Supporting Information for Electrocatalytic Hydrogenation of 5-Hydroxymethylfurfural to 2,5-Bis(hydroxymethyl)furan Using CuIr Bimetallic Nanowires

Chen Chen [1], Chenhao Yang [1], Hongke Li [1], Yiran Liu [1], Yao Chen [2,*] and Yunlei Zhang [1,*]

[1] Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China
[2] School of the Environment and Safety, Jiangsu University, Zhenjiang 212013, China
* Correspondence: chenyao1390@ujs.edu.cn (Y.C.); jsdxzyl@ujs.edu.cn (Y.Z.)

1. Experimental section

1.1. Catalyst Characterizations

The X-ray diffraction (XRD) patterns were obtained on a Bruker D8 diffractometer using Cu Kα radiation. The scanning range was 10-80° with a scan speed of 7° min^{-1}. The images of samples were obtained by scanning electron microscope (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). The Brunauer–Emmett–Teller (BET) surface area of the materials was measured by N_2 adsorption-desorption isotherms at 77 K in an Autosorb-6B (Quantachrome Instruments). X-ray photoelectron spectroscopy (XPS) was measured by using a Thermo Fisher Scientific ESCALAB 250 with a monochromatized Al X-ray source. All XPS results were corrected by referencing the C1s speak at 284.8 eV. Electron spin resonance (ESR) spectra were recorded at room temperature on a Bruker E7407 spectrometer operating at X-band for radical intermediate detection.

1.2. Electrochemical Experimental Parameters

Electrochemical measurements were conducted using a 40 mL H-type three-electrode electrolytic cell, in which the two compartments were separated by a cation exchange membrane. The electrolyte was 0.1 M KOH solution with a pH of 13. In the experiments, the prepared catalyst served as the working electrode, a platinum sheet as the counter electrode, and a mercury oxide electrode as the reference electrode. The geometric surface area of the working electrode was 1 cm^2. Chronoamperometry was applied during each electrocatalytic test, and all measured potentials were converted to the reversible hydrogen electrode (RHE) scale using Equation 1. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s^{-1}, while cyclic voltammetry (CV) was conducted at a scan rate of 100 mV s^{-1}. The electrochemical reduction of HMF was carried out under magnetic stirring at 500 rpm. All experiments were performed at room temperature and repeated three times to ensure data reliability and reduce standard error.

$$E_{RHE} = E_{(Hg/HgO)} + 0.0592 \times pH + 0.098 \quad (1)$$

1.3. Product Analysis

After the electrochemical reaction, a 90 μL aliquot of the reaction mixture was withdrawn and diluted to 9 mL. The sample was filtered through a 0.22 μm membrane filter prior to analysis. Product analysis was conducted using high-performance liquid chromatography (HPLC) equipped with an Agilent Eclipse C18 column (250.0 × 4.6 mm, 5.0 μm). The mobile phase was composed of 0.1 wt% ammonium sulfate and acetonitrile in a 90:10 volume ratio. The flow rate was gradually increased from 0.2 mL min^{-1} to 0.6 mL min^{-1}, with the final system pressure stabilizing at approximately 103 bar. The infrared detection wavelength was set to 223 nm, and the column temperature was maintained at 40°C. HMF eluted at approximately 6.5 minutes, while

BHMF appeared at around 5.7 minutes. The standard calibration curves for HMF and BHMF are shown in Figure S1.

