# **Supplementary Information**

# The influence of the MOF shell thickness in the catalytic performance of composites made of inorganic (hollow) nanoparticles encapsulated into MOFs

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# **Experimental details**

#### Materials

All reagent and solvents used were purchased from Sigma Aldrich and used without further purification.

#### Synthesis of hollow nanoparticles

Synthesis of silver nanoparticles (Ag NPs): Ag NPs of ~ 24 nm in diameter were prepared by scaling up the seeded-growth method previously reported by Bastús *et al.*<sup>1</sup> In this method, silver seeds were first obtained by filling a three-neck round-bottomed flask with 750 mL of an aqueous solution containing 5 mM sodium citrate (SC) and 0.1 mM of tannic acid (TA). This mixture was then heated up to 100 °C using a heating mantle. After boiling had started, 7.5 mL of 25 mM AgNO<sub>3</sub> was injected into this solution under vigorous stirring. The obtained silver seeds were then grown by cooling down the solution to 90 °C, and sequentially injecting 0.75 mL of 25 mM SC, 1.875 mL of 2.5 mM TA and 1.875 mL of 25 mM AgNO<sub>3</sub>. This process was repeated up to four times, progressively growing the Ag NPs up to ~ 24 nm. The obtained Ag NPs were purified by centrifugation and further re-suspended in water. See Figure S1 for STEM images.

**Synthesis of hollow nanoparticles:** The standard protocol for the preparation of hollow nanoparticles consisted in two simple steps. First, 200 mL of the synthesized Ag NPs solution were precipitated by centrifugation, re-dispersed in 15 mL of PVP (5 mM, 275 mg/mL), and the resulting solution was left in a glass vial under soft stirring for 24 h. And second, 2.5 mL of HCl (250 mM) and 0.5 mL of 1 mM of K<sub>2</sub>PtCl<sub>4</sub> or K<sub>2</sub>PdCl<sub>6</sub> were simultaneously added into this solution. After this very first injection, an additional volume of 9.5 mL of the precursor was added into the vial in 19 consecutive 0.5 mL injections with a time delay of 5 min between each one. During the whole process, the solution was kept under vigorous stirring at room temperature until the reaction was completed; which can be clearly identified by a progressive change in color: from yellow (Ag NPs) to dark gray in the case of the hollow Pt NPs, and from yellow to blue/purple for the hollow Pd NPs. See Figure S2 for the schematic representation of this synthetic process.

**Purification of the hollow nanoparticles:** 20 min after the last precursor injection, the solution was diluted by adding 16 mL of mQ-water and 4 mL of acetone, and then centrifuged at 10,000 g for 60 min. The supernatant was then removed to discard the unreacted precursor species, and the pellet was re-dispersed in 10 mL of 5 mM PVP. After that, the solution was supersaturated with NaCl and gently stirred for 30 min to remove the insoluble AgCl (by-product of the galvanic reaction) from the hollow NP surface. The obtained hollow NPs where then precipitated and re-suspended in mQ-water three times to get rid of the excess PVP in solution. Finally, the solution was left overnight without stirring to let possible remaining AgCl to precipitate at the bottom of the vial (white pellet), which was finally discarded.

#### Size determination of the composites

The size of the rhombic dodecahedral MOF@iNP composites (defined as c) was calculated by the average of the distance between opposite vertices ( $c_2$ ) and the distance between opposite rhombic faces ( $c_1$ ). The average MOF shell thickness **b** of each composite was obtained from b = c/2 - a ( $\Delta b = \Delta c/2 + \Delta a$ ).



 $c=(c_1+c_2)/2$ 

#### **Reduction of 4-nitrophenol**

The catalytic reactions were conducted by mixing 0.5 mL of an aqueous solution of NaBH<sub>4</sub> (1.3 M) with 3.0 mL of an aqueous solution of 4-NP (0.125 mM). After 2 min, 0.2 mL of an aqueous solution of 0.6, 1.68, 2.1 and 2.1 mg·mL<sup>-1</sup> of ZIF-8@PtNP-1, ZIF-8@PtNP-2, ZIF-8@PtNP-3 and ZIF-8@PtNP-4, respectively, and 0.4, 1.1 and 1.76 mg·mL<sup>-1</sup> of ZIF-8@PdNP-1, ZIF-8@PdNP-2 and ZIF-8@PdNP-3, respectively, were injected into the reaction mixture, and the reaction was followed every 10 min by UV-vis spectroscopy in the range of 280–460 nm.<sup>2</sup>

### **Reduction of Eosin Y**

The catalytic reactions to study the reduction of  $EY^{2-}$  were conducted by mixing 1.5 mL of an aqueous solution of  $EY^{2-}$  (4 × 10<sup>-5</sup> M) with 0.6 mL of an aqueous solution of 0.6, 1.68, 2.1 and 2.1 mg·mL<sup>-1</sup> of ZIF-8@PtNP-1, ZIF-8@PtNP-2, ZIF-8@PtNP-3 and ZIF-8@PtNP-4, respectively, and 0.4, 1.1 and 1.76 mg·mL<sup>-1</sup> of ZIF-8@PdNP-1, ZIF-8@PdNP-2 and ZIF-8@PdNP-3, respectively. Then, the volume of the resulting mixture was adjusted to 2.5 mL by the addition of 0.4 mL of deionized water. After 3 min, 0.5 mL of an aqueous solution of NaBH<sub>4</sub> (0.12 M) was injected into the reaction mixture, and the reaction was followed every 10 min by UV-vis spectroscopy in the range of  $300-600 \text{ nm.}^3$ 

## Characterization

Field-emission scanning electron microscopy (FESEM) images were collected on a scanning electron microscope (FEI Magellan 400L XHR) at acceleration voltage of 2.0 kV, using aluminium as support. The size of crystals was calculated from high angle annular dark field scanning transmission electron microscope (HAADF-STEM) images by averaging the diameter of at least 100 particles from images of different areas of the same samples. HAADF-STEM and TEM images and EDX composition profiles were collected on a Transmission Electron Microscopy (TEM; FEI Tecnai G2 F20) at 200 KV. X-ray powder diffraction (XRPD) measurements were performed using an X'Pert PRO MPDP analytical diffractometer. ICP-MS measurements were performed using an ICP\_MS Agilent Serie 7500. UV–Vis Spectroscopy. UV–visible spectra were acquired with a Shimadzu UV-2400 spectrophotometer. Samples were placed in a cell, and spectral analysis was performed at room temperature.

