

Supplementary Materials

***In-Situ* Spectroscopic Studies for One-Pot Synthesis of Composition-Controlled Cu-Ni Nanowires with Enhanced Catalytic Activity**

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Experimental Procedure

Materials

Nickel(II) acetate tetrahydrate, nickel(II) chloride anhydrous, nickel chloride(II) hexahydrate, nickel(II) nitrate hexahydrate, nickel(II) acetylacetonate anhydrous, nickel(II) acetylacetonate dihydrate, copper(II) chloride anhydrous, copper(I) chloride anhydrous, copper(II) chloride dihydrate, copper(II) acetate anhydrous, copper(II) nitrate trihydrate, 1-hexanol, 1-heptanol, 1-octanol, benzyl alcohol, oleylamine (OAm), sodium borohydride, and methylene blue tetrahydrate were provided by Wako Chemicals Co. Ltd, Japan. And the above chemicals were used without any treatment or purification.

Synthesis of Cu-Ni NWs

In a typical synthesis of Ni-coated Cu NWs, 2 mmol of CuCl_2 , 8 mmol of $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ and 34 g OAm were dissolved in 100 mL of 1-heptanol in a 300 mL separable four-necked flask. The reactants were heated from room temperature (RT) to 172 °C under nitrogen atmosphere and kept at this temperature for 3 h. After the reaction was completed, the system was cooled to RT, naturally. Then the sediments were washed using isopropanol-toluene mixture, and finally stored in toluene.

In situ measurements of oxidation states and structural changes of metal complexes in 1-heptanol solution during the formation of Cu-Ni NWs

In-situ X-ray Absorption Spectroscopy (XAS) measurements were carried out at Engineering Science Research II beamline (BL14B2) at Spring8, Japan using a reaction cell designed by the authors to perform XAFS-UV-Vis measurements of the reactants simultaneously from RT to 170 °C. The reaction cell was made of aluminum with quartz glass window at the lower section of the cell for UV-Vis measurements and a Kapton window for XAS measurements. The schematic diagram of the cell and the photograph of the experimental setup are given in Fig. 4. The reactants used for the measurements are as follow: 1.25 mmol of CuCl_2 anhydrous, 1.25 mmol $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ and 10 ml of OAm were dissolved in 25 ml of 1-heptanol. Then, 3 ml of the above solution was introduced into the reaction cell and was heated from R.T to 170 °C at a heating rate of 0.4 °C/min and maintained at this temperature for 3 h. The XAFS measurements were made at Cu- and Ni-K edges using 19 element SSD in the fluorescence mode.

Characterization

The identification of the crystal phases of the precipitates was carried out using an X-ray diffractometer (XRD, Rigaku SmartLab) with $\text{Cu-K}\alpha$ radiation between 10 and 90 degrees. The samples used for the above measurements were vacuum dried at 70 °C.

The size and morphology of the particles were analysed by using scanning and transmission electron microscopes operated at 10 kV (SEM, Hitachi S4500) and 200 kV (TEM, Hitachi H8100), respectively. Samples for the microscopic measurements were prepared by depositing toluene dispersed Cu-Ni particles or nanowires on a silicon holder (SEM) or amorphous carbon-coated grids (TEM). Also, high angle annular dark field (HAADF) microscopy coupled with STEM as well as energy dispersive

spectroscopy (EDS) elemental mapping were performed on a JEOL JEM-ARM200F instrument operated at 200 kV with a spherical aberration corrector; the nominal resolution was 0.8 Å.

The chemical composition of Cu-Ni products was analysed using ICP-MS (Inductively-Coupled Plasma mass spectrometer, SII SPS3100). The as-synthesized Cu Ni samples were dissolved in aqua regia and the Cu and Ni contents were evaluated from the calibration curves obtained using the standard Cu and Ni solutions.

Catalytic properties of Cu-Ni NWs

In a typical method, 5 mL NaBH₄ solution (20 mmol) and 22.5 mL methylene blue solution (9×10^{-2} mmol) were mixed in a glass beaker. In another beaker, 1 mg of NWs or NPs were dispersed in 12.5 mL distilled water. Both solutions were mixed and then 4 mL of the solution was withdrawn every minute for UV-Vis absorbance measurement (Hitachi U-3900) in the range between 500 and 800 nm. The methylene blue solution absorbs part of the visible light and exhibits maximum absorbance at 664.5 nm.