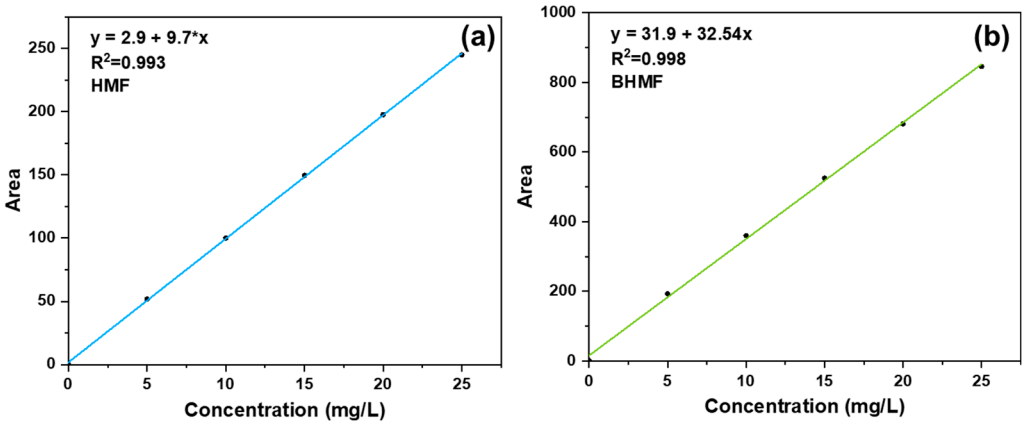

Figure S1. The standard curves of HMF (a) and BHMF (b).

1.4. In Situ Infrared Analysis

To investigate the surface adsorption behavior of the catalyst and the evolution of reaction intermediates during the electrocatalytic hydrogenation of HMF, Fourier-transform infrared (FTIR) spectroscopy was employed. The spectra were recorded within the range of 1000–4000 cm^{-1}. To improve data quality and suppress background noise, each spectrum was obtained by accumulating 600 scans and analyzed at a resolution of 4 cm^{-1}. An in situ FTIR electrochemical cell with a three-electrode configuration was used, where Ag/AgCl served as the reference electrode, Pt as the counter electrode, and the $CuIr_x$ material as the working electrode, directly exposed beneath the infrared transmission window.

At the beginning of the experiment, 0.5 M Na_2SO_4 was introduced as the supporting electrolyte. The system was left at rest for 10 minutes without the substrate to achieve pre-equilibration of the electrode/electrolyte interface. Subsequently, 20 mM HMF was added to the electrolyte, and a static adsorption test was conducted for 30 minutes under open-circuit conditions. After adsorption equilibrium, a constant potential of -0.45 V vs RHE was applied for 30 minutes, during which in situ FTIR spectra were continuously collected to monitor the evolution of functional groups and the generation of intermediates throughout the reaction.

1.5. Electron Spin Resonance (ESR) Spectroscopy

ESR spectroscopy was employed to detect radical intermediates generated during the electrocatalytic hydrogenation process using the spin-trapping agent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). For the measurement, the catalyst was dispersed in the reaction electrolyte (0.1 M KOH containing 20 mM HMF) under a nitrogen atmosphere.

DMPO was added to the mixture at a final concentration of 50 mM. The suspension was transferred to a quartz ESR flat cell and placed in the spectrometer cavity. In-situ ESR measurements were performed under a constant applied potential of 1.4 V vs. RHE. Aliquots of the reaction mixture were extracted at defined time intervals (0, 5, 10, and 15 min) for ex-situ ESR analysis to track the evolution of radical species over time. Spectra were recorded at room temperature on a Bruker E7407 spectrometer operating at X-band.For mathematical simulation and quantitative comparison of the ESR signals, the obtained spectra were processed by integration after careful baseline correction. The area under the curve corresponding to the characteristic signals of DMPO-H* and DMPO-C* was calculated. The integrated area from the CuIr40 catalyst was then compared to that from the Cu NW reference to obtain the signal enhancement factors reported in the main text.

