Supporting Information

One-Pot Protocol for Synthesis of Non-noble Metal-based Core-Shell Nanoparticles under Ambient Conditions: Toward Highly Active and Cost-effective Catalysts for Hydrolytic Dehydrogenation of NH_3BH_3

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S1. Materials and Instrumentation

All chemicals were purchased from commercial and used without further purification: Ammonia-borane (AB, NH_3BH_3, Aldrich, 90%), sodium borohydride ($NaBH_4$, Sigma-Aldrich, 99%), copper(II) chloride (Wako Pure Chemical Industries, Ltd., 98%), cobalt (II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, Wako Pure Chemical Industries, Ltd., >99%), iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, Wako Pure Chemical Industries, Ltd., >99%), nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, Wako Pure Chemical Industries, Ltd., >98%), hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$, Wako Pure Chemical Industries, Ltd., >99%), polyvinylpyrrolidone K 30 (PVP, $(C_6H_9NO)_n$, Viscosity Average Molecular Wt. 40000, Tokyo Chemical Industry Co., Ltd.), and ethanol (CH_3CH_2OH, Kishida Chemical Co., Ltd., >99.8%). Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer of Rigaku, Rint 2000. A glass substrate holding the powder sample was covered by an adhesive tape on the surface to prevent the sample from exposure to air during the measurements. The UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The size and morphology of Cu@Co sample were observed by using a transmission electron microscope (TEM, JEOL, JEM-3000F) equipped with an energy dispersive X-ray detector (EDX) and Gatan Imaging Filter (GIF) for EELS analysis at an acceleration voltage of 300 kV. The X-ray photoelectron spectra (XPS) were acquired with an ESCA-3400 spectrometer (Shimadzu Corp.) equipped with an Mg Kα X-ray exciting source (1253.6 eV) operating at 10 kV and 10 mA. The binding energies (BE) were referred to the C 1s peak at 285.0 eV. A 2 kV Ar^+ sputter beam was used for depth profiling of Cu@Co sample after the initial data were collected.

S2. Preparation of Cu@M (M = Co, Fe, Ni) Core-Shell NPs

The composition of Cu@M core-shell NPs can be expressed as $Cu_x@M_{5-x}$ (x = 0.5, 1, 2, 3, 4), where the total mol number of Cu and M is fixed to be 0.0525 mmol whereas Cu/M molar ratio is x/(5-x).

For $Cu_1@Co_4$ NPs (x = 1): 1.05×10^{-2} mmol of $CuCl_2$ (1.41 mg) and 4.20×10^{-2} mmol of $CoCl_2\cdot6H_2O$ (9.99 mg) were dissolved with PVP (100 mg) in 10 mL distilled water. The solution was pre-stirred to be uniform before introduced into the flask containing 90 mg of NH_3BH_3. The mixture was shaken (~250 rpm) under ambient conditions. It should be noted that magnetic stirring is not preferred owing to the aggregation of the prepared magnetic particles resulting from the strong magnetism.

For $Cu_{0.5}@Co_{4.5}$ NPs (x = 0.5): the same procedure as for $Cu_1@Co_4$ except that 5.25 $\times10^{-3}$ mmol of $CuCl_2$ (0.71 mg) and 4.73×10^{-2} mmol of $CoCl_2\cdot6H_2O$ (11.24 mg) were used.

For $Cu_2@Co_3$ (x = 2): the same procedure as for $Cu_1@Co_4$ except that 2.10 $\times10^{-2}$ mmol of $CuCl_2$ (2.82 mg) and 3.15×10^{-2} mmol of $CoCl_2\cdot6H_2O$ (7.49mg) were used.

For $Cu_3@Co_2$ (n = 3), the same procedure as for $Cu_1@Co_4$ except that 3.15 $\times10^{-2}$ mmol of $CuCl_2$ (4.23 mg) and 2.10×10^{-2} mmol of $CoCl_2\cdot6H_2O$ (5.00mg) were used.

For $Cu_4@Co_1$ (n = 4), the same procedure as for $Cu_1@Co_4$ except that 4.20 $\times10^{-2}$ mmol of $CuCl_2$ (5.65 mg) and 1.05×10^{-2} mmol of $CoCl_2\cdot6H_2O$ (2.50mg) were used.

For $Cu_x@Fe_{5-x}$ and $Cu_x@Ni_{5-x}$ (x = 0.5, 1, 2, 3), the same preparation procedure as for $Cu_x@Co_{5-x}$ described above was applied except that $CoCl_2\cdot6H_2O$ was replaced by $FeSO_4\cdot6H_2O$ and $NiCl_2\cdot6H_2O$, respectively.

