Supporting Information for

Electrochemical Semi-hydrogenation of Adiponitrile over Copper Nanowire as a Key Step for the Green Synthesis of Nylon-6

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1. Method and synthesis

1.1 Material preparation

Self-supported CuO nanowire arrays (CuO NWAs). Initially, the copper foam (CF) was cut into a rectangular shape measuring 5 cm × 1 cm × 0.15 cm. The CF was subsequently treated with acetone and a 3.0 M aqueous solution of HCl for 10 min, respectively. Subsequently, the CF was rinsed multiple times with deionized water and promptly dried under ambient conditions. $Cu(OH)_2$ nanowires were synthesized through the oxidation of CF substrate in an alkaline environment. Under vigorous stirring, 3.0 g NaOH and 0.68 g ammonium persulfate were dissolved in 30 ml deionized water, and the pre-treated CF was immersed in the solution. After 20 minutes, the CF coated with nanowires was extracted from the solution, subjected to multiple rinses with deionized water, and subsequently dried at ambient temperature. Following the drying process, a noticeable blue hydroxide layer was evident on the surface of CF after drying. The $Cu(OH)_2$ NWAs precursor was placed in a boat and subjected to heating at 300 °C for 2.5 h under an air atmosphere. After that, the materials were allowed to cool to room temperature, resulting in the formation of black CuO NWAs.

Self-supported Cu NWAs: CuO NWAs were electrochemically reduced to Cu NWAs in a 1M KOH solution. In a three-electrode system, a carbon sheet was used as counter electrode, Ag/AgCl (saturated KCl) as the reference electrode, and CuO NWAs as the work electrode with an exposed surface area of 1∅1 cm^2). Linear sweep voltammetry (LSV) was conducted within the potential range of -0.55 V ~ -1.5 V at a scan rate of 10 mV s^{-1} until the cathodic reduction peak was no longer observable.

1.2 Structure characterization

The morphology of the synthesized samples was characterized using a field emission scanning electron microscope (FE-SEM, JSM-7600F, Jeol Co., Ltd., Tokyo, Japan) equipped with energy scattering X-ray spectroscopy. X-ray photoelectron spectroscopy (XPS) analysis was conducted using the Thermo ESCALAB 250Xi with an Al Kα X-ray source. All XPS data were adjusted using a binding energy of 284.6 eV for the C_{1s} peak. X-ray diffraction (XRD) data were obtained using a

PANalytical X'pert instrument with a step rate of 2° min^{-1}. Transmission electron microscopy (TEM) images were acquired yusing a Zeiss LIBRA 200 instrument operating at 200 kV.

1.3 Electrochemical test

All electrochemical tests were conducted at CHI 660e workstation with a three-electrode system. In a divided cell, the working electrode has a defined geometric area of 1 × 1 cm^2, the anode consists of a graphite sheet measuring 2 cm × 2 cm, and the reference electrode is composed of Ag/AgCl with a saturated KCl solution. The electrolyte consists of a 1M KOH solution at 25 °C, with extra 4 ml methanol in the cathode chamber. All the potentials mentioned in this study were standardized against Ag/AgCl. Prior to conducting the ADN electroreduction test, linear sweep voltammetry (LSV) curves were recorded before and after the addition of the reactant at a scan rate of 5 mv s^{-1}. Electrolysis experiments were conducted at various current densities and potentials. Unless specified otherwise, the concentration of ADN is 0.1 M.

1.4 Product analysis

The electrochemical hydrogenation of ADN was conducted in 20 ml 1M KOH solution (methanol/water = 1/4) with 229 μL of organic reactant. Following the reaction, the cathodic reaction solution is subjected to chloroform extraction, after which a small sample is analyzed using gas chromatography. ACN and HMDA are the main products, and no cycloheximide was detected. The conversion, selectivity, and FE were determined using the following equations:

$$\text{Conversion}\ (\%) = \frac{n_{\text{ADN}}^{0} - n_{\text{ADN}}}{n_{\text{ADN}}^{0}} \times 100\% \quad \#(1)$$

$$\text{Selectivity(ACN)}\ (\%) = \frac{n_{\text{ACN}}}{n_{\text{ADN}}^{0} - n_{\text{ADN}}} \times 100\% \quad \#(2)$$

$$\text{Selectivity(HMDA)}\ (\%) = \frac{n_{\text{HMDA}}}{n_{\text{ADN}}^{0} - n_{\text{ADN}}} \times 100\% \quad \#(3)$$

$$\text{FE(ACN)}\ (\%) = \frac{n_{\text{ACN}} \times 4\text{F}}{\text{Q}} \times 100\% \#(4)$$

Where n_{ADN}^{0} is the initial mole amount of ADN, n_{ADN} is the final mole amount of ADN. The n_{ACN} and n_{HMDA} is the mole amount of generated ACN and HMDA, respectively. F is the Faradaic constant (96485 C mol^{-1}), and Q is the total consumed charge.

