

Electronic Supplementary Material (ESI) for CrystEngComm.

Controlled Growth of Metal-Organic Framework on Gold Nanoparticles

Jiating He,^a Ray Chin Chong Yap,^a Siew Yee Wong,^a Yu Zhang,^a Yating Hu,^b Chao Chen,^a Xikui Zhang,^a John Wang,^b Xu Li^{a, c, *}

^aInstitute of Materials Research and Engineering, A*STAR, 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634

^bDepartment of Materials Science and engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575

^cDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

Materials and Methods

Materials

4-mercaptobenzoic acid (MBA, 90%, Sigma Aldrich), 2-naphthalenethiol (NPT, 90%, Sigma Aldrich), hydrogen tetrachloroaurate(III) (99.9%, Au 49% on metals basis, Alfa Aesar), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), Polyvinylpyrrolidone (PVP, 99%, Alfa Aesar), Zinc nitrate (Sigma Aldrich), 2-methylimidazole (Sigma Aldrich) and methanol (analytical grade) were used as received. Au nanorods (NR-40-700-100) were purchased from Nanoseedz Ltd. Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from XinXing BaiRui (T10023).

Characterization

Transmission electron microscopy (TEM) images were collected on a high-resolution transmission electron microscope (Philips CM 300). X-ray diffraction data was collected on Panalytical X'pert Pro X-ray diffractometer. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer. The loading amount of the catalyst in nano-hybrids was calculated based on the data collected on an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS). For ICP characterization, the Au-ZIF-8 nano-hybrids were dissolved in aqua regia solution. Then, the resulting solutions were diluted with additional water and purified by filtration for ICP characterization. The Brunauer–Emmett–Teller (BET) surface area was evaluated using N₂ adsorption data in the relative pressure (P/P₀) range of 0.06–0.33 using a micromeritics ASAP 2020 system. ¹H nuclear magnetic resonance (NMR) spectra of reactant 4-nitrophenol and product 4-aminophenol were recorded at JEOL 300 MHz spectrometer and Bruker 300 MHz spectrometer, respectively.

Synthesis of Au nanospheres

Citrate-stabilized Au nanoparticles (Au NPs) with diameter of about 30 nm were synthesized using wet chemistry. Hydrogen tetrachloroaurate(III) (10 mg) was dissolved in 100 mL of water and then the

solution was heated to boiling. Under vigorous stirring, 1 ml of sodium citrate tribasic dihydrate solution (1 wt%) was injected into the above solution. The mixture was kept at 100 °C for 1 h under stirring and then cooled down to room temperature in the air.

Controlled Synthesis of Au-ZIF-8 nano-hybrids

To synthesize concentric core-shell Au-ZIF-8 nano-hybrids, Au NP solution (2 mL) was concentrated to a total of 50 μ L by centrifugation at 4000 g for 7 min. After the removal of supernatant, the residual NPs were re-dispersed into 2 mL of methanol. Methanol solution of MBA (5 mM, 40 μ L) was used as sole ligand and added into the Au NP solution under mild stirring. After 5 min of reaction, Zinc nitrate (200 mM, 3 mL) was added in the solution. The above solution was stirred for another 5 min to make sure that zinc ions adsorbed on the surface of Au NPs. Subsequently, methanol solution of 2-methylimidazole (200 mM, 6 ml) was injected into the mixture and the solution was stirred for overnight. To isolate the product, the reaction mixture was centrifuged at 1200 g for 4 min and the supernatant removed. The resulting nano-hybrids particles were dried in vacuum oven for overnight. The loading of Au in these nano-hybrids is 22 wt%, which is determined by ICP.

For the synthesis of eccentric core-shell nano-hybrids, MBA (5 mM, 20 μ L) and NPT (5 mM, 20 μ L), was used as competitive ligand with all other conditions unchanged. The loading of Au in these nano-hybrids is 25 wt%, which is determined by ICP. To prepare Janus Au-ZIF-8 nano-hybrids, the amount of ligands added into the solution were changed to the mixture of MBA (5 mM, 10 μ L) and NPT (5 mM, 30 μ L), with all other conditions unchanged. The loading of Au in these nano-hybrids is 20 wt%, which is determined by ICP.