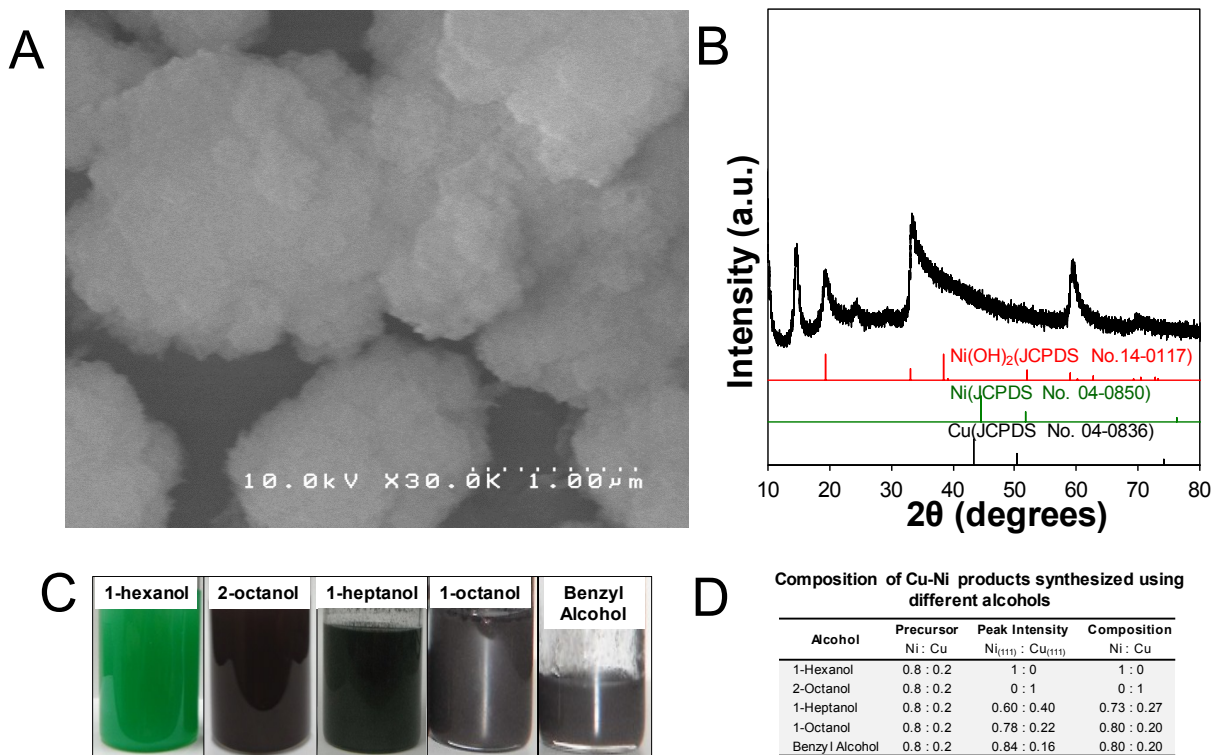


Fig. S1 (A) SEM image and (B) XRD pattern of product synthesized in 1-hexanol as solvent. (C) Photographs of Cu-Ni product suspensions in toluene and (D) chemical analysis and XRD peak intensity ratios of (111) planes of Cu and Ni in sediments obtained using different alcohols as reducing agent and solvent.

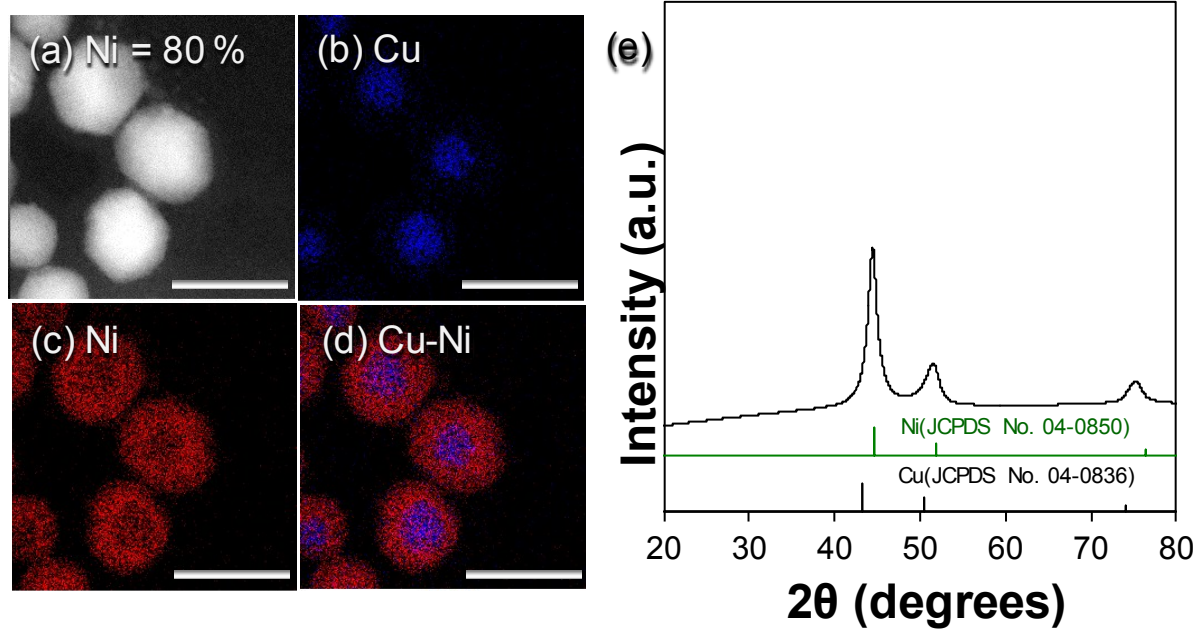


Fig. S2 Elemental mapping and XRD pattern of Cu-Ni NPs (80 % Ni) synthesized by using metallic acetates as precursors.

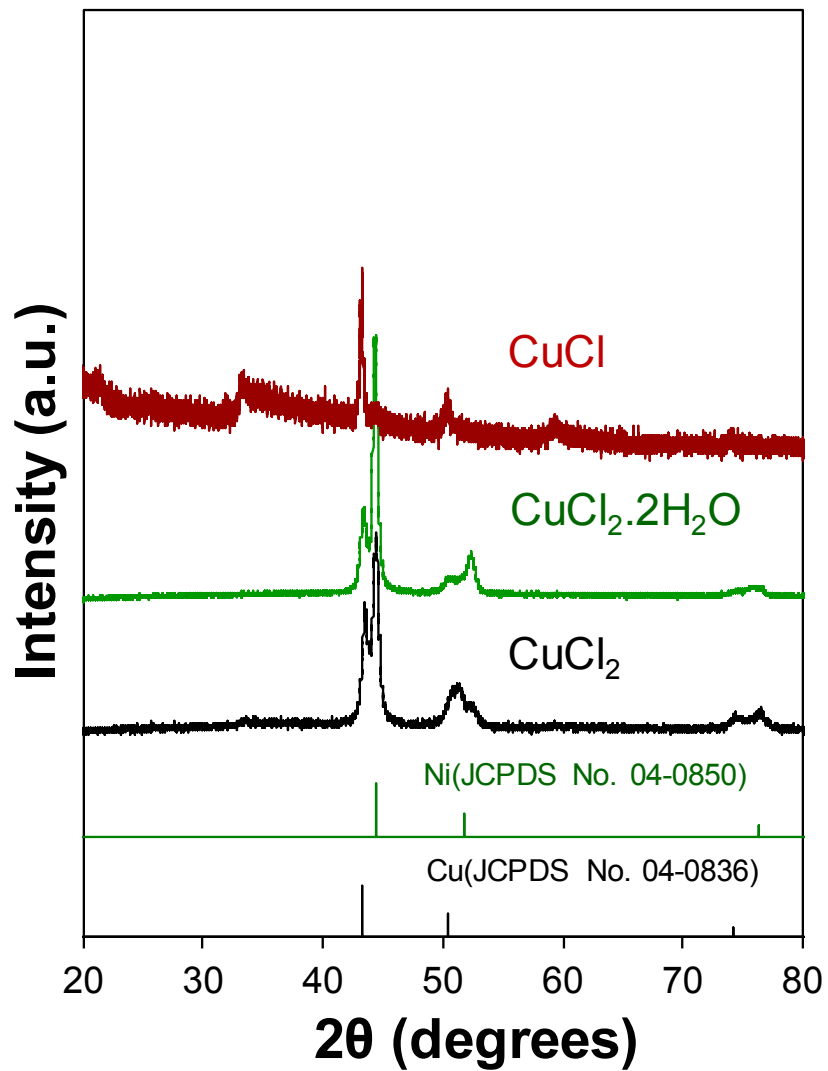


Fig. S3 XRD patterns of Cu-Ni NPs (80 % Ni) synthesized by using $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and different Cu chlorides sources.