1.5 DFT calculation

The DFT calculations were performed using the Vienna ab initio simulation package (VASP). The entire process utilized a projection enhanced wave (PAW) and a plane wave truncation energy of 400 eV. The K-point sampling was conducted following the Monkhorst Pack protocol (3 × 3 × 1). In all DFT optimizations, the third vector was oriented perpendicular to the surface. During the calculation, the top two metal layers were allowed to relax, while the remaining metal layers were fixed. The weak interaction force was corrected using the DFT-D3 method proposed by Grimme et al. Ion relaxation should be allowed until the absolute value force acting on each atom is below 0.01 eV/Å. The adsorption energy can be determined using the following formula:

$$\Delta E_{ads} = \frac{1}{n}\left(E_{metal+adsorbate} - E_{metal} - E_{adsorbate}\right)\#(5)$$

1.6 Kinetic modelling method

In this study, the one-order reactor model was used for kinetic fitting. The hydrogenation of ADN is known to be a typical sequential reaction:

$$\text{ADN} \xrightarrow{k_1} \text{ACN} \xrightarrow{k_2} \text{HMDA}$$

Where k_1 and k_2 are the rate constants of the two steps. The rate equations for the three components are expressed as follows:

$$\frac{dc_{ADN}}{dt} = -k_1 c_{ADN} \#(6)$$

$$\frac{dc_{ACN}}{dt} = k_1 c_{ADN} - k_2 c_{ACN} \#(7)$$

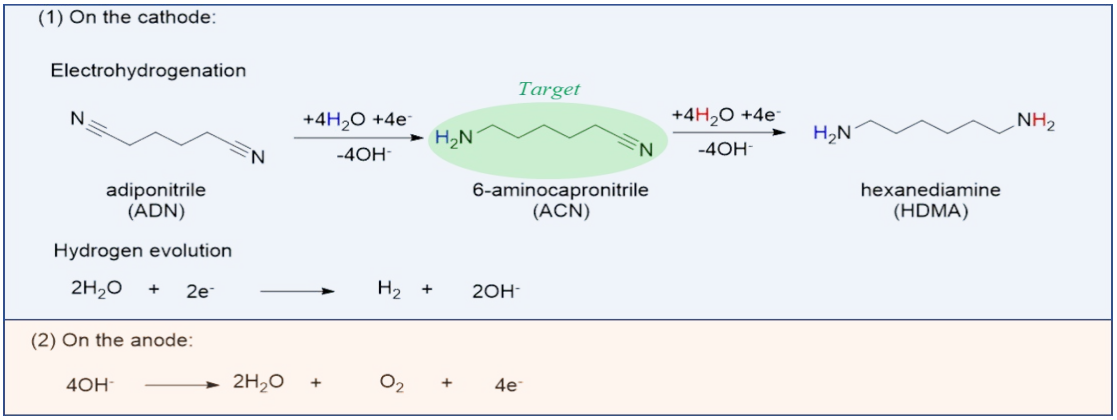
$$\frac{dc_{HMDA}}{dt} = - k_2 c_{ACN} \#（8）$$

Since electrochemical reaction is dependent on temperature and electrode potential, the expression for the electroreduction reaction rate constant is expressed by a combination of Arrhenius formula and Tafel formula:

$$k_i = k_i^{ref} \cdot \exp\left[-\frac{E_{a,i}}{R}\left(\frac{1}{T} - \frac{1}{T^{ref}} \right) \right] \cdot \exp\left[-\alpha_i \left(E - E^{ref} \right) \right]$$

Where T^{ref} and E^{ref} are the reference temperature (298.15 K) and the reference electrode potential (-1.4 V vs. Ag/AgCl), k_i^{ref} is the k value at reference temperature and reference potential, R is the gas constant, and E_a is the activation energy.

2. Supporting Figures ang Table



Scheme 1 Electrode reactions involved during the electrochemical hydrogenation of adiponitrile.