Control experiments were carried out to elucidate the growth mechanism of eccentric Au-ZIF-8 nano-hybrids. (a) To synthesize pure ZIF-8, methanol solution of Zinc nitrate (200 mM, 3 mL) was directly mixed with methanol solution of 2-methylimidazole (200 mM, 6 ml). The solution was stirred at room temperature for overnight. TEM image of the ZIF-8 crystals are shown in Fig. S1; (b) When NPT (5 mM, 40 μ L) was used as sole ligand, the Au NPs aggregated together without any encapsulation of ZIF-8. TEM image of the products are shown in Fig. 4a; (c) When PVP (5 mM, 10 μ L) and NPT (5 mM, 30 μ L) were used as ligands, nano-hybrids with random structures were obtained. TEM image of the products are shown in Fig. 4b.

Catalytic reactions in the presence of Au-ZIF-8 nano-hybrids monitored by successive UV-vis spectra

For testing the catalytic performance of the achieved nano-hybrids, three types of nano-hybrids with almost same amount of Au were weighed (the amounts of concentric core-shell, eccentric core-shell, and Janus nano-hybrids are 2.0 mg, 2.3 mg, and 1.8 mg, respectively). Then they were added into the aqueous solution of 4-nitrophenol (2.5 mM) and NaBH₄ (500 mM), respectively. The reaction progress was recorded by UV-vis spectra at 2 min interval, as shown in Figure 5. The reaction solution was shaken before each run to ensure full contact of catalysts with the reactants.

For testing the catalytic performance of Au NSs (d=30 nm), water solution (9 ml) of Au NSs was centrifuged at 4000 g for 7 min and the concentrated nanoparticles were added into the reaction solution of 4-nitrophenol (2.5 mM) and NaBH₄ (500 mM) directly. The successive UV-vis spectra are shown in Fig. S2 and the reaction rate constant is calculated to be $1.8 \times 10^{-2} \text{ s}^{-1}$.

To compare the activity of Janus Au-ZIF-8 nano-hybrids and Au NSs after recycling, Au-ZIF-8 nano-hybrids and Au NSs were collected from reaction solution via centrifugation after the reaction finished. Subsequently, the recycled particles were used as catalysts in another solution of 4-nitrophenol (2.5 mM) and NaBH₄ (500 mM), respectively. After recycled from 4 times reactions, Au-ZIF-8 and Au NSs were used as added into another solution of 4-nitrophenol (2.5 mM) and NaBH₄ (500 mM) and the successive UV-vis spectra are shown in Fig. S5. Fig. S5b. Shows that the catalytic reaction is unable to finish in 8 min, probably due to the aggregation of Au NSs during the reaction (Fig. S3).