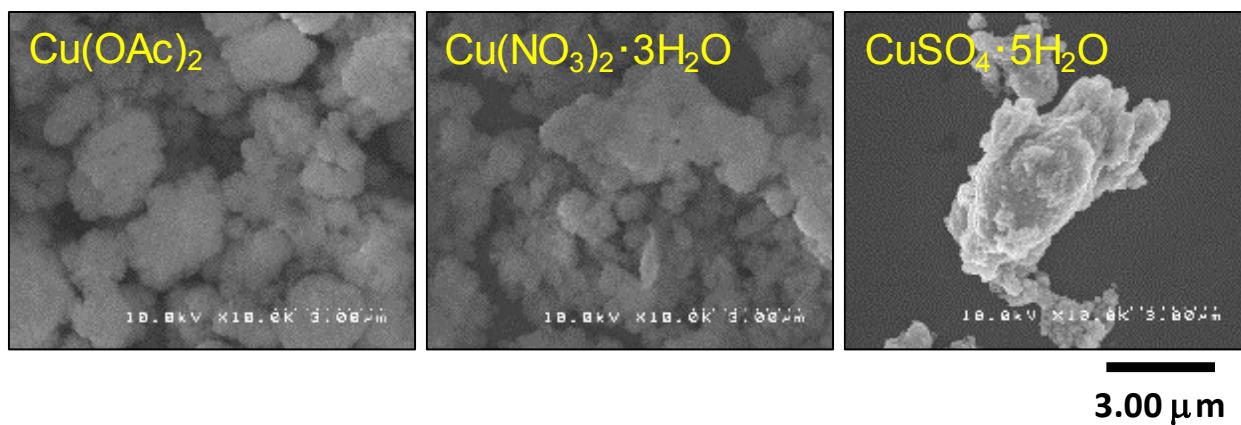
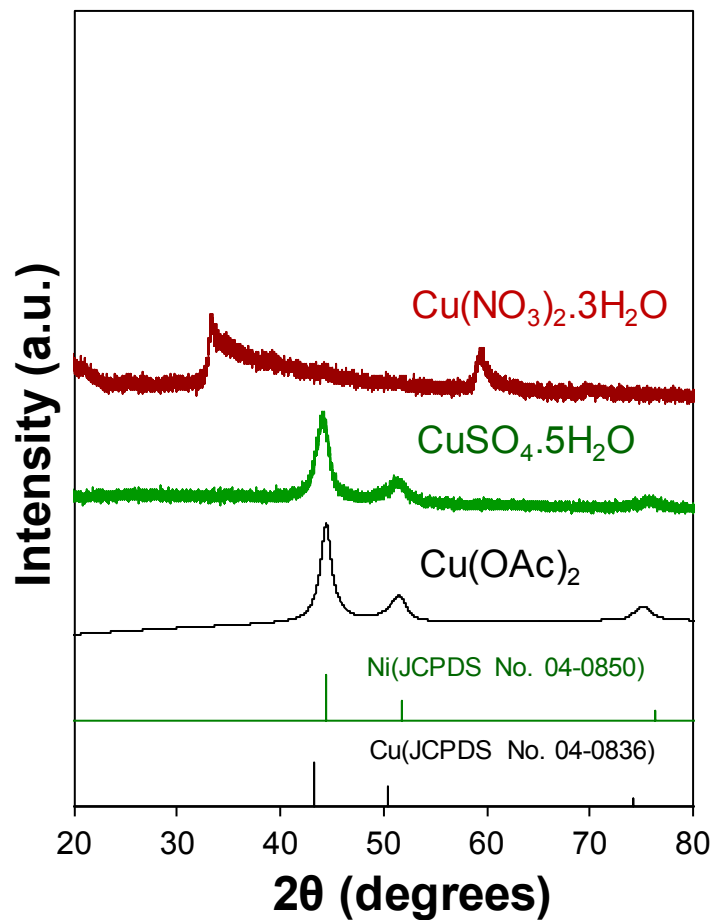


Fig. S4 XRD patterns of Cu-Ni products synthesized in 1-heptanol- OAm system using $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (8 mmol) as Ni source and different Cu sources (2 mmol): $\text{Cu}(\text{OAc})_2$ anhydrous, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Table S1 Summary of Cu-Ni products obtained at different conditions

Alcohol Type	Cu Precursor	Ni Precursor	Precursor Ratio	Product
1-Hexanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Ni(OH) ₂ : layered particles
2-Octanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu: nanoparticles, few rods
1-Heptanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires
1-Octanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires, few nanoparticles
Benzyl Alcohol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires, few nanoparticles
1-Heptanol	Cu(OAc) ₂ ·H ₂ O	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanoparticles
1-Heptanol	CuCl ₂ ·2H ₂ O	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires
1-Heptanol	CuCl	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu: nanowires Ni(OH) ₂ : layered particles
1-Heptanol	Cu(NO ₃) ₂ ·3H ₂ O	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Ni(OH) ₂ : layered particles
1-Heptanol	CuSO ₄ ·5H ₂ O	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanoparticles
1-Heptanol	CuCl ₂	Ni(acac) ₂	20 : 80	Cu-Ni: nanowires, nanoparticles
1-Heptanol	CuCl ₂	Ni(acac) ₂ ·2H ₂ O	20 : 80	Cu-Ni: nanowires, nanoparticles
1-Heptanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires
1-Heptanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	50 : 50	Cu-Ni: nanowires, few nanoparticles
1-Heptanol	CuCl ₂	Ni(OAc) ₂ ·4H ₂ O	70 : 30	No particles
1-Heptanol	CuCl	Ni(OAc) ₂ ·4H ₂ O	20 : 80	Cu-Ni: nanowires, nanoparticles
1-Heptanol	CuCl	Ni(OAc) ₂ ·4H ₂ O	50 : 50	Cu-Ni: few nanowires, nanoparticles
1-Heptanol	CuCl	Ni(OAc) ₂ ·4H ₂ O	70 : 30	Cu-Ni: few nanowires, nanoparticles
1-Heptanol	Cu(OAc) ₂ ·H ₂ O	NiCl ₂	20 : 80	Cu-Ni: nanowires, few nanoparticles
1-Heptanol	Cu(OAc) ₂ ·H ₂ O	NiCl ₂	50 : 50	Cu-Ni: nanowires, few nanoparticles
1-Heptanol	Cu(OAc) ₂ ·H ₂ O	NiCl ₂	70 : 30	Cu-Ni: nanoparticles

