Electronic Supplementary Information

Experimental section

Materials

Sodium hypophosphite (NaH_2PO_2) was purchased from Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), and ammonium persulfate (APS) were bought from Beijing Chemical Corporation. CF was supplied by Changsha Liyuan New Material Co. , Ltd. All the reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

Preparation of $Cu(OH)_2$/CF:

Typically, a piece of CF (1 × 2 cm^2) was washed with HCl, ethanol and deionized water several times to remove the surface impurities. The cleaned CF was immediately immersed into a aqueous solution of 2.5 mol L^{-1} sodium hydroxide and 0.1 mol L^{-1} ammonium persulphate at room temperature for about 20 min. The CF was taken out of the solution and washed with de-ionized water several times and dried in air.

Preparation of Cu_3P/CF and Cu_3P film:

$Cu(OH)_2$/CF and NaH_2PO_2 (0.2 g) were placed at two separate positions in one closed porcelain crucible with NaH_2PO_2 at the upstream side of the furnace. Subsequently, the samples were heated at 250 °C for 1 h with a heating speed of 2 °C min^{-1} in Ar atmosphere. Cu_3P/CF was collected after naturally cooled to ambient temperature under Ar. The loading of Cu_3P nanoarray on CF was measured by inductively coupled plasma mass spectrometry (ICP-MS) (loading: 9.2 mg cm^{-2}). Cu_3P film was prepared

by direct phosphidation of CF.

Characterizations

XRD data were collected on Bruker D8 ADVANCE Diffractiometer (λ = 1.5418 Å). SEM measurements were carried out on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. TEM image was collected on a Hitachi H-8100 electron microscope with an accelerating voltage of 200 kV. ICP-AES analysis was performed on Model ARCOS FHS12 (SPECTRO Analytical Instruments Inc., Germany).

Electrochemical measurements:

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Cu_3P/CF as working electrode, Pt wire as the counter electrode, and a saturated calomel electrode (SCE) used as the reference electrode. Since hydrazine hydrate is toxic, we need to wear gloves during the entire experiment. All potentials measured were calibrated to RHE using the following equation: E (RHE) = E (SCE) + 1.068 V. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1}. All experiments were carried out at room temperature (~ 25 °C).