S3. Preparation of Monometallic NPs

For preparation of Cu NPs, 5.25 ×10^{-2} mmol of $CuCl_2$ (7.06 mg) were dissolved with PVP (100 mg) in 10 mL distilled water. The solution was pre-stirred to be uniform before introduced into the flask containing 90 mg of NH_3BH_3. The mixture was shaken (~250 rpm) under ambient conditions.

For preparation of Co NPs, the same as that for Cu NPs except that only 5.25 ×10^{-2} mmol of $CoCl_2 \cdot 6H_2O$ (12.5 mg) was used.

For preparation of Fe NPs, the same as that for Cu NPs except that only 5.25 ×10^{-2} mmol of $FeSO_4 \cdot 6H_2O$ (13.65 mg) was used.

For preparation of Ni NPs, the same as that for Cu NPs except that only 5.25 ×10^{-2} mmol of $NiCl_2 \cdot 6H_2O$ (19.92 mg) was used.

S4. Preparation of Cu_1M_4 (M = Co, Fe, Ni) Alloy NPs

For preparation of Cu_1Co_4 alloy NPs: 1.05 × 10^{-2} mmol of $CuCl_2$ (1.41 mg) and 4.20 × 10^{-2} mmol of $CoCl_2 \cdot 6H_2O$ (9.99 mg) were dissolved with PVP (100 mg) in 10 mL distilled water. The solution was pre-stirred to be uniform before introduced into the flask containing 10 mg of $NaBH_4$ while shaking (~250 rpm) under ambient conditions. Black particles were immediately generated without obvious color changing from brick-red to black.

For preparation of Cu_1Fe_4 and Cu_1Ni_4 alloy NPs, the same procedures as those for Cu_1Co_4 alloy NPs were applied except that $CoCl_2 \cdot 6H_2O$ was replaced by $FeSO_4 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$, respectively.

S5. Catalytic Activity Investigations

Under ambient conditions (around 26 ºC), 90 mg of NH_3BH_3 was kept in a two-necked round-bottom flask (30 mL). One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce the aqueous solution (10 mL) of metal precursors with PVP, where the molar ratio of $(Cu^{2+} + M^{2+})/ NH_3BH_3$ is fixed to be a constant of 0.02 although the Cu^{2+}/M^{2+} molar ratios are changed in different batches of experiments. The reaction started once the aqueous solution was introduced to NH_3BH_3 with shaking (~250 rpm). The evolution of gas was monitored using the gas burette. The reaction was carried out at room temperature under ambient atmosphere. The hydrolysis of NH_3BH_3 can be briefly expressed as follows:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \qquad (1)$$

For catalytic activity examination for monometallic and alloy NPs, the aqueous solution containing monometallic precursors or alloy NPs was introduced into the flask containing 90 mg NH_3BH_3. The monitor of H_2 release was the same as described above.

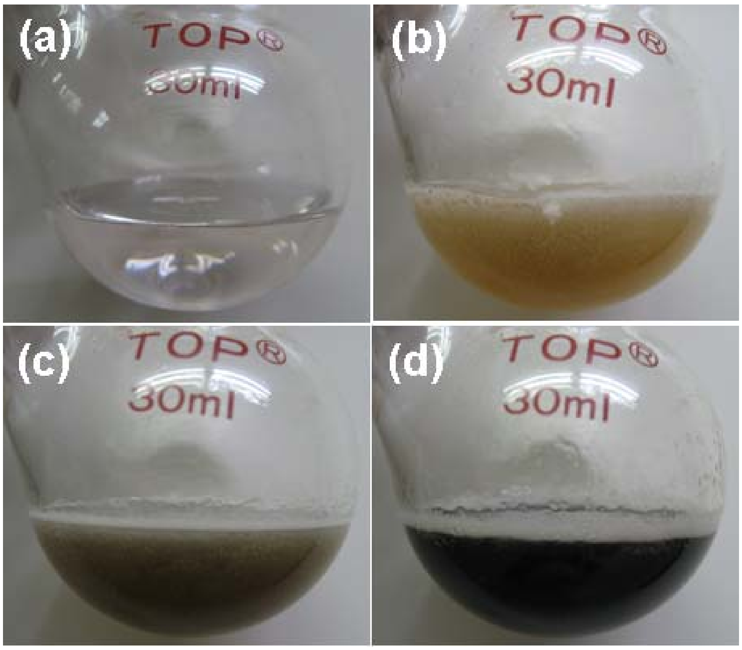
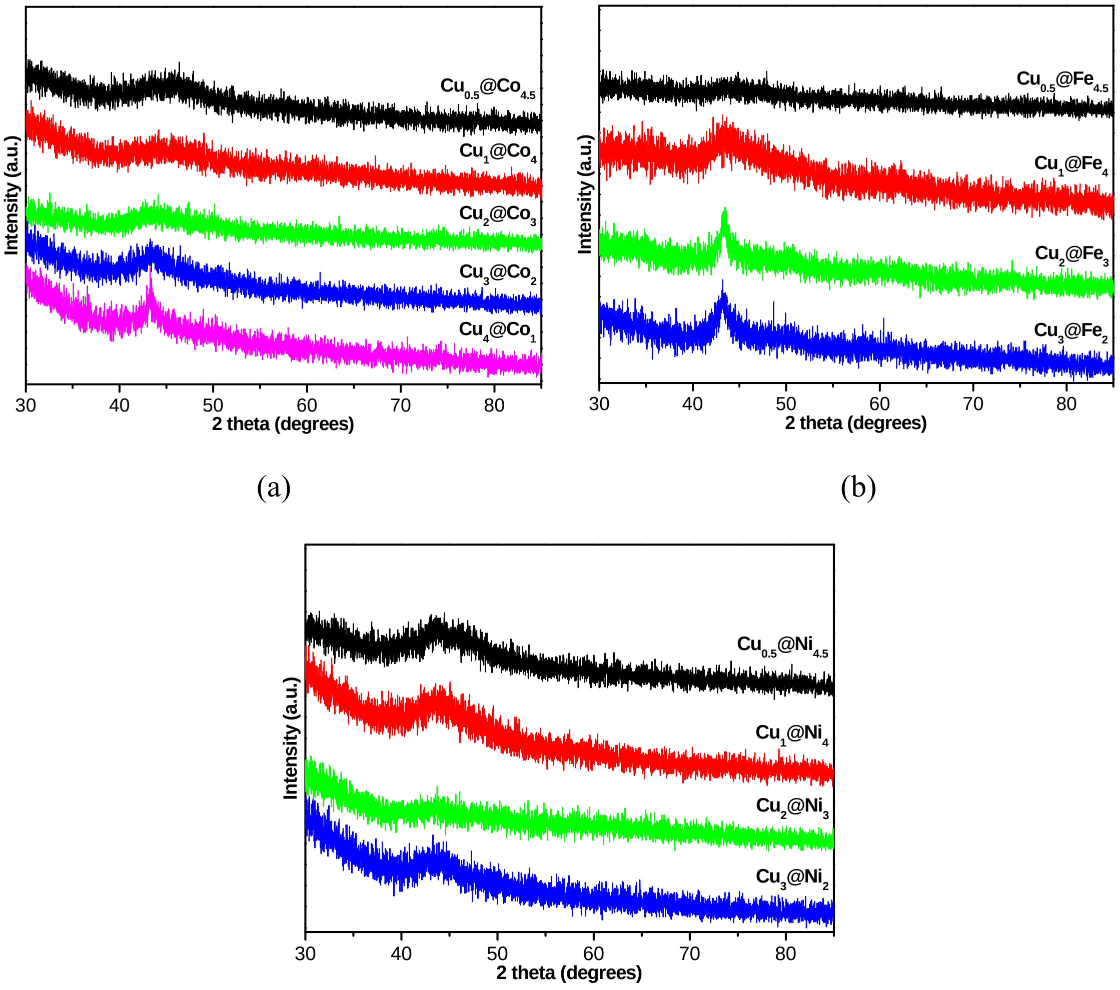


Fig. S1 Color evolution pictures of the solution during the reaction process. (a) the light-pink aqueous solution with Cu^{2+}/Co^{2+}/PVP before the addition of NH_3BH_3; (b) solution in khaki after introducing NH_3BH_3; and (c, d) solution becomes darker and darker during the H_2 generation and reduction process.



(a) (b)

(c)

Fig. S2 Powder XRD patterns of $Cu_x@M_{5-x}$ (M = Co, Fe, Ni; x = 0.5, 1, 2, 3, 4) samples.

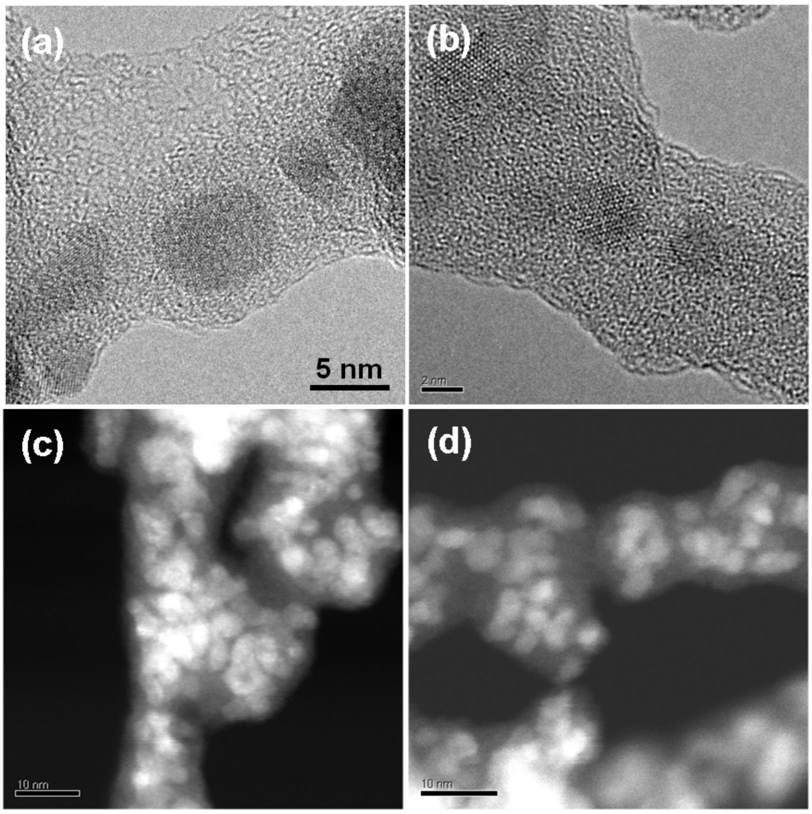


Fig. S3 Additional (a) TEM, (b) HRTEM and (c,d) HAADF-STEM images for Cu@Co core-shell sample showing its nanochain-like shape.

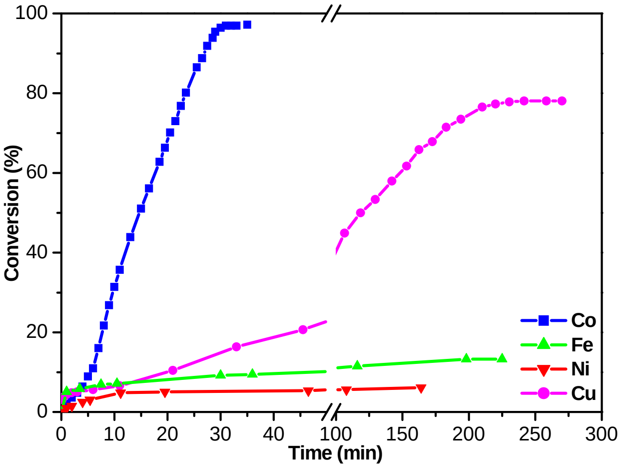


Fig. S4 Hydrogen generation from NH_3BH_3 aqueous solution (0.26 mol/L, 10 mL) over monometallic NPs under ambient conditions. The molar ratio of catalyst/NH_3BH_3 = 0.02.

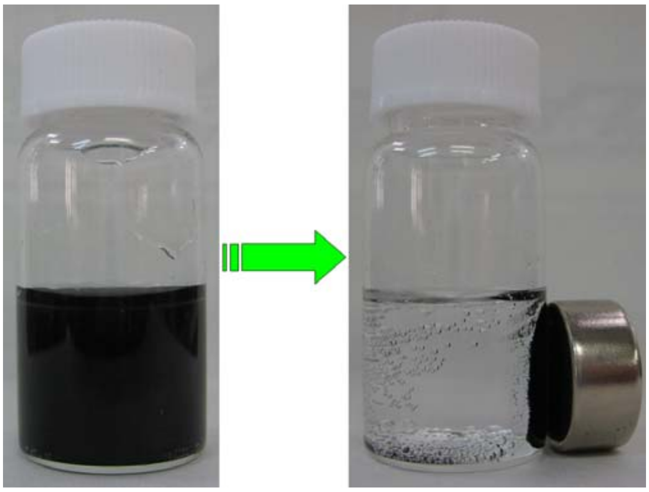


Fig. S5 Photograph showing the magnetic separation for the Cu@Co NPs in the solution.