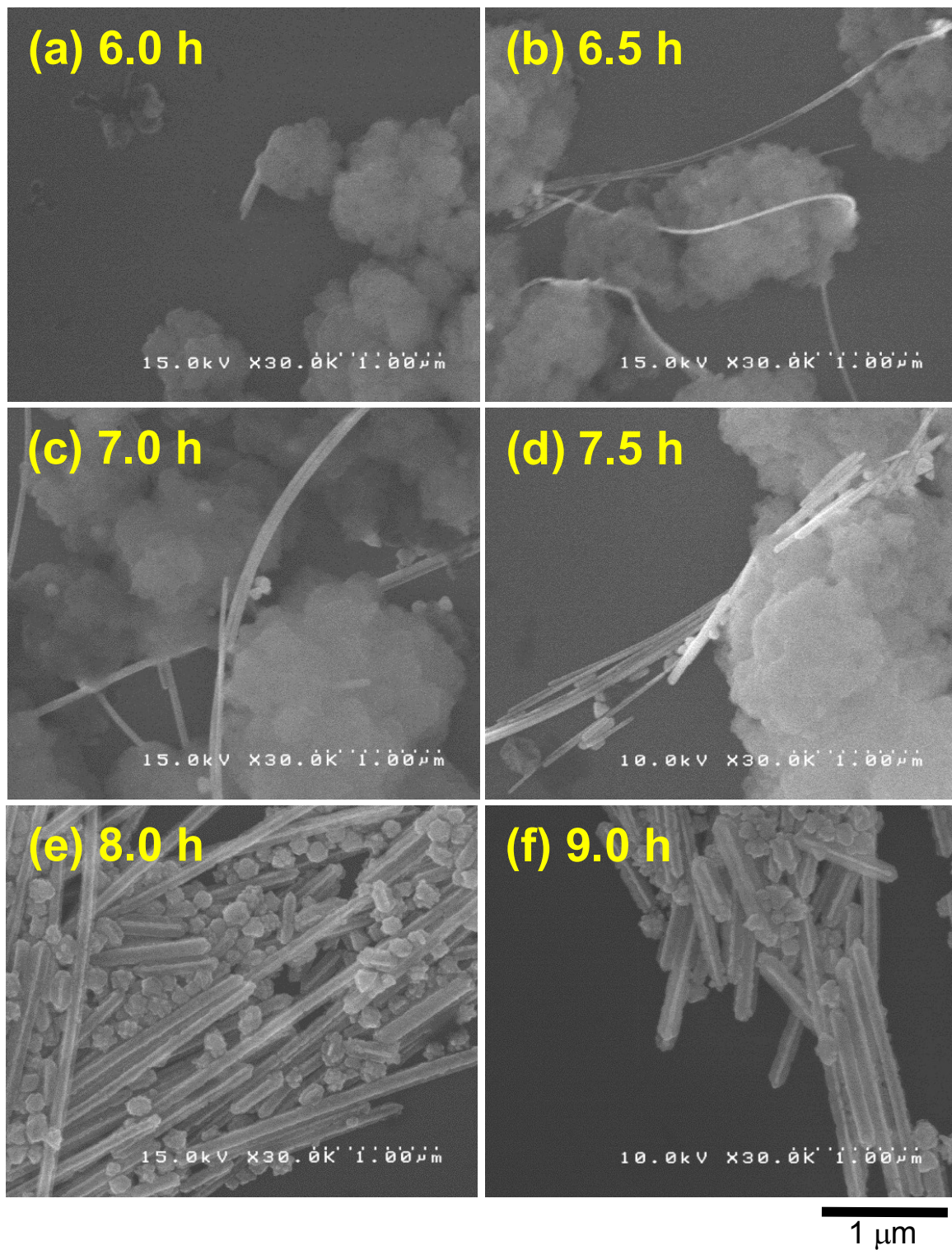


Fig. S5 SEM photographs of samples collected at different reaction times.