Supplementary Figures

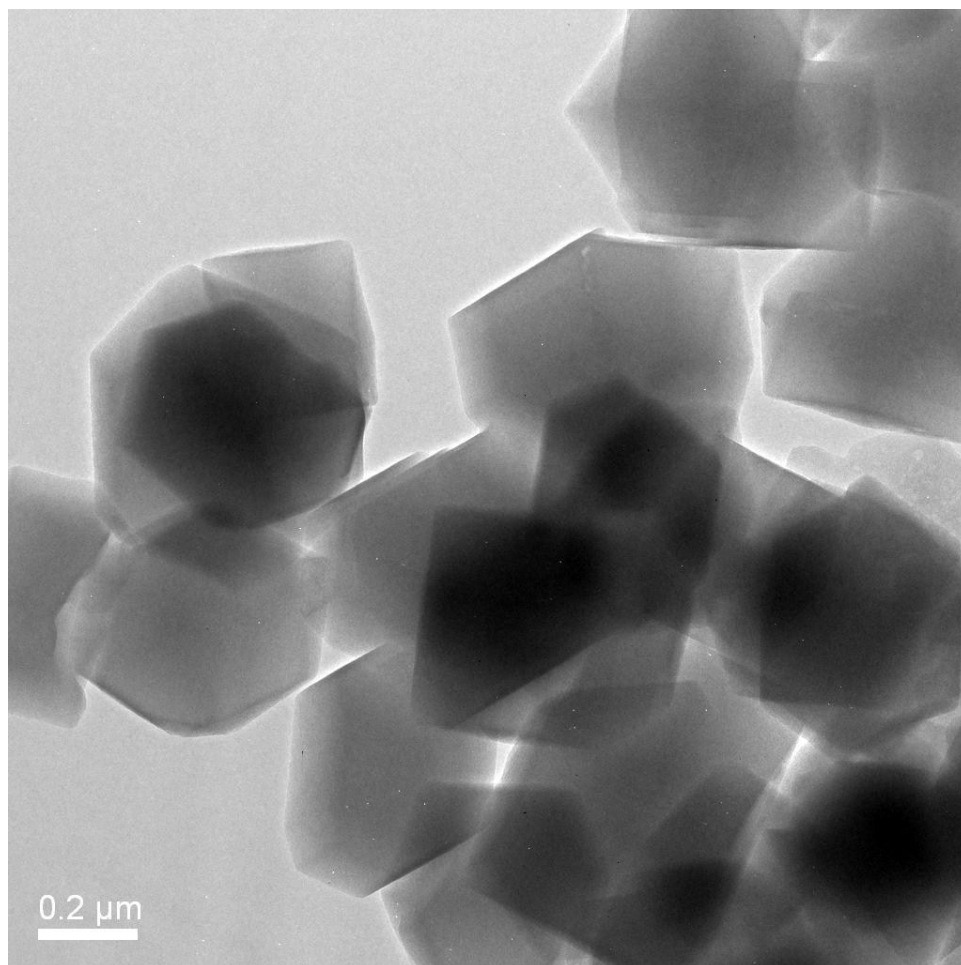


Fig. S1. TEM image of pure ZIF-8 crystals.

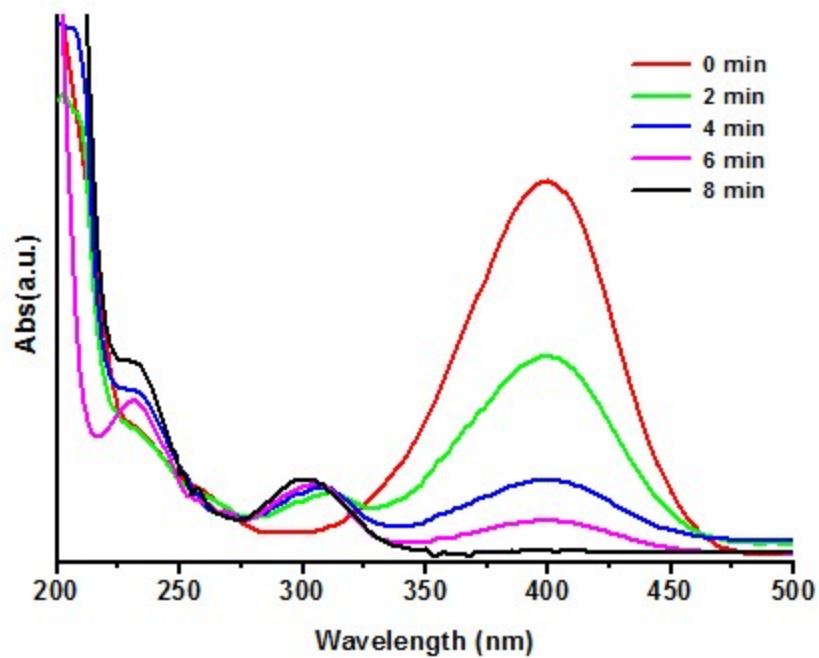


Fig. S2. Successive UV-vis spectra of the reaction mixture (2.5 mM of 4-nitrophenol and 500 mM of NaBH_4) using Au NPs as catalyst. The reaction rate constant is calculated to be $1.8 \times 10^{-2} \text{ s}^{-1}$.

