Electronic Supplementary Information

Highly active AuCo alloy nanoparticles encapsulated in the pores of metal–organic frameworks for hydrolytic dehydrogenation of ammonia borane

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Experimental Section

Chemicals

All chemicals were commercial and used without further purification. Chromic nitrate nonahydrate $(Cr(NO_3)_3 \cdot 9H_2O, Sigma-Aldrich, 99\%)$, aqueous hydrofluoric acid (HF, Kishida Chemical Co. Ltd., 46%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, Wako Pure Chemical Industries, Ltd., >99%), hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄·4H₂O, Wako Pure Chemical Industries, Ltd., >99%), sodium borohydride (NaBH₄, Aldrich, 99%), ammonia borane (NH₃BH₃, JSC Aviabor, >99%), terephthalic acid (HOOCC₆H₄COOH, Tri Chemical Laboratories Inc., 99%), anhydrous n-hexane (Sigma-Aldrich) and ethanol (C₂H₅OH, Kishida Chem. Co., >99.8%) were used as received. De-ionized water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd., Japan).

Synthesis of MIL-101

MIL-101 was synthesized using the reported procedure.¹ Terephthalic acid (1.661 g, 10.0 mmol), Cr(NO₃)₃·9H₂O (4.002 g, 10.0 mmol), aqueous HF (0.5 mL, 46 wt%) and de-ionized water (70 mL) were placed in a 100 mL Teflon-liner autoclave and heated at 220 °C for 8 h. After cooling, the resulting green powder of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3$ ·nH₂O (n ≤ 25) were doubly filtered off using two glass filters with pore sizes between 40 and 100 µm to remove the unreacted crystals of terephthalic acid, and then further purified by solvothermal treatment in ethanol at 80 °C for 24 h. The resulting green solid was soaked in NH₄F (1 M) solution at 70 °C for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered, washed with hot water several times, and finally dried overnight at 150 °C under vacuum for further use.

Preparation of Au@MIL-101, Co@MIL-101, AuCo@MIL-101

Encapsulation of Au³⁺ and Co²⁺ precursors were carried out via double solvents method.² Typically, 100 mg of activated MIL-101 was suspended in 20 mL of dry n-hexane as hydrophobic solvent and the mixture was sonicated for 15 min until it became homogeneous. After stirring for 2 h, 0.15 mL of aqueous HAuCl₄·4H₂O and/or CoCl₂·6H₂O solution with desired concentrations as the hydrophilic solvent was added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for 2 h. After filtration, the green powder was dried in air at room temperature. These synthesized samples were further dried at 150 °C under vacuum for 12 h. The molar ratio of Au³⁺/(Au³⁺+Co²⁺) were changed with several values (0, 0.015, 0.03, 0.06, 0.075, 0.09, 0.125, 0.25 and 1.00), while the molar contents of (Au³⁺+Co²⁺) added to 100 mg MIL-101 matrix were kept to be 0.034 mmoL. After dehydration of the Au³⁺Co²⁺@MIL-101 with different molar ratios of Au³⁺ to Co²⁺, an overwhelming reduction approach was employed by using 3.5 mL freshly prepared 0.6 M aqueous NaBH₄ solution while vigorous shaking (220 rpm),³ resulting in the

generation of catalysts as a dark green suspension. The synthesized samples were collected by centrifuging, and used for the catalytic reactions.

Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku RINT-2000 X-ray diffractometer with Cu K α source (40 kV, 40 mA). X-ray photoelectron spectroscopic (XPS) measurements were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg K α source (10 kV, 10 mA). The Ar sputtering experiments were carried out under the conditions of background vacuum of 3.2×10^{-6} Pa, sputtering acceleration voltage of 2 kV and sputtering current of 10 mA. The surface area measurements were performed with N₂ adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after dehydration under vacuum at 150°C for 12 h using automatic volumetric adsorption equipment (Belsorp-max). The pore volume was calculated by a single point method at P/P₀=0.99. Transmission electron microscope (TEM, TECNAI G² F20) equipped with energy dispersed X-ray detector (EDS) was applied for the detailed microstructure and composition information for the prepared samples.

Catalytic activity investigations

The hydrolysis of ammonia borane (NH₃BH₃, AB) can be briefly expressed as the formula: NH₃BH₃ + 4H₂O \rightarrow NH₄⁺ + B(OH)₄⁻ + 3H₂. Reaction apparatus for measuring the hydrogen evolution from the aqueous AB solution is the same as previously reported.⁴ In general, a mixture of catalyst (50 mg) and distilled water (4.8 mL) was placed in a two-necked round-bottomed flask (30 mL), which was placed in a water bath at room temperature under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of hydrogen. The reaction started when aqueous AB solution (1 mmol in 200 µL water) was injected into the mixture using a syringe. The volume of the evolved hydrogen gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generation. In addition, the molar ratios of (Au+Co)/AB were theoretically fixed at 0.017 for all the catalytic reactions, corresponding to 50 mg catalysts.

Durability/stability of AuCo@MIL-101 catalyst

After the hydrogen generation reaction was completed, another aliquot of AB (1.0 mmol in 200 µL water) was added into the reaction system and the released gas was monitored by the gas burette. After the reaction, the as-synthesized AuCo@MIL-101 was separated from the reaction solution by centrifugation and dried under vacuum at room temperature. The obtained sample after hydrolysis of AB was used for PXRD (See Fig. S2) and TEM (See Fig. S8) analyses.



Fig. S1. Powder XRD patterns of (a) as-synthesized MIL-101, (b) AuCo@MIL-101 (Au/Co = 6:94), (c) Co@MIL-101 and (d) Au@MIL-101.



Fig. S2. Powder XRD patterns of (a) as-synthesized MIL-101 and AuCo@MIL-101 (Au/Co = 6:94) (b) before and (c) after the catalytic hydrolysis of AB.



Fig. S3. XPS spectra for (a) Au@MIL-101, (b) Co@MIL-101 and (c, d) AuCo@MIL-101 (Au/Co = 6:94) before and after Ar etching for 60 min (Au $4f_{7/2}$ and $4f_{5/2}$ peaks, and Co $2p_{3/2}$ and $2p_{1/2}$ peaks).



Fig. S4. N₂ sorption isotherms of (a) as-synthesized MIL-101, (b) AuCo@MIL-101 (Au/Co = 6:94) and (c) Au³⁺Co²⁺@MIL-101 at 77 K. The BET surface areas of the three samples are 3452, 1930 and 1455 m²/g, respectively. Filled and open symbols represent adsorption and desorption branches, respectively.



Fig. S5. HAADF-STEM images of AuCo@MIL-101 (Au/Co = 6:94).



Fig. S6. EDX spectrum for the as-synthesized AuCo@MIL-101 (Au/Co = 6:94). The copper signal originates from Cu grid.



Fig. S7. Size distribution of AuCo alloy nanoparticles in AuCo@MIL-101 sample (Au/Co = 6:94).



Fig. S8. TEM image of AuCo@MIL-101 after AB hydrolysis (Au/Co = 6:94).



Fig. S9. Plots of time versus volume of hydrogen generated from AB (1.0 mmol, 5 mL) by AuCo@MIL-101 catalysts with different Au molar contents ((Au+Co)/AB=0.017).



Fig. S10. Durability characterization of AuCo@MIL-101 in five runs for hydrogen generation from hydrolysis of aqueous AB solution (1.0 mmol, Au/Co = 6:94, (Au+Co)/AB=0.017).

References

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