Supporting Information

Upgrading of palmitic acid over MOF catalysts in supercritical fluid of n-hexane

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**MOF-5 hollow nanospheres**

In a typical procedure, Zn(NO$_3$)$_2$·6H$_2$O 11.6 mg, H$_2$BDC 2.4 mg, and PVP (MW=30000, 150 mg) were dissolved in DMF-ethanol mixture (6.4 mL, v/v = 5:3) under magnetic stirring for 10 minutes at room temperature. The resulting homogeneous solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150 °C for 12 h before it was cooled to room temperature. The products were separated via centrifugation at 11000 rpm for 15 minutes and further purified with DMF and ethanol for several times. [1]

**PTA@MOF-5 hollow nanospheres**

11.6 mg Zn(NO$_3$)$_2$·H$_2$O, 2.4 mg H$_2$BDC, 150 mg PVP and 2.4 mg PTA were dissolved in 6.4 mL DMF-ethanol mixture (v/v = 5:3) under magnetic stirring for 10 minutes at room temperature. The resulting homogeneous solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. After heating the sealed vessel at 150 °C for 12 h it was cooled to room temperature. The products were separated via centrifugation at 11000 rpm for 15 min and further purified with DMF and ethanol for several times.

**Preparation of Fe$^{III}$-MOF-5 hollow octahedral nanostructures.**

In a typical procedure, Fe(acac)$_3$, 60 mg, Zn(NO$_3$)$_2$·6H$_2$O 46.4 mg, H$_2$BDC 9.6 mg, and PVP (M$_W$= 30000, 200 mg) were dissolved in DMF-ethanol mixture (25.6 mL, v/v = 5:3) under magnetic stirring for 10 minutes at room temperature. The resulting
homogeneous solution was transferred to a 40 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 100 °C for 6 h before it was cooled to room temperature. The products were separated via centrifugation at 11000 rpm for 15 min and further purified with DMF and ethanol for several times. [1]

**Synthesis of PdCu dendrites.**

In a typical synthesis, PdCu dendrites were synthesized according to the previous report [1]. Briefly, Pd(acac)$_2$ (7.6 mg), Cu(acac)$_2$ (6.5 mg), and PVP (M$_w$ = 30000, 50 mg) were dissolved in DMF (4 mL) with stirred for 10 min at room temperature and heated to 150 °C for 4 h in a 12 mL Teflon-lined stainless-steel autoclave. The resulting products were separated via centrifugation at 11000 rpm for 15 minutes and further purified with ethanol for several times.

**Synthesis of Pd NPs.**

Pd NPs were synthesized using the same procedure as PdCu alloy NPs but without the addition of Cu(acac)$_2$ in the reaction solution. [1]

**Synthesis of Au NPs.**

Briefly, PVP (M$_w$= 30000, 50 mg), and H$_2$C$_2$O$_4$ (0.5 mmol, 63 mg) were dissolved in formamide (5 mL) and heated to 120 °C, and HAuCl$_4$·4H$_2$O aqueous solution (0.25mL, 0.2 M) was injected and the solution was maintained at 120 °C for 10 min. The products were separated via centrifugation at 10000 rpm for 5 minutes and
further purified with ethanol for several times. [2]

**General nanoparticle encapsulation procedure.**

For all nanoparticles ethanol was used as solvent. Typically, a 2 mL nanoparticles solution of desired concentration and PVP (M_w = 30000, 200 mg) were mixed with DMF-ethanol mixture (23.6 mL, v/v =5:3) under magnetic stirring for 10 min at room temperature. Then, Fe(acac)_3 60mg, Zn(NO_3)_2·6H_2O 46.4 mg, H_2BDC 9.6 mg were added to the above solution under magnetic stirring for another 10 minutes. The resulting solution was transferred to a 40 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 100 °C for 6 h before it was cooled to room temperature. The products were separated via centrifugation at 11000 rpm for 15 minutes and further purified with DMF and ethanol for several times. [1]

**Characterization**

Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Bruker D8-advance X-ray powder diffractometer operated at 40 kV voltage and 40 mA current with CuKα radiation (λ=1.5406 Å). Transmission electron microscopy (TEM) was performed on a JEM 2100 LaB6 TEM (JEOL). X-ray photoelectron spectroscopy (XPS) was performed on scanning X-ray microprobe (Quantera SXM, ULVAC-PHI. INC) operated at 250 kV, 55 eV with monochromated Al Kα radiation. Binding energies were corrected by reference to the C 1s peak at 284.8 eV. Fourier-transformed infrared resonance (FT-IR) spectra were obtained in transmission
mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA). Thermogravimetric (TG) analysis was carried out at a constant heating rate of 10 °C min⁻¹ from room temperature to 700 °C in N₂ atmosphere, using a TA-50 thermal analyzer. Elemental analysis of Pd, Cu and W in the solid samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, ThermoFisher). The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated by the Barrett - Joyner - Halenda (BJH) method.
Figure captions:

**Fig. S1** TEM image of MOF-5.

**Fig. S2** TEM image of PTA@MOF-5.

**Fig. S3** TEM image of FeIII-MOF-5.

**Fig. S4** TEM image of PdCu@FeIII-MOF-5.

**Fig. S5** TEM image of Pd NPs@FeIII-MOF-5.

**Fig. S6** TEM image of Au NPs@FeIII-MOF-5.

**Fig. S7** TEM image of PdCu dendrites.

**Fig. S8** TEM image of Pd NPs.

**Fig. S9** TEM image of Au NPs.

**Fig. S10** XRD analysis of FeIII-MOF-5.

**Fig. S11** XPS spectra of PTA@FeIII-MOF-5 hollow octahedral nanostructures: (a) The survey spectrum; (b) XPS Fe 2p spectrum; (c) XPS Zn 2p spectrum.

**Fig. S12** XRD analysis of Au NPs.

**Table S1** Catalytic HDO of palmitic acid in traditional meida.
Fig. S1 TEM image of MOF-5.

Fig. S2 TEM image of PTA@MOF-5.
Fig. S3 TEM image of Fe$^{III}$-MOF-5.

Fig. S4 TEM image of PdCu@Fe$^{III}$-MOF-5.
Fig. S5 TEM image of Pd NPs@Fe$^{III}$-MOF-5.

Fig. S6 TEM image of Au NPs@Fe$^{III}$-MOF-5.

Fig. S7 TEM image of PdCu dendrites.
Fig. S8 TEM image of Pd NPs.

Fig. S9 TEM image of Au NPs.
Fig. S10 XRD analysis of Fe$^{III}$-MOF-5.
Fig. S11. XPS spectra of PTA@Fe$^{\text{III}}$-MOF-5 hollow octahedral nanostructures: (a) The survey spectrum; (b) XPS Fe 2p spectrum; (c) XPS Zn 2p spectrum.

As shown in Figure S11b, the Fe 2p peaks of Fe$^{\text{III}}$-MOF-5 hollow spheres at $\sim$711 eV and $\sim$725 eV are assigned to Fe 2p3/2 and Fe 2p1/2 for iron (III) oxide, and the additional satellite peaks at $\sim$718 eV and $\sim$733 eV are associated with Fe 2p3/2 and Fe 2p1/2, which exhibits similar spectra with those of Fe$_2$O$_3$. [3] The Zn 2p peaks at $\sim$1021 eV and $\sim$1044 eV are assigned to Zn 2p3/2 and Zn 2p1/2 for zinc (II) oxide. [4]

Fig. S12. XRD analysis of Au NPs.

As shown in Fig. S12, the XRD analysis of the as-synthesized Au NPs coincides
with the literatures [1, 2].

Table S1 Catalytic HDO of palmitic acid in traditional media.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T / °C</th>
<th>t / h</th>
<th>P_{H2} / MPa</th>
<th>Conv. / %</th>
<th>Product distribution / %</th>
</tr>
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<tbody>
<tr>
<td>5 % MoO_2/CNTs [5]</td>
<td>220</td>
<td>4</td>
<td>4</td>
<td>100</td>
<td>Pentadecane / 7.60, Hexadecane / 92.20</td>
</tr>
<tr>
<td>1.5 % Co-5 % MoO_2/CNTs [6]</td>
<td>180</td>
<td>4</td>
<td>4</td>
<td>100</td>
<td>Pentadecane / 5.20, Hexadecane / 89.30</td>
</tr>
<tr>
<td>5 % Ni/CNTs [7]</td>
<td>240</td>
<td>4</td>
<td>2</td>
<td>97.25</td>
<td>Pentadecane / 89.64</td>
</tr>
<tr>
<td>Mo/HZ-R [8]</td>
<td>260</td>
<td>4</td>
<td>4</td>
<td>100</td>
<td>n-C_{15} / multi-iso-C_{16} / mono-iso-C_{16} / n-C_{16}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.6 / 15.6 / 44.1 / 15.8</td>
</tr>
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References