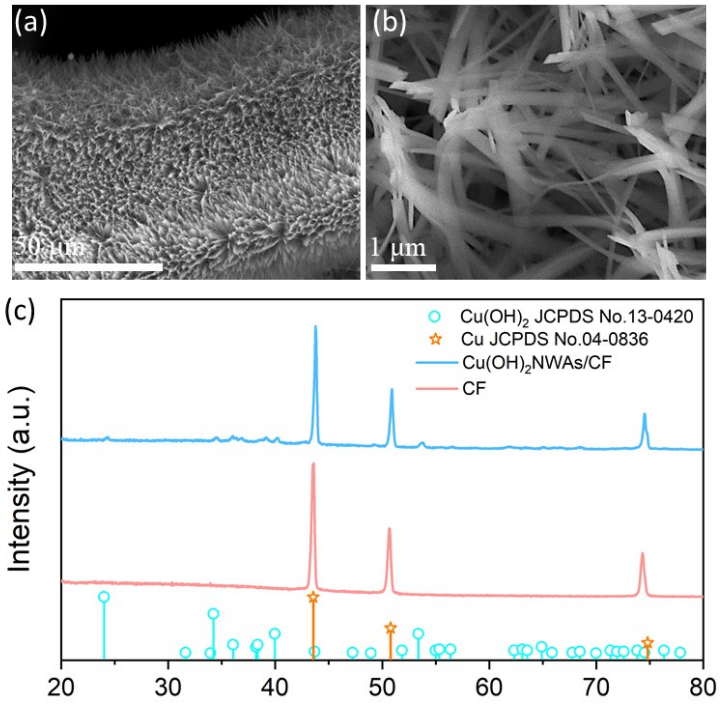


Fig. S1 Characterization results of Cu $(OH)_2$ NWAs. (a) Low-magnification and (b) high-magnification SEM images (c) XRD patterns of CF substrate and prepared $Cu(OH)_2$ NWAs.

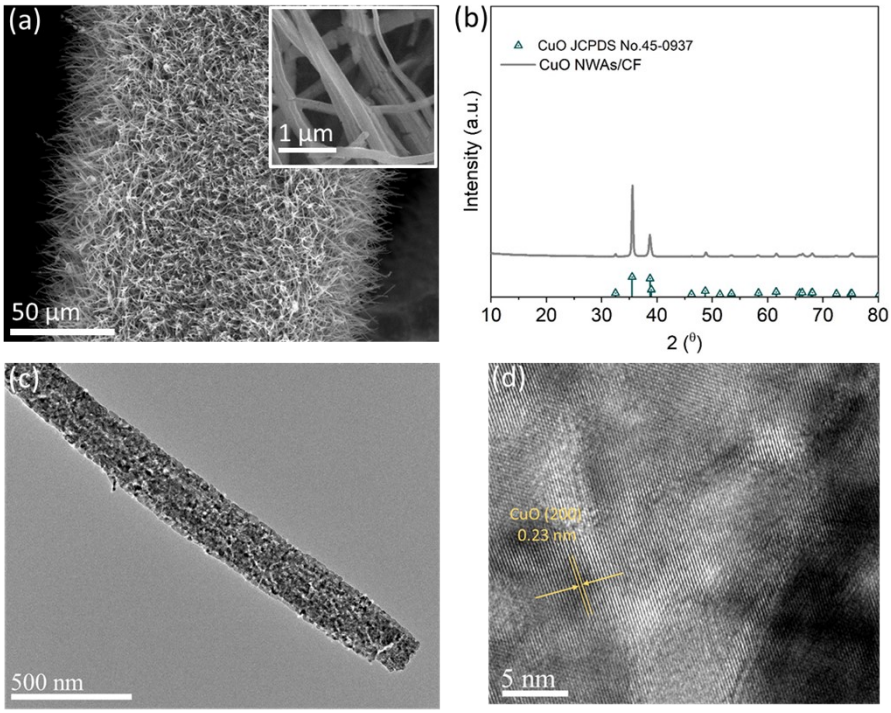


Fig. S2 Characterization results of CuO NWAs. (a) Low-magnification and high-magnification (insert figure) SEM images，(b) XRD patterns, (c) TEM and (d) HR-TEM images for prepared CuO NWAs.