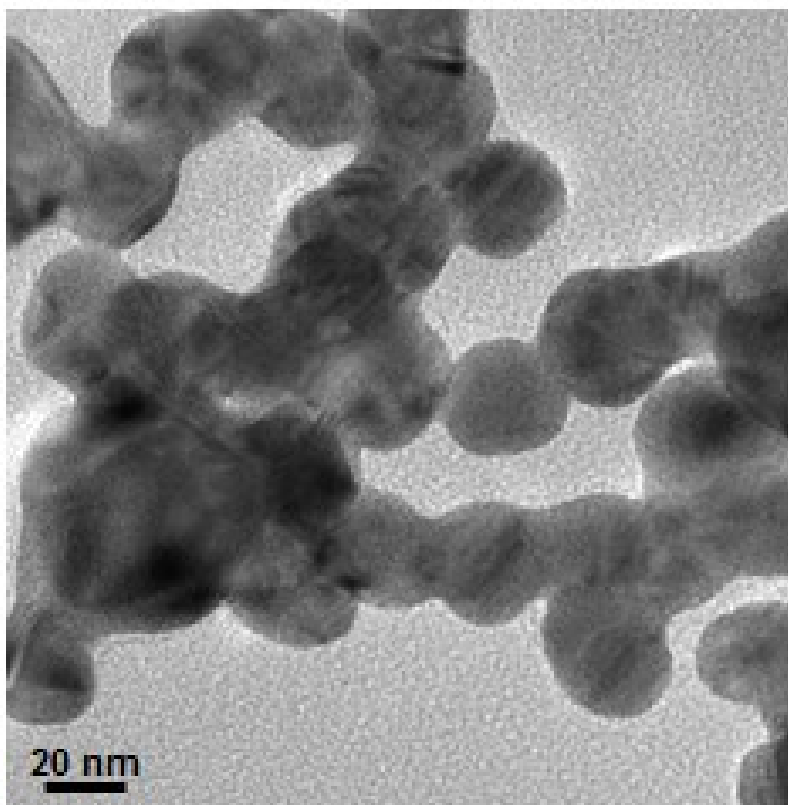


Fig. S3. TEM image of aggregated Au NSs after the reaction using it as catalyst.

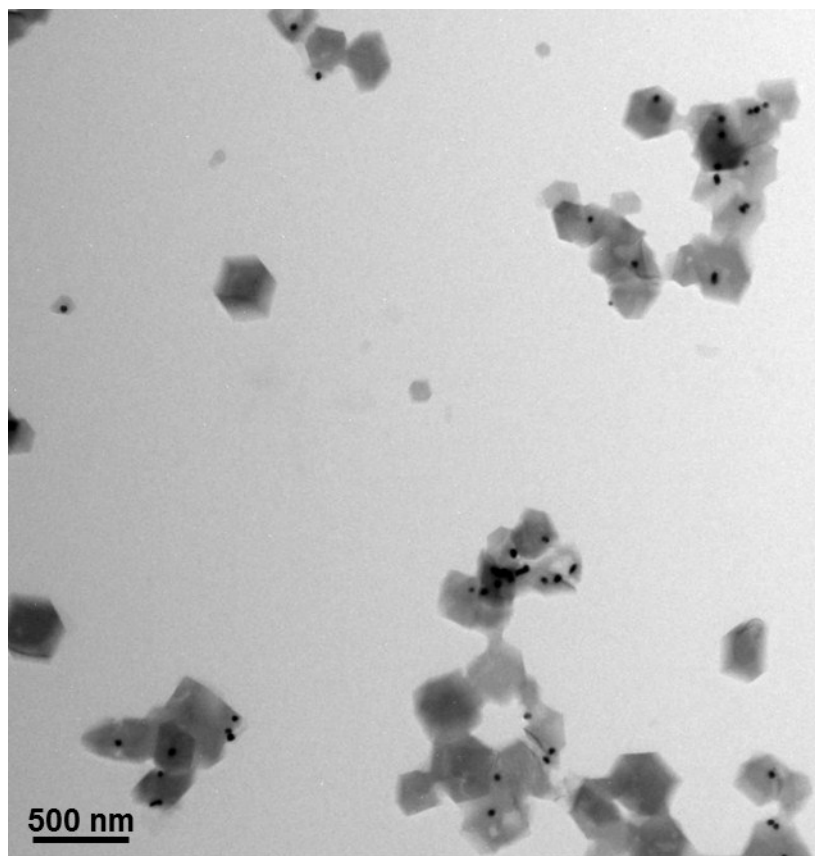


Fig. S4. TEM image of Janus Au-ZIF-8 nano-hybrids after the reaction using it as catalyst.