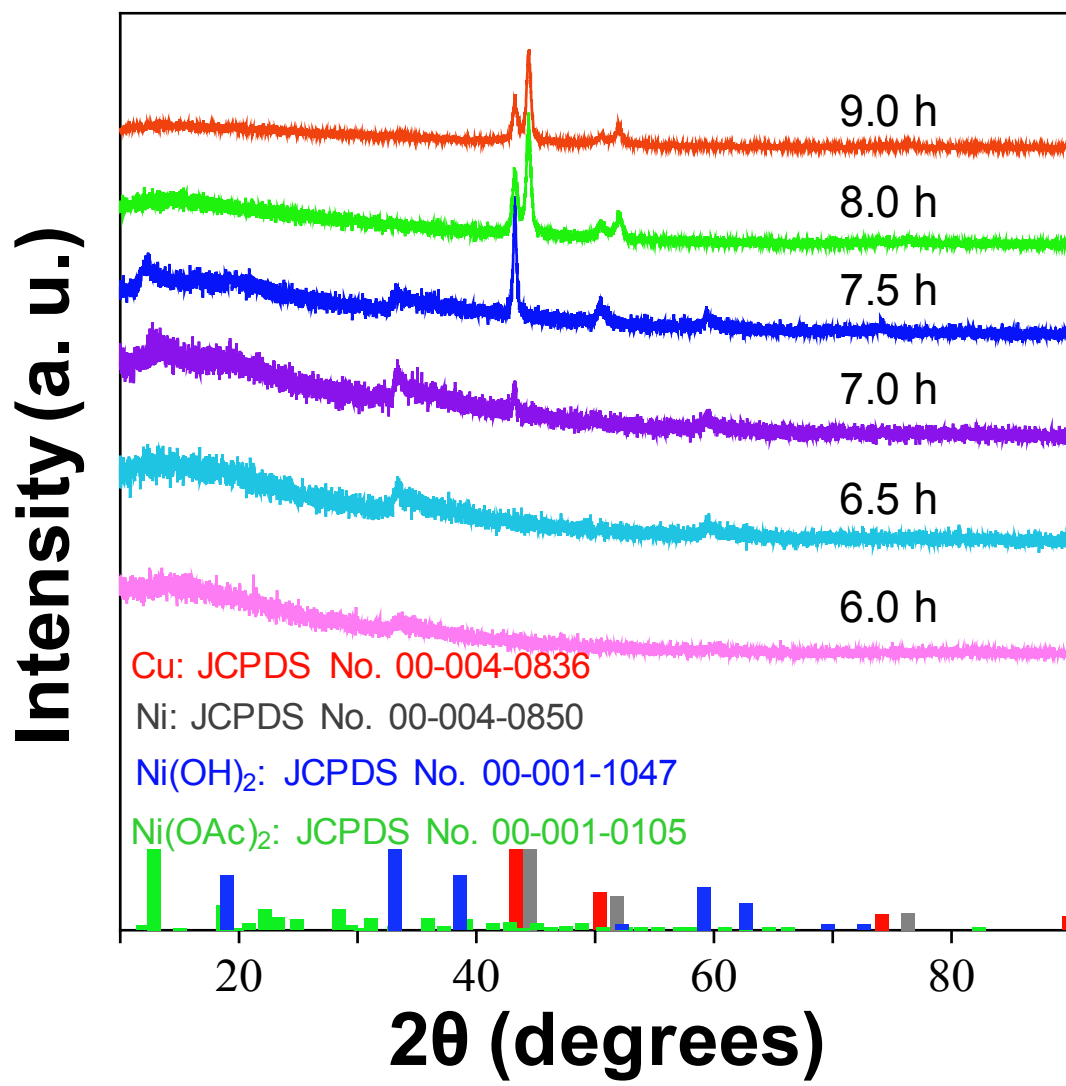


Fig. S6 XRD patterns of Cu-Ni NWs synthesized at different reaction times.

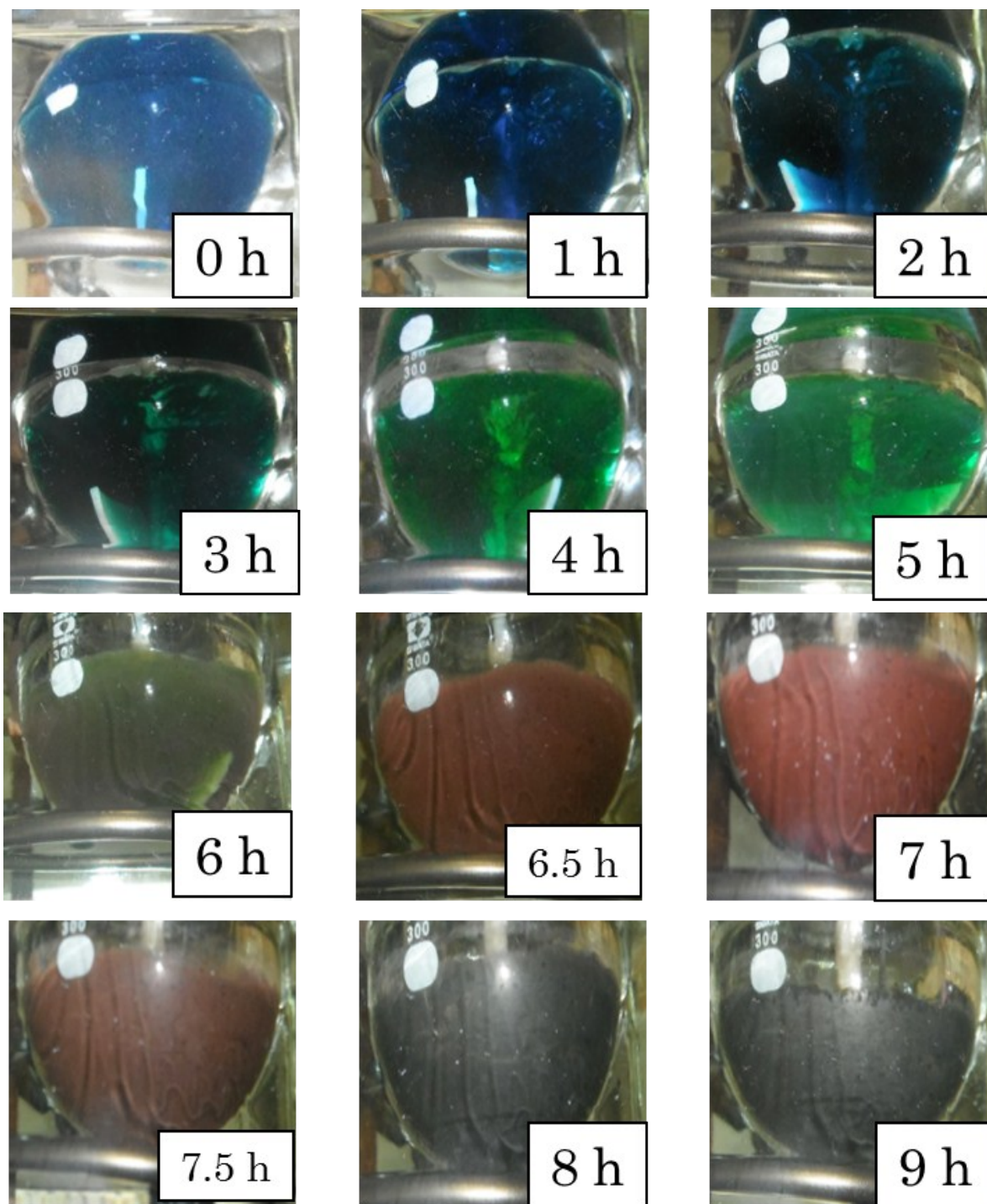


Fig. S7 Colour of the solutions obtained during the synthesis of Cu-Ni NWs at 177 °C for different reaction times.