#### References

- 1. N. G. Bastús, F. Merkoçi, J. Piella and V. Puntes, *Chemistry of Materials*, 2014, **26**, 2836-2846.
- 2. Z. Li and H. C. Zeng, *Chemistry of Materials*, 2013, **25**, 1761-1768.
- 3. G. Weng, M. A. Mahmoud and M. A. El-Sayed, *The Journal of Physical Chemistry C*, 2012, **116**, 24171-24176.

**Figure S1**. STEM images of the Ag NPs used as templates for the synthesis of the hollow Pt and Pd NPs. Inset shows the size distribution after counting more than 600 NPs.



Figure S2. Schematic procedure of the synthesis of the hollow Pt and Pd NPs.



**Figure S3**. (a) TEM images of the synthesized hollow Pt NPs; and (b) corresponding size distribution of both diameter and shell thickness.



**Figure S4**. (a) STEM images of the synthesized hollow Pd NPs; and (b) corresponding size distribution of both diameter and shell thickness.



Figure S5. EDX profile of (a) ZIF-8@PtNP-3 and (b) ZIF-8@PdNP-2.



**Figure S6.** X-Ray Powder Diffraction (XRPD) patterns of ZIF-8@PtNP and ZIF-8@PdNP composites, as compared to the simulated pattern for the crystal structure of ZIF-8 (black).



**Figure S7.** UV-vis spectra evolution of the  $EY^{2^{-}}$  reduction with NaBH<sub>4</sub> in the absence of hollow iNPs as catalysts: in (a), with the presence of 3 mg of ZIF-8; and in (b), with the absence of ZIF-8. For all spectra: 0 min (black), 10 min (red), 20 min (blue), 30 min (pink), 40 min (green), and 50 min (navy). Both control experiments confirm that the reduced  $EY^{3^{-}}$  (peak at 405 nm) is not formed in the absence of hollow iNPs.





**Figure S8.** FESEM images of ZIF-8@PdNP-1 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of *4-NP* reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are  $1 \mu m$ .





**Figure S9.** FESEM images of ZIF-8@PdNP-1 after (a) 10 min, (b) 20 min, (c) 30 min and (d) 40 min of EY reduction. White arrows in (d) highlight the etching of ZIF-8. Scale bars for all images are 1 μm.



**Figure S10.** FESEM images of ZIF-8@PdNP-2 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of *4-NP* reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1 μm.



**Figure S11.** FESEM images of ZIF-8@PdNP-2 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of EY reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1 μm.





**Figure S12.** FESEM images of ZIF-8@PdNP-3 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min and (f) 60 min of *4-NP* reduction. White arrows in (f) highlight the etching of ZIF-8. Scale bars for all images are 2  $\mu$ m.



**Figure S13.** FESEM images of ZIF-8@PdNP-3 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min and (f) 60 min of EY reduction. White arrows in (f) highlight the etching of ZIF-8. Scale bars for all images are 2 μm.



**Figure S14.** FESEM images of ZIF-8@PtNP-1 after (a) 10 min, (b) 20 min, (c) 30 min and (d) 40 min of 4-NP reduction. White arrows in (d) highlight the etching of ZIF-8. Scale bars for all images are  $1 \mu m$ .



**Figure S15.** FESEM images of ZIF-8@PtNP-1 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of EY reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1  $\mu$ m.



**Figure S16.** FESEM images of ZIF-8@PtNP-2 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of *4-NP* reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1 μm.



**Figure S17.** FESEM images of ZIF-8@PtNP-2 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of EY reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1  $\mu$ m.





**Figure S18.** FESEM images of ZIF-8@PtNP-3 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of *4-NP* reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1 μm.



**Figure S19.** FESEM images of ZIF-8@PtNP-3 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min and (e) 50 min of EY reduction. White arrows in (e) highlight the etching of ZIF-8. Scale bars for all images are 1  $\mu$ m.





**Figure S20.** FESEM images of ZIF-8@PtNP-4 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min and (f) 60 min of *4-NP* reduction. White arrows in (f) highlight the etching of ZIF-8. Scale bars for all images are 2  $\mu$ m.



**Figure S21.** FESEM images of ZIF-8@PtNP-4 after (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, (f) 60 min and (g) 70 min of EY reduction. White arrows in (g) highlight the etching of ZIF-8. Scale bars for all images are 2 μm.



**Figure S22.** Representative X-Ray Powder Diffraction (XRPD) patterns of ZIF-8@PtNP-4 and ZIF-8@PdNP-3 composites after stopping the catalytic reactions, as compared to the simulated pattern for the crystal structure of ZIF-8 (black). These spectra confirm that these composites retain the crystallinity under the studied conditions.



**Figure S23**. The calibration line of the absorbance maxima at wavelength, 400 nm, versus the *4-NP* concentration, giving an extinction coefficient value of  $12.8 \times 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$ .