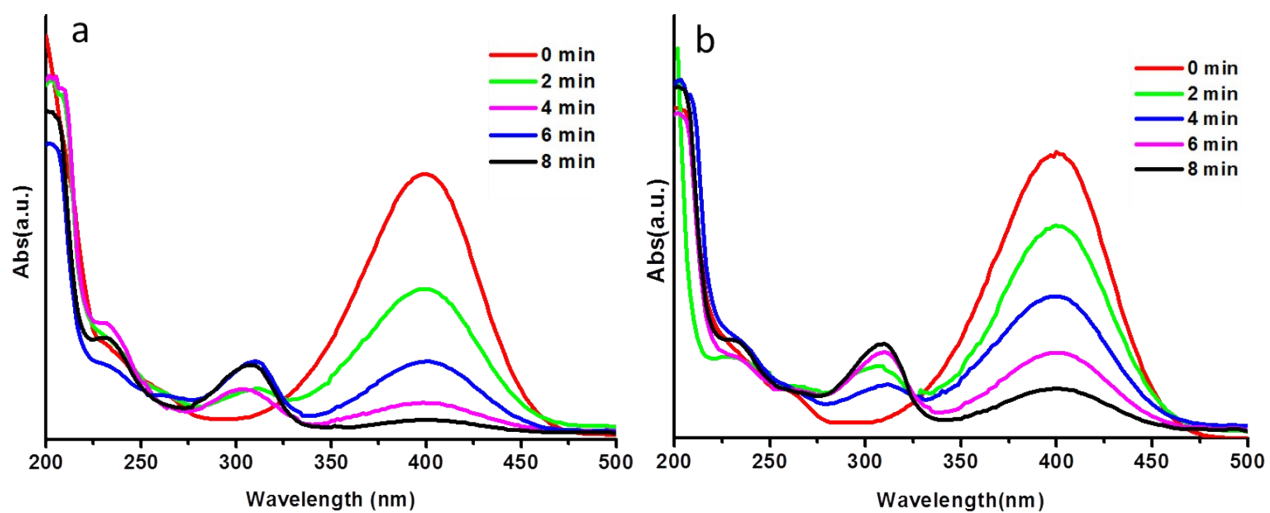


Fig. S5. Successive UV-vis spectra of the reaction mixture (2.5 mM of 4-nitrophenol and 500 mM of NaBH_4) using (a) Janus Au-ZIF-8 nano-hybrids and (b) Au NSs recycled from 4 times reactions.