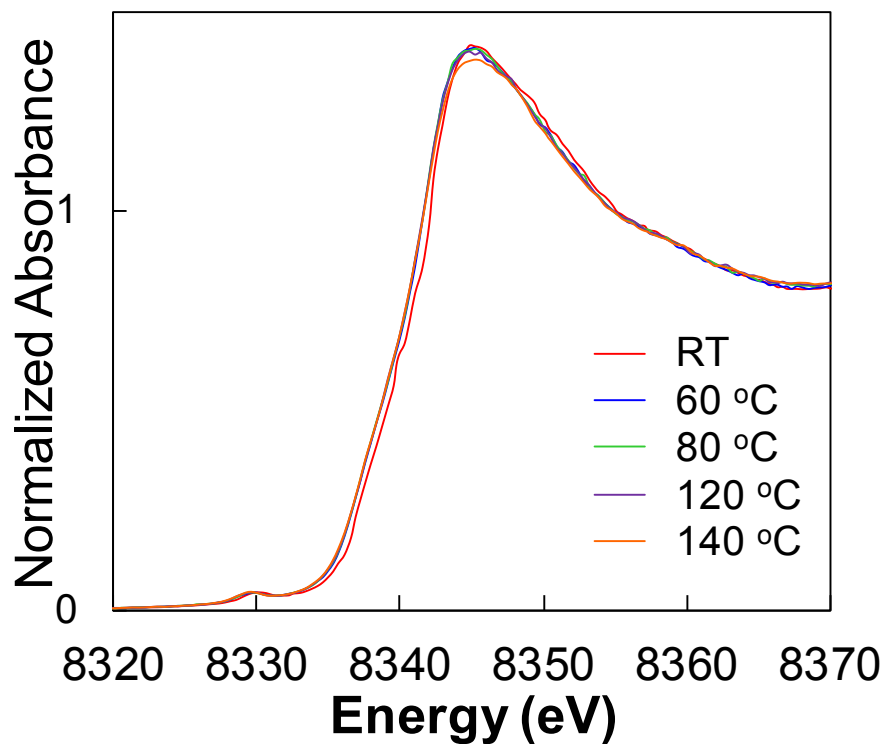


Fig. S8 (a) Changes in profiles of XANES spectra at Ni K-edge for Cu-Ni solution at various temperatures during heating.

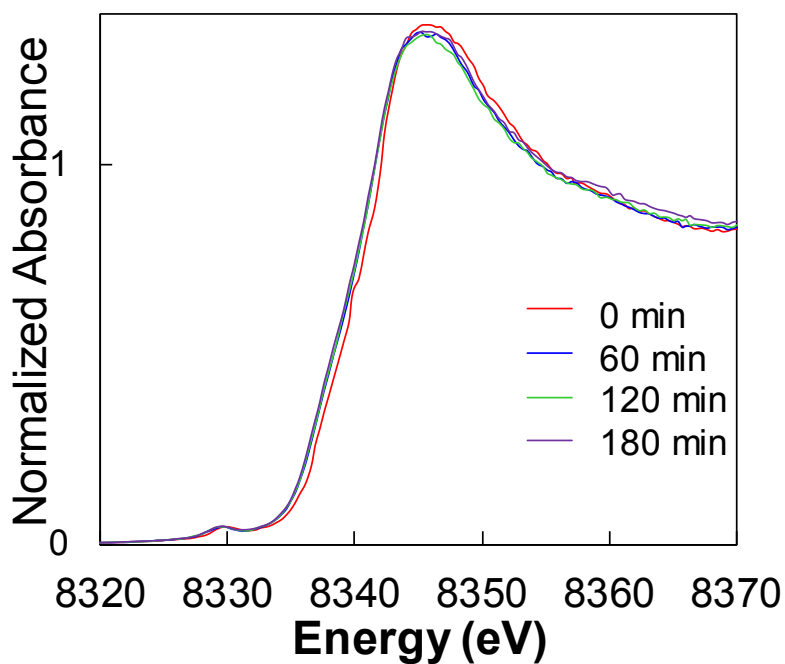


Fig. S8 (b) Changes in profiles of Ni K-edge XANES spectra for CuNi solution at 170°C for different durations.

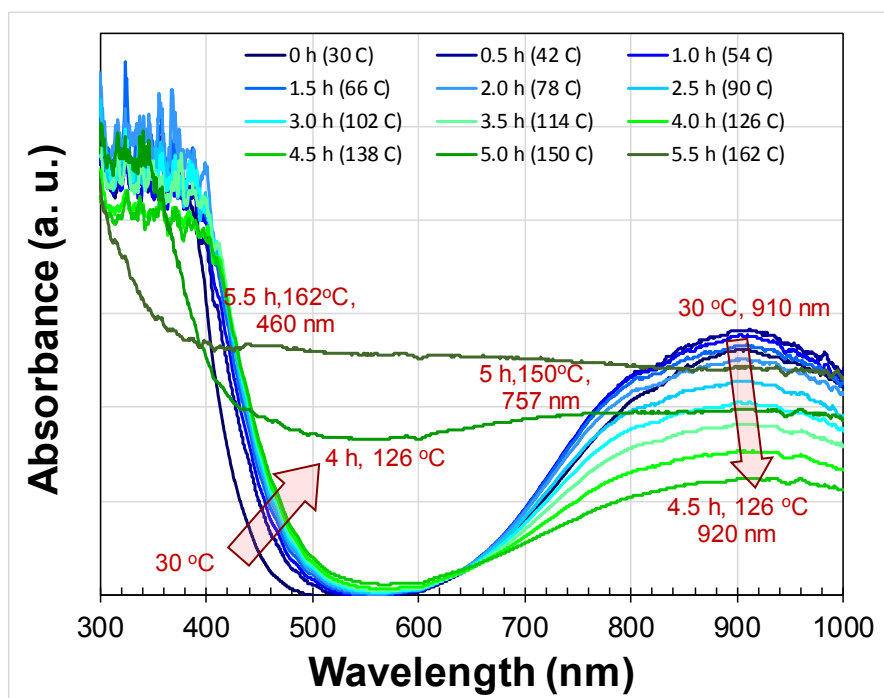


Fig. S9(a) In situ UV-Vis spectra taken at different times and temperatures during heating of CuCl_2 in 1-heptanol.

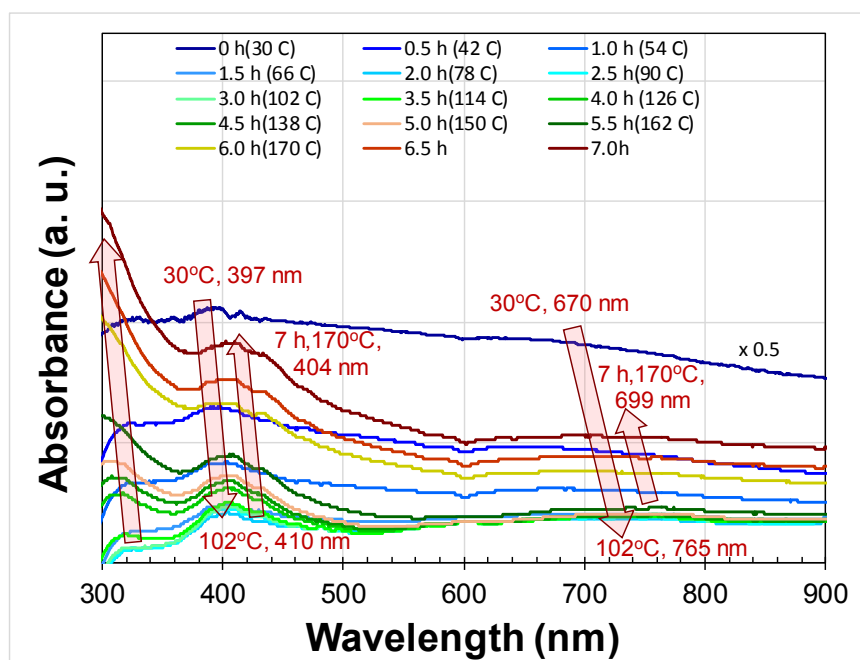


Fig. S9(b) In situ UV-Vis spectra taken at different times and temperatures during heating of $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ in 1-heptanol.

