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Flexible cupric oxide photocathode with enhanced stability for renewable hydrogen energy production from solar water splitting

Yang Li[a,b,c*] and Kai Luo[a]

a. School of Energy and Power, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu, 212003, P. R. China.

b. School of Science, Tianjin University, Tianjin, 300072, China.

c. Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin, 300072, China.

*Corresponding author: Yang Li (yang_li@just.edu.cn)

Experimental details:

Material preparation

Cu foil (thickness 50 μm) purchased from Hebei Hangxu Metal Manufacturing Co.,Ltd. was cut into strips before use. In a typical procedure, Cu strips were dipped into acetone and ethanol, ultrasonic cleaning for 5 minutes, respectively. The Cu strips were burned with an alcohol burner, and keep moving for 10 s to prevent local overheating. After air cooling at ambient conditions, a black CuO film formed on the Cu substrate.

Titanium butoxide (Sinopharm chemical reagent Co.,Ltd.), lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, Sinopharm chemical reagent Co.,Ltd.) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sinopharm chemical reagent Co.,Ltd.) were dissolved into absolute ethanol, respectively, and the concentrations were controlled to 0.1 M, respectively. The TiO_2, La_2O_3 and NiO precursors were deposited on CuO strips via a dip-coating method (withdrawal rate: 1 mm/s), followed by a fast fire treatment with an alcohol burner. To obtain the desired film construction, the dip-coating processes of the different layers were conducted twice for TiO_2, five times for La_2O_3 and once for NiO, respectively. The film growth rates per cycle and the film thicknesses were measured by both ellipsometry and profilometer on films deposited on optically polished silicon wafers with a native surface oxide. Before the deposition, the CuO substrates were conditioned for 10 min under plasma in a Plasma Cleaner (13.56 MHz, Hongming Tech.).

Characterization

The surface morphologies were observed with a field-emission scanning electron microscopy (SEM; Hitachi, S-4800). The oxidation states were analyzed with an X-ray photoelectron spectroscopy (XPS, Perkinelmer, PHI1600 ESCA). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.

For the analyses in the basic solutions, all the CuO photocathodes were activated in pH 13 at 0.5 V_{RHE} for 2000 s before experiments. Photoelectrochemical response measurements were carried out using a three-electrode setup, with a platinum counter-electrode and a Ag/AgCl/KCl(sat.) reference electrode (E = 0.210 V vs. NHE). The scan rate for the cyclic voltammetry was 100 mVs^{-1}. All the potentials in this work are converted using the reversible hydrogen electrode (RHE) as the reference electrode, according to the following equation:

$$E(RHE) = E(Ag/AgCl) + 0.21 + 0.059 \times pH \qquad (1)$$

The surface area of the film in contact with the electrolyte was 1.0 cm^2. The electrochemical behavior was monitored with an IVIUM compactstat, while the light was provided by a 500 W Xenon-arc lamp, calibrated to provide 1 sun (100 $mW \cdot cm^{-2}$) of AM 1.5 illumination to the sample. The measurement of H_2 and O_2 was carried out by connecting the photoelectrochemical cell to an automatic sealed analysis system (HM-A300, Changzhou Hongming Instrument Technology Co.,Ltd.) to circulate the gas toward the gas chromatograph (GC, PerkinElmer Clarus 500, TCD detector, carrier gas (Ar) flow rate = 36 mL/min; oven temperature = 50 °C; detector temperature = 120 °C) for the detection. The sealed system was previously vacuumed to evacuate the air and the dissolved oxygen.

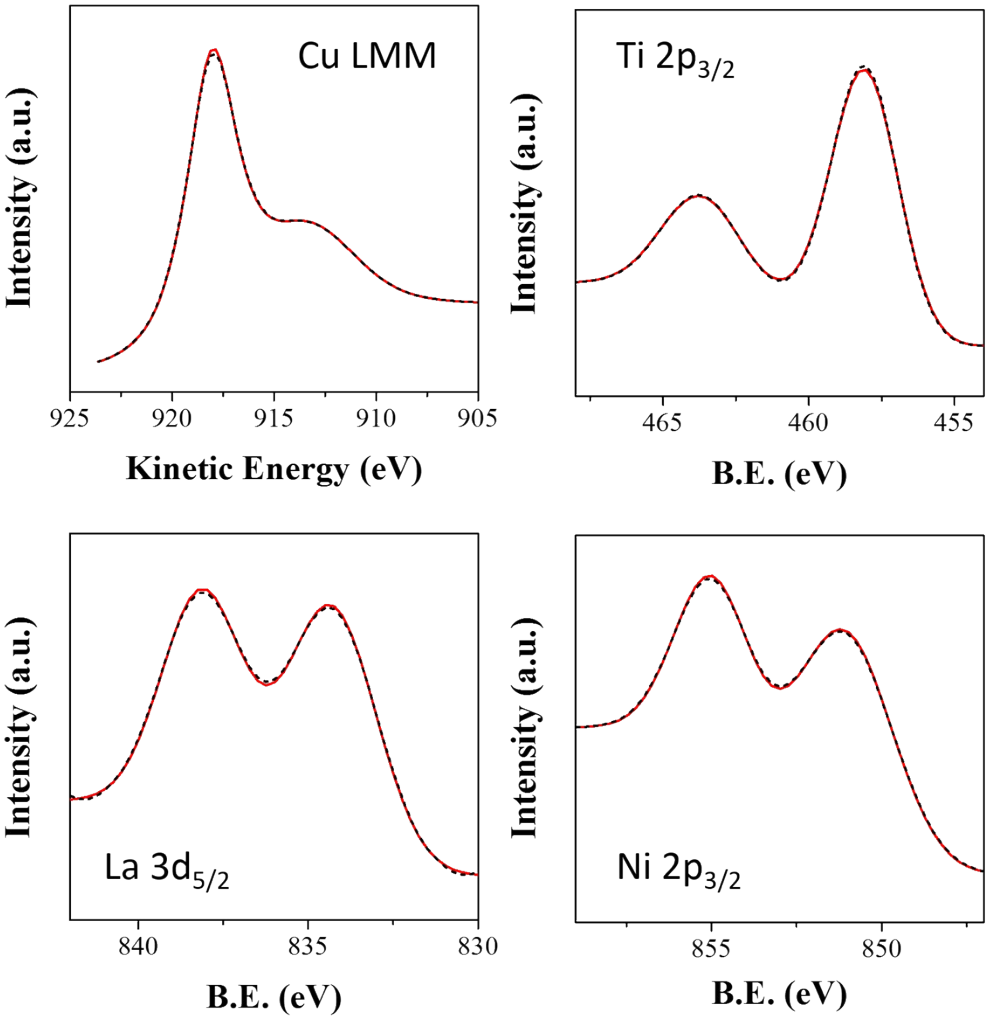

Figure S1. X-ray photoelectron spectra (XPS) of Cu LMM, Ti 2p, La 3d and Ni 2p before (solid lines) and after (dash lines) 30 min reaction.