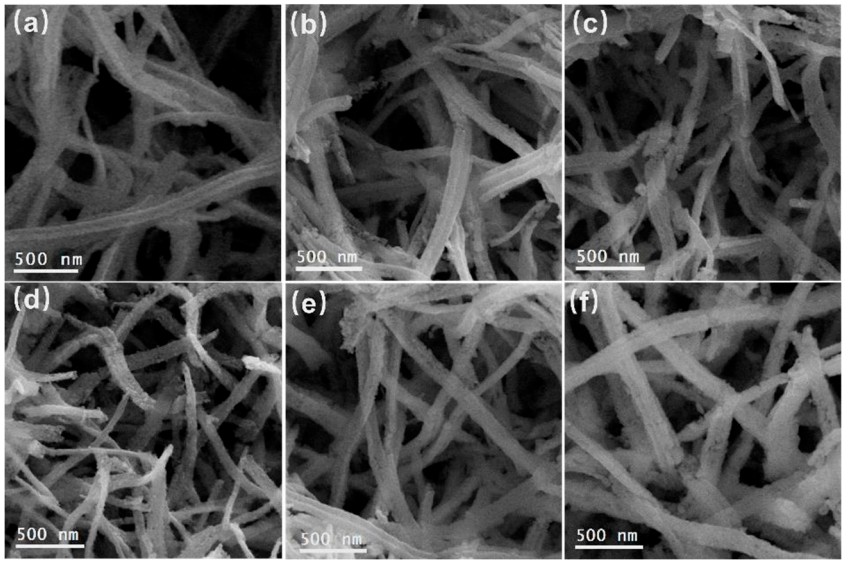

Figure S2. SEM images of Cu NW (a), $CuIr_{10}$ (b), $CuIr_{20}$ (c), $CuIr_{30}$ (d), $CuIr_{40}$ (e), and $CuIr_{50}$ (f).

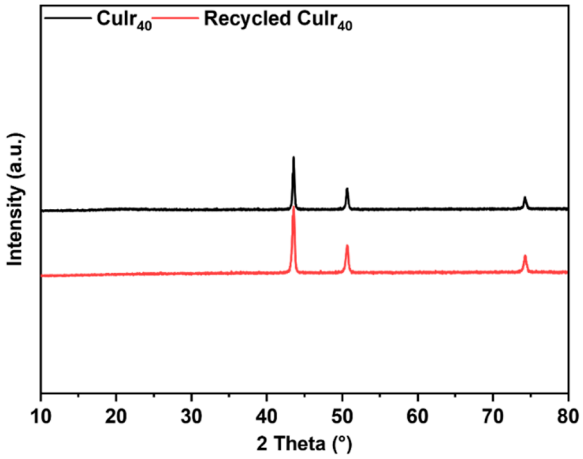

Figure S3. XRD patterns before and after cycles.

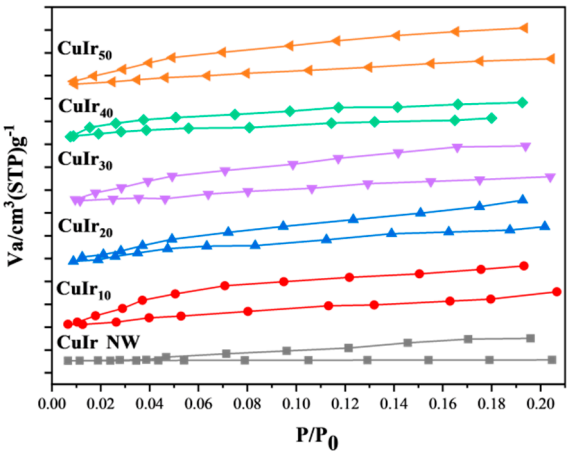

Figure S4. Magnified view of the low-pressure region of N_2 adsorption isotherms.

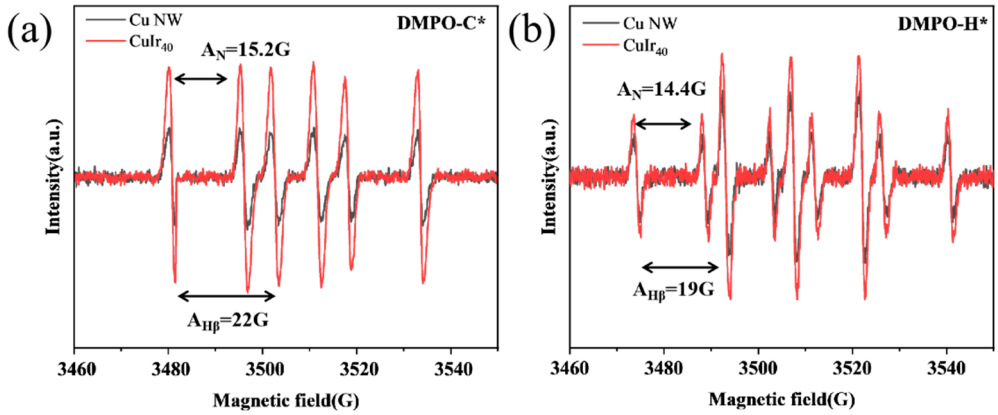

Figure S5. ESR spectra of DMPO-C*(a) and DMPO-H*(b) adducts generated over different catalysts after 15 min of reaction.