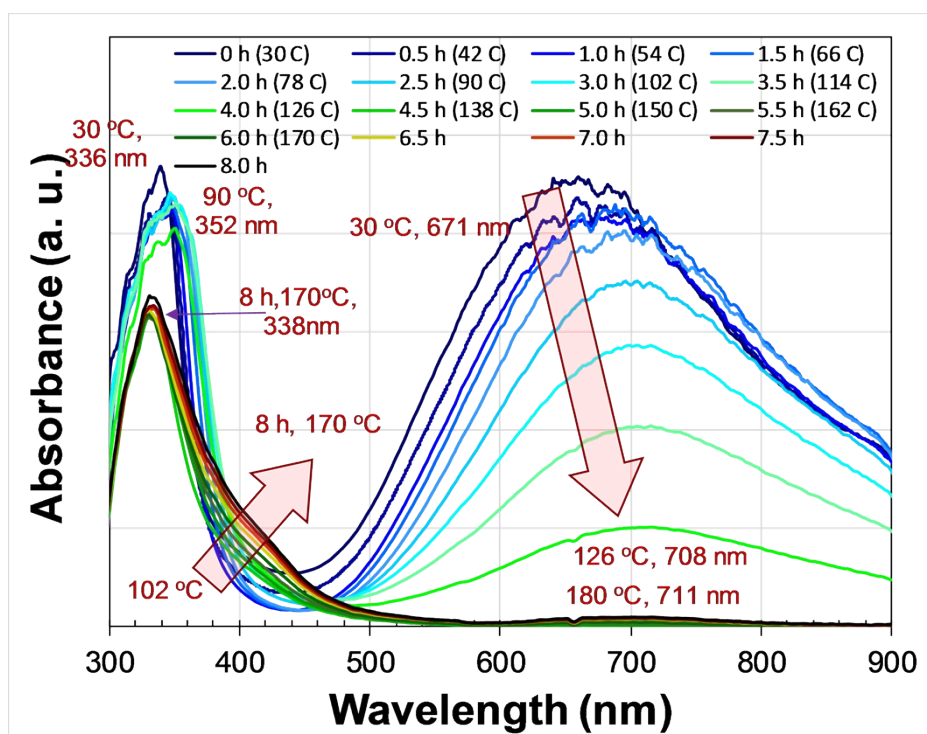


Fig. S10(a) In situ UV-Vis spectra taken at different times and temperatures during heating of CuCl₂ in oleylamine.

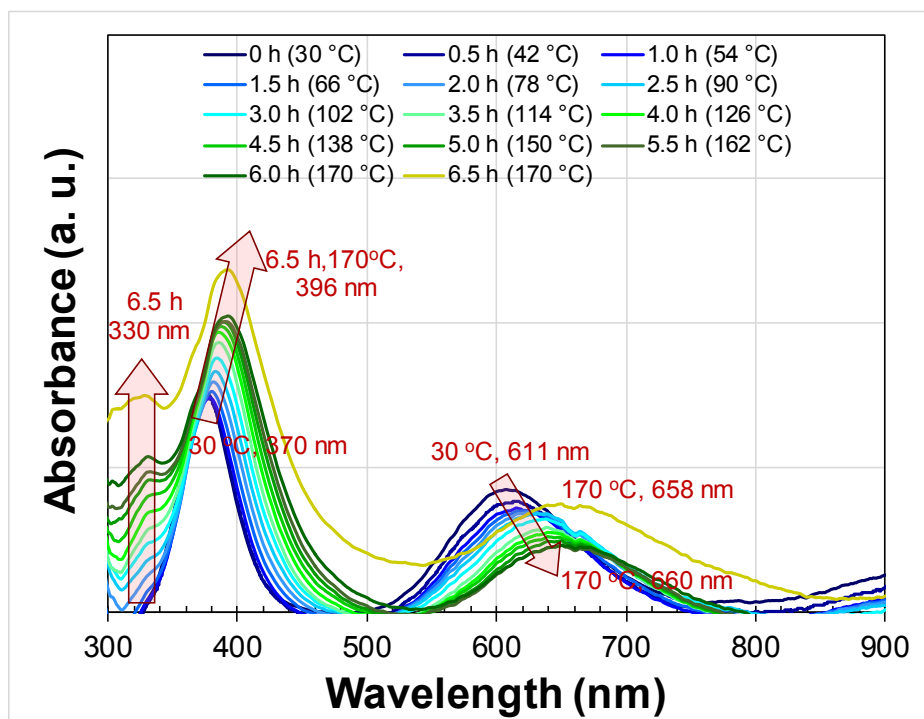


Fig. S10(b) In situ UV-Vis spectra taken at different times and temperatures during heating of Ni(OAc)₂·4H₂O in oleylamine

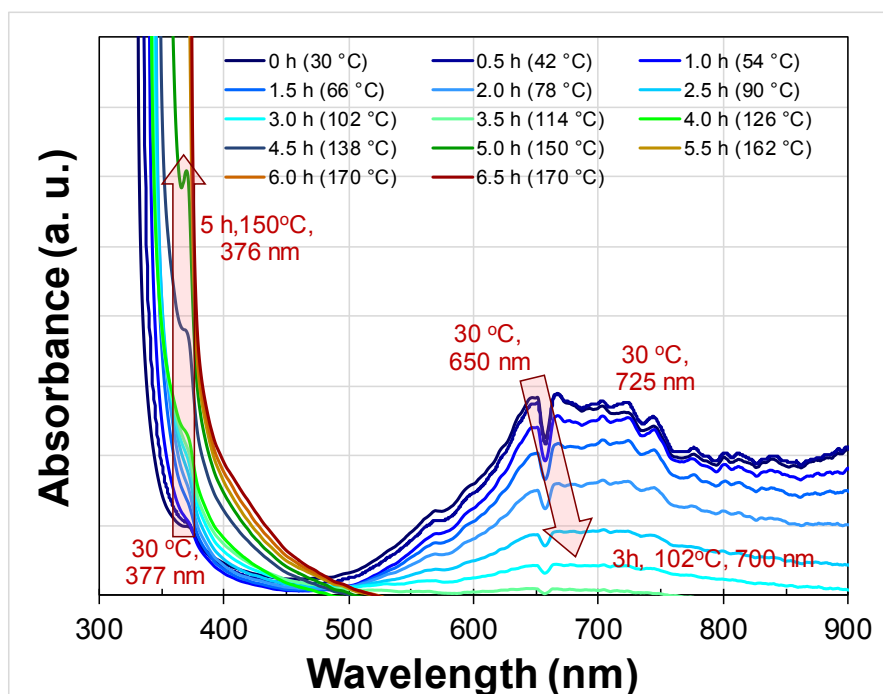


Fig. S11(a) In situ UV-Vis spectra taken at different times and temperatures during heating of CuCl_2 in 1-heptanol and oleylamine.