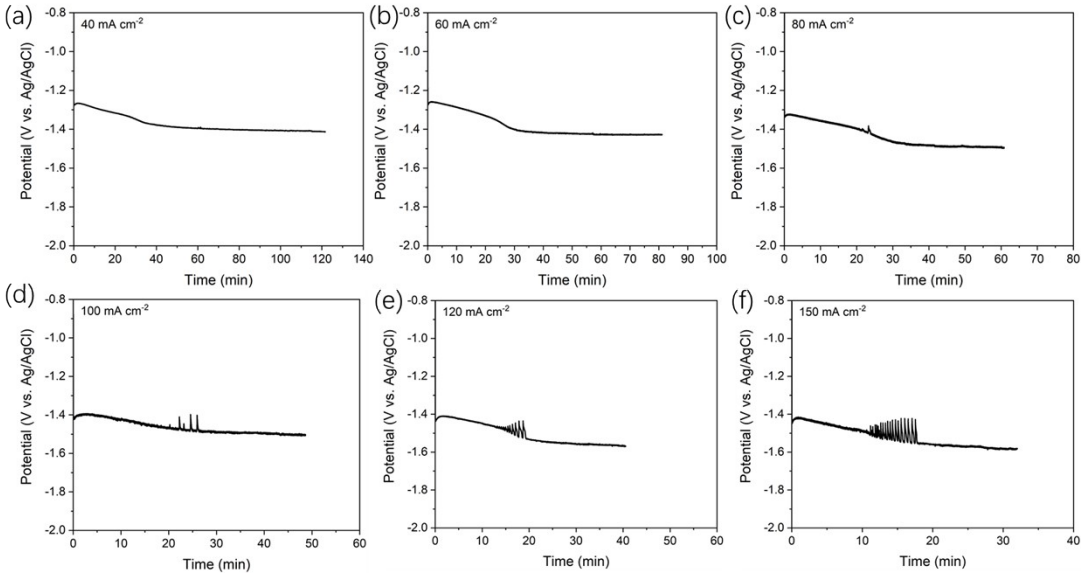


Fig. S3 The time-dependent potential of ADN electroreduction reaction under different current density on Cu NWAs/CF cathode in 1 M KOH containing methanol.

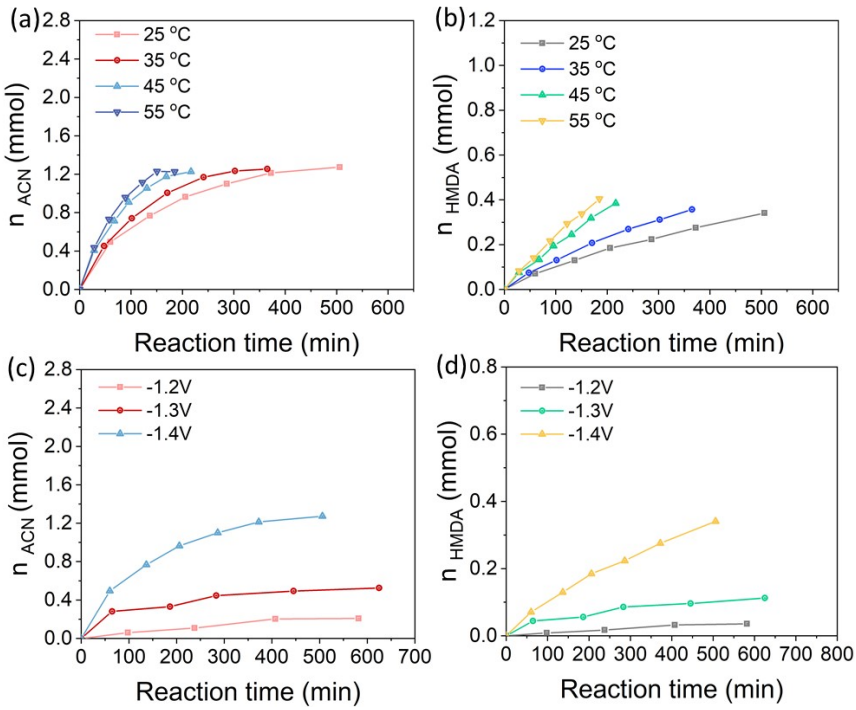


Fig. S4 Effect of temperature and potential on the ADN reduction products over Cu NWAs electrode. (a, b) Time-dependent generation of ACN and HMDA at different reaction temperature. Applied potential: −1.4 V vs. Ag/AgCl. (c, d) Time-dependent generation of ACN and HMDA under different applied potential. Reaction temperature: 25 ℃.