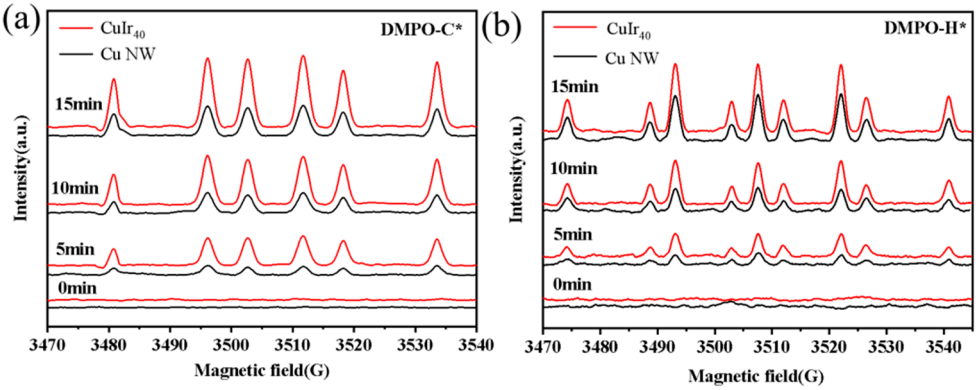

Figure S6. Integral fitting of ESR spectra of DMPO-C*(a) and DMPO-H*(b) for Cu NW and $CuIr_{40}$.

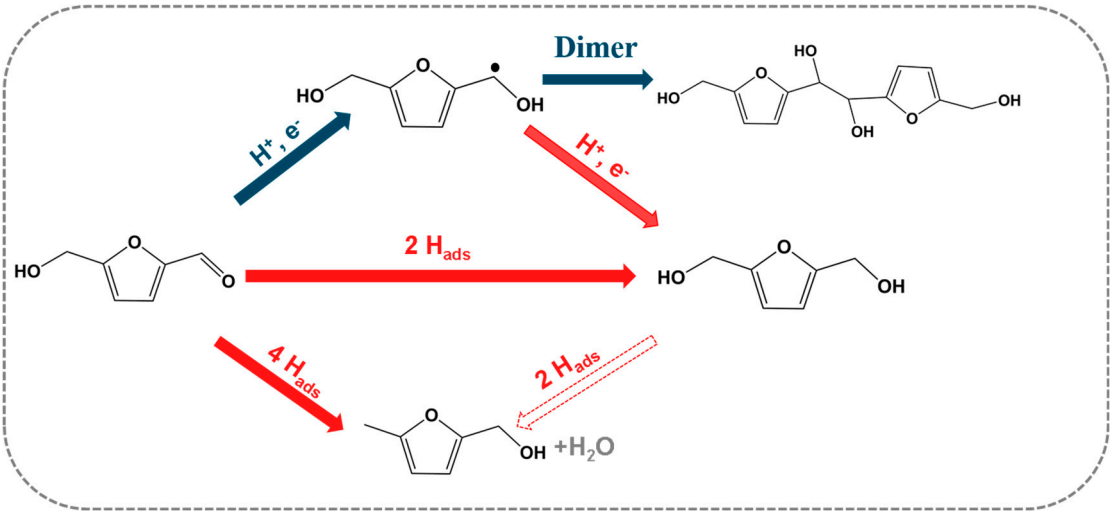

Figure S7. The hydrogenation path of BHMF prepared by HMF.

Table S1. The Ir content on the catalyst surface.

Catalysts	Time (min)	Ir loaded (mg)	Ir loaded (wt%)
$CuIr_{10}$	10	0.135	0.125
$CuIr_{20}$	20	0.217	0.20
$CuIr_{30}$	30	0.274	0.25
$CuIr_{40}$	40	0.336	0.30
$CuIr_{50}$	50	0.373	0.35