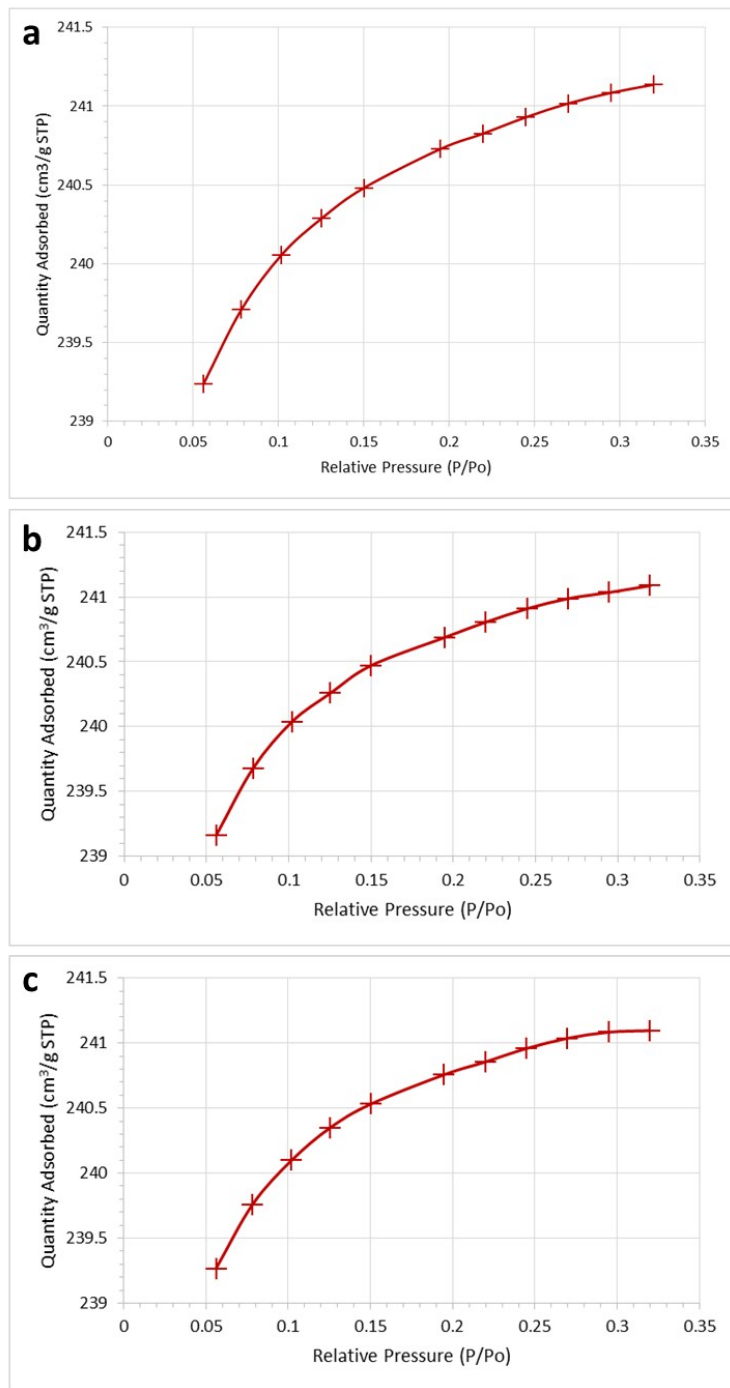


Fig. S6. N₂ adsorption isotherm curves of (a) concentric core-shell, (b) eccentric core-shell and (c) Janus nano-hybrids. The surface area of concentric core-shell, eccentric core-shell, and Janus nano-hybrids are 700.74, 704.85 and 704.05 m²/g, respectively.

