtained from Pd K-edge EXAFS oscillations for the series of PdAu@Ti-HMSS samples with different Pd/Au ratios and Pd foil as a reference.