Supporting Information:

In Situ Synthesis of Magnetically Recyclable Graphene Supported Pd@Co Core-Shell Nanoparticles as Efficient Catalysts for Hydrolytic Dehydrogenation of Ammonia Borane

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1. Chemicals and materials.

Ammonia borane (NH₃BH₃, AB, Aldrich, 90%), cobalt (Ⅱ) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Sinopharm Chemical Reagent Co., Ltd, ≥99%), palladium (Ⅱ) chloride (PdCl₂, Aladdin Reagent, Pd: ≥60%), nickel (Ⅱ) chloride hexahydrate (NiCl₂·6H₂O, Aladdin Reagent, ≥98%), iron (Ⅲ) sulfate heptahydrate (FeSO₄·7H₂O, Aladdin Reagent, ≥99%), sodium borohydride (NaBH₄, Beijing Chemical Works, ≥98%), sodium chloride (NaCl, Aladdin Reagent, ≥99%), sulfuric acid (H₂SO₄, Beijing Chemical Works, 98%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), potassium peroxodisulfate (K₂S₂O₈, Aldrich, ≥99%), phosphorus pentoxide (P₂O₅, Aldrich, ≥99.99%), potassium permanganate (KMnO₄, Sinopharm Chemical Reagent Co., Ltd, ≥99%), hydrogenperoxide (H₂O₂, Beijing Chemical Works, 30%), graphite powder (Alfa, 325 mesh) and nylon filter membranes (Aldrich, pore size 0.2 μm) 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.

2. Graphite Oxide (GO) preparation.

GO was made by a modified Hummers method.¹,² Briefly, graphite powder (3 g, 325 mesh) was put into an 80 °C solution of concentrated H₂SO₄ (12 mL), K₂S₂O₈
(2.5 g), and P2O5 (2.5 g). After keeping at 80 °C for 4.5 h using a hotplate, the mixture was cooled to room temperature and diluted with 0.5 L of de-ionized water and left overnight. Then, the mixture was filtered and washed with de-ionized water using a 0.2 micron Nylon Millipore filter to remove the residual acid. The product was dried under ambient condition overnight. Next, the pretreated graphite powder was put into cold (0 °C) concentrated H2SO4 (120 mL) in a 250-mL round-bottom flask equipped with a magnetic stir bar. 15 g KMnO4 was added gradually under stirring while the temperature of the mixture was kept below 20 °C. The solution was then stirred at 35 °C for 2 h. Afterwards, 250 mL of de-ionized water was added and the suspension was stirred for another 2 h. Subsequently, additional 0.7 L of de-ionized water was added. Shortly after that, 20 mL of 30% H2O2 was added to the mixture to destroy the excess of permanganate. The suspension was then repeatedly centrifuged and washed first with 5% HCl solution and then with water. Exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 30 min.

3. In situ synthesis of graphene supported Pd@Co core-shell NPs (Pd/Co=0.1/0.9) and their catalytic activities toward the hydrolysis of AB (catalysts/AB=0.02).

First, Na2PdCl4 was prepared by mixing PdCl2 and NaCl with the molar ratio of 1:2 in aqueous solution. Then, a 6 mL of aqueous solution containing Na2PdCl4 (51.72 mM, 77.3 μL), Co(NO3)2·6H2O (10.5 mg) and GO solution (1g, containing 8‰ GO) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce 4 mL of aqueous solution containing AB (65 mg). The reactions were started when the aqueous AB solution was added to the mixture solution of precursors and GO with vigorous stirring. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere.

In order to find an optimized reaction condition for catalytic dehydrogenation from AB, the molar ratio of Pd/Co was varied from 0 to 1, while the molar ratio for catalysts to AB was kept a constant of 0.02. For comparison, Pd@M/graphene
(Pd/M=0.1/0.9, M=Fe and Ni) nanocatalysts was synthesized using the similar method as for Pd@Co/graphene nanocatalysts.

4. **In situ synthesize Pd@Co core-shell NPs (Pd/Co=0.1/0.9) and their catalytic activities toward the hydrolysis of AB (catalysts/AB=0.02).**

   Except for the absence of GO, the experiment procedures were similar to that of synthesis of Pd@Co/graphene.

5. **Pre-synthesis of graphene supported PdCo alloy NPs (Pd/Co=0.1/0.9) and their catalytic activities toward the hydrolysis of AB (catalysts/AB=0.02).**

   The graphene supported PdCo alloy NPs were pre-synthesized by adding NaBH₄ (5 mg) into 6 mL of the mixture solution containing equivalent precursors and GO with vigorous stirring. After the absence of gas evolution from the solution was verified, 4 mL of aqueous solution containing AB (65 mg) was introduced to test the catalytic activities at ambient conditions.

6. **Stability tests.**

   For stability test, catalytic reactions were repeated 5 times by adding another equivalent of AB (65 mg) into the mixture after the previous cycle.

7. **Catalyst characterization.**

   Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation (λ = 0.15405 nm). Transmission electron microscope (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Samples for all of these TEM experiments were prepared by dispersing the samples in ethanol with sonication for 30 min to ensure adequate dispersion of the nanostructures, and evaporating one drop of the solution onto a 300 mesh Cu grid, coated with a lacey
carbon film. Fourier transform infrared spectroscopy was obtained with BRUKER Vertex 70 FT-IR spectrometer. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter at ambient conditions.
Fig. S1 Fourier transform infrared spectroscopy of GO.
Fig. S2 XRD pattern of in situ synthesized Pd@Co/graphene (Pd/Co=0.1/0.9) catalysts.
Fig. S3 Raman spectra of GO (a), GO reduced by AB (b) and GO reduced by AB in the presence of metal catalysts (c).
Fig. S4 Time plots of catalytic dehydrogenation of AB over in situ synthesized Pd$_x$@Co$_{(1-x)}$/graphene (x=0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) catalysts at ambient conditions. Catalyst/AB=0.02 (molar ratio).
**Fig. S5** Time plots of catalytic dehydrogenation of AB over the in situ synthesized Pd$_{0.1}$@M$_{0.9}$/graphene (M=Co, Ni, and Fe) catalysts at ambient conditions. Catalyst/AB=0.02 (molar ratio).
**Fig. S6** The recycle ability of Pd@Co/graphene catalysts after catalytic reaction.

**Reference**