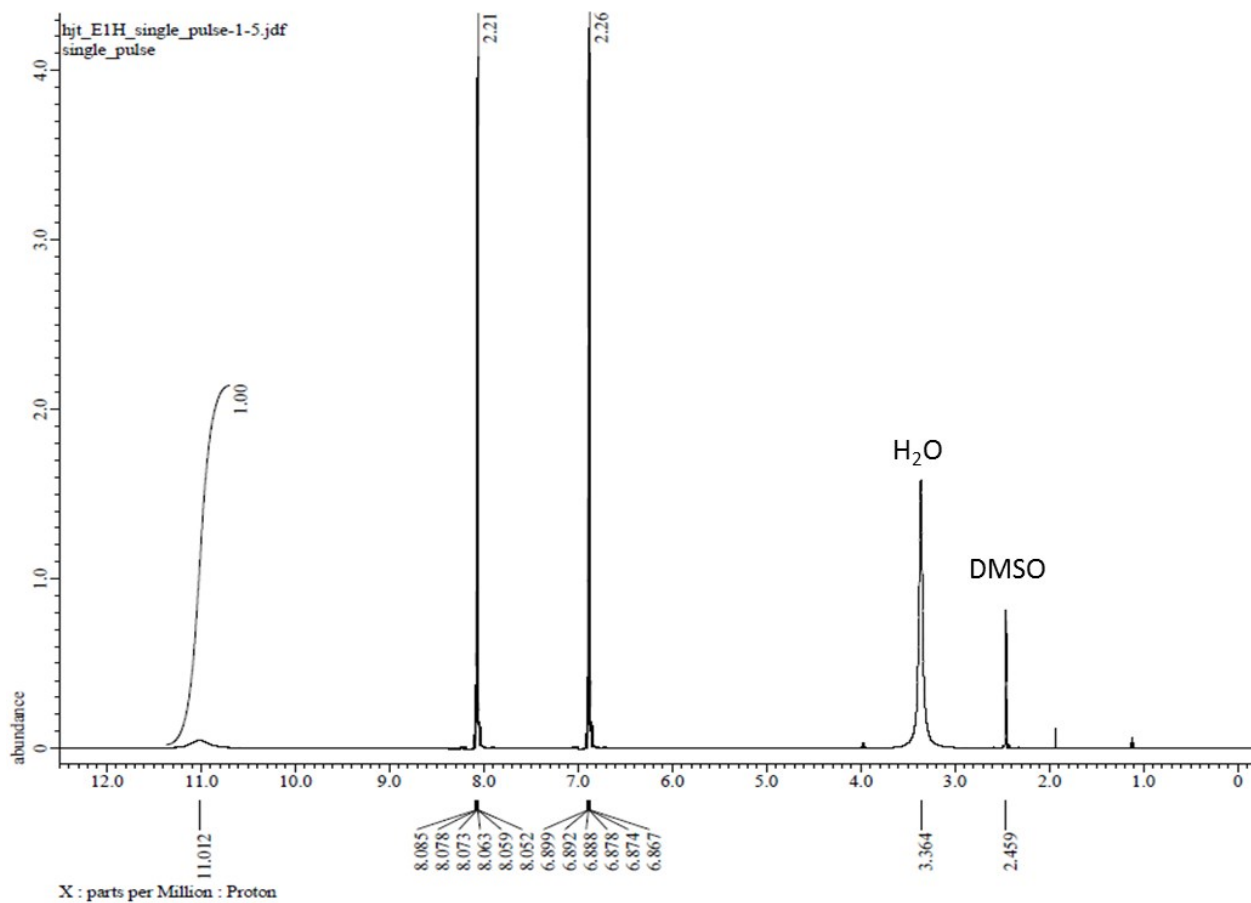


Fig. S7. ¹H NMR spectrum of reactant 4-nitrophenol.

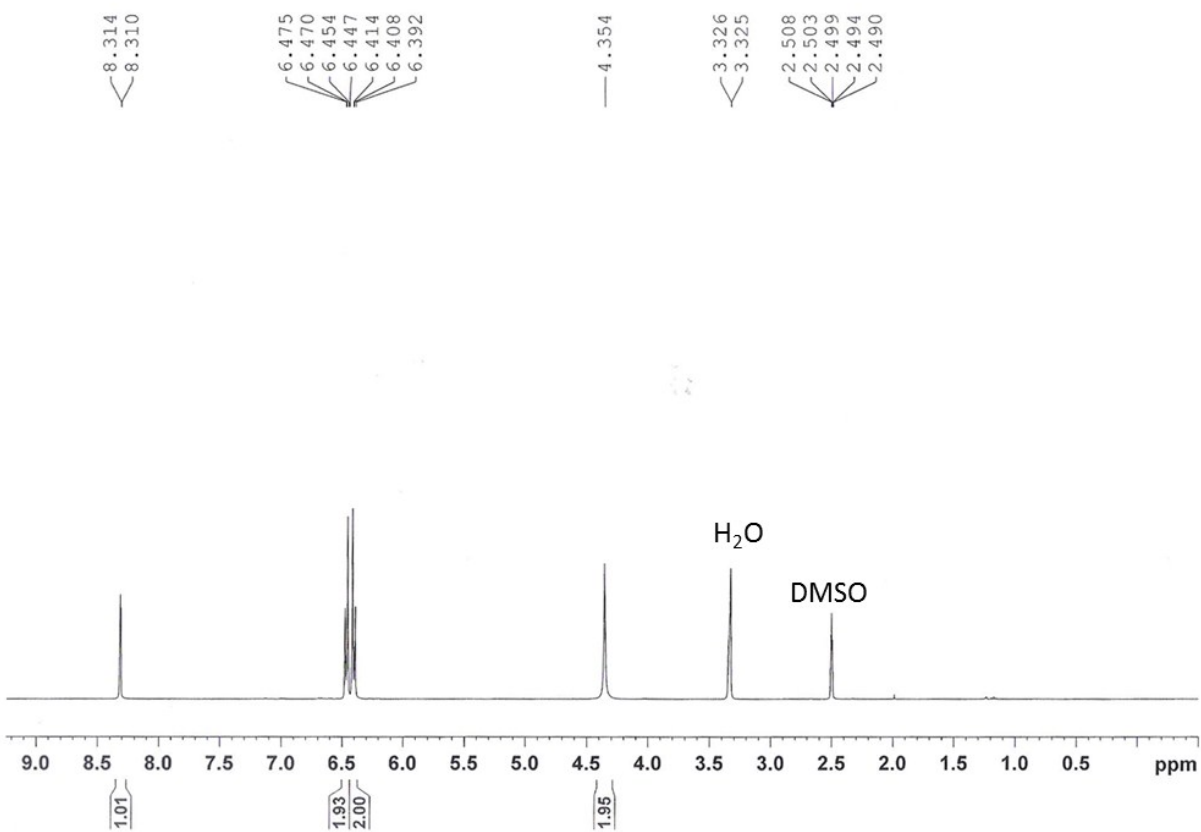


Fig. S8. ¹H NMR spectrum of the product 4-aminophenol.