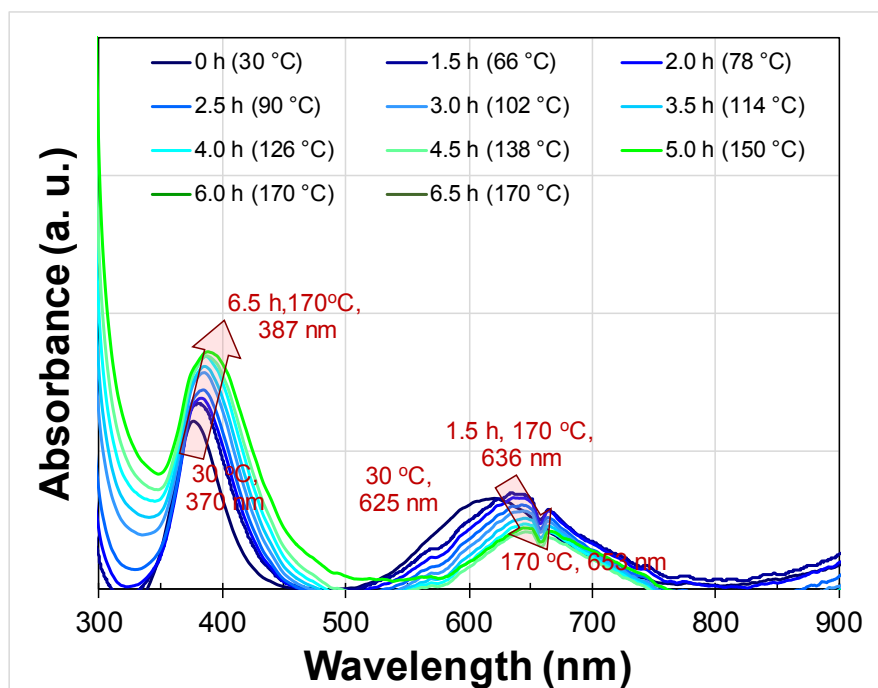


Fig. S11(b) In situ UV-Vis spectra taken at different times and temperatures during heating of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in 1-heptanol and oleylamine.

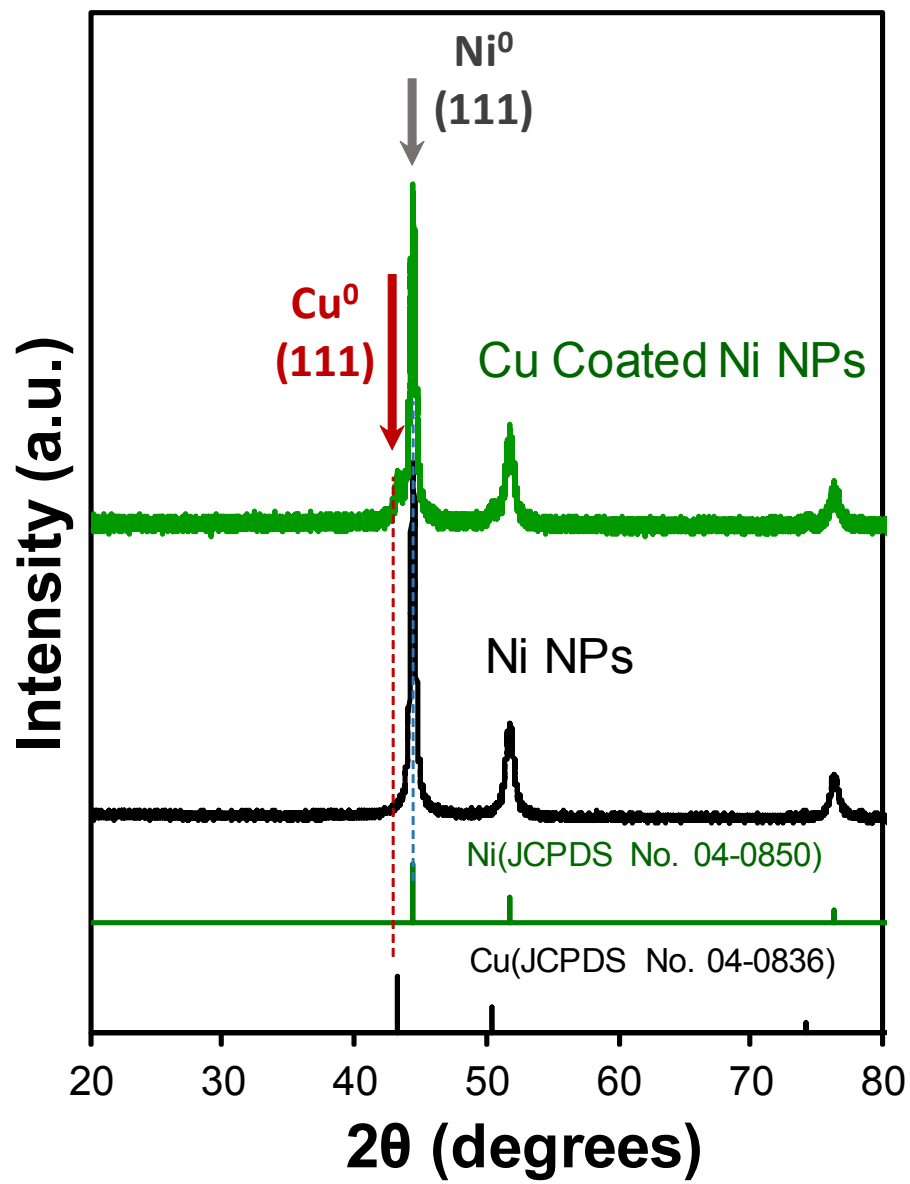


Fig. S12 XRD patterns of Ni NPs and Cu coated Ni NPs.