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$_3$BH$_3$

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S1. Materials and Instrumentation

All chemicals were purchased from commercial and used without further purification: Ammonia-borane (AB, NH$_3$BH$_3$, Aldrich, 90%), sodium borohydride (NaBH$_4$, Sigma-Aldrich, 99%), copper(II) chloride (Wako Pure Chemical Industries, Ltd., 98%), cobalt (II) chloride hexahydrate (CoCl$_2$·6H$_2$O, Wako Pure Chemical Industries, Ltd., >99%), iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, Wako Pure Chemical Industries, Ltd., >99%), nickel (II) chloride hexahydrate (NiCl$_2$·6H$_2$O, Wako Pure Chemical Industries, Ltd., >98%), hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl$_4$·4H$_2$O, Wako Pure Chemical Industries, Ltd., >99%), polyvinylpyrrolidone K 30 (PVP, (C$_6$H$_9$NO)$_n$, Viscosity Average Molecular Wt. 40000, Tokyo Chemical Industry Co., Ltd.), and ethanol (CH$_3$CH$_2$OH, 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 K$_\alpha$ 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 Cuₙ@M₅₋ₙ (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 Cu₁@Co₄ NPs (x = 1): 1.05 × 10⁻² mmol of CuCl₂ (1.41 mg) and 4.20×10⁻² mmol of CoCl₂·6H₂O (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 NH₃BH₃. 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 Cu₀.₅@Co₄.₅ NPs (x = 0.5): the same procedure as for Cu₁@Co₄ except that 5.25 × 10⁻³ mmol of CuCl₂ (0.71 mg) and 4.73×10⁻² mmol of CoCl₂·6H₂O (11.24 mg) were used.

For Cu₂@Co₃ (x = 2): the same procedure as for Cu₁@Co₄ except that 2.10 × 10⁻² mmol of CuCl₂ (2.82 mg) and 3.15×10⁻² mmol of CoCl₂·6H₂O (7.49 mg) were used.

For Cu₃@Co₂ (n = 3), the same procedure as for Cu₁@Co₄ except that 3.15 × 10⁻² mmol of CuCl₂ (4.23 mg) and 2.10×10⁻² mmol of CoCl₂·6H₂O (5.00 mg) were used.

For Cu₄@Co₁ (n = 4), the same procedure as for Cu₁@Co₄ except that 4.20×10⁻² mmol of CuCl₂ (5.65 mg) and 1.05×10⁻² mmol of CoCl₂·6H₂O (2.50 mg) were used.

For Cuₓ@Fe₅₋ₓ and Cuₓ@Ni₅₋ₓ (x = 0.5, 1, 2, 3), the same preparation procedure as for Cuₓ@Co₅₋ₓ described above was applied except that CoCl₂·6H₂O was replaced by FeSO₄·6H₂O and NiCl₂·6H₂O, respectively.
S3. Preparation of Monometallic NPs

For preparation of Cu NPs, $5.25 \times 10^{-2}$ 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$_3$BH$_3$. The mixture was shaken (~250 rpm) under ambient conditions.

For preparation of Co NPs, the same as that for Cu NPs except that only $5.25 \times 10^{-2}$ mmol of CoCl$_2$·6H$_2$O (12.5 mg) was used.

For preparation of Fe NPs, the same as that for Cu NPs except that only $5.25 \times 10^{-2}$ mmol of FeSO$_4$·6H$_2$O (13.65 mg) was used.

For preparation of Ni NPs, the same as that for Cu NPs except that only $5.25 \times 10^{-2}$ mmol of NiCl$_2$·6H$_2$O (19.92 mg) was used.

S4. Preparation of Cu$_1$M$_4$ (M = Co, Fe, Ni) Alloy NPs

For preparation of Cu$_1$Co$_4$ alloy NPs: $1.05 \times 10^{-2}$ mmol of CuCl$_2$ (1.41 mg) and 4.20 × $10^{-2}$ mmol of CoCl$_2$·6H$_2$O (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$_1$Fe$_4$ and Cu$_1$Ni$_4$ alloy NPs, the same procedures as those for Cu$_1$Co$_4$ alloy NPs were applied except that CoCl$_2$·6H$_2$O was replaced by FeSO$_4$·6H$_2$O or NiCl$_2$·6H$_2$O, respectively.
S5. Catalytic Activity Investigations

Under ambient conditions (around 26 °C), 90 mg of NH₃BH₃ 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 (Cu²⁺ + M²⁺)/NH₃BH₃ is fixed to be a constant of 0.02 although the Cu²⁺/M²⁺ molar ratios are changed in different batches of experiments. The reaction started once the aqueous solution was introduced to NH₃BH₃ 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 NH₃BH₃ can be briefly expressed as follows:

\[
\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2
\]  \hspace{1cm} (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 NH₃BH₃. The monitor of H₂ 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$_3$BH$_3$; (b) solution in khaki after introducing NH$_3$BH$_3$; and (c, d) solution becomes darker and darker during the H$_2$ generation and reduction process.
Fig. S2 Powder XRD patterns of Cu\textsubscript{x}M\textsubscript{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$_3$BH$_3$ aqueous solution (0.26 mol/L, 10 mL) over monometallic NPs under ambient conditions. The molar ratio of catalyst/NH$_3$BH$_3$ = 0.02.
**Fig. S5** Photograph showing the magnetic separation for the Cu@Co NPs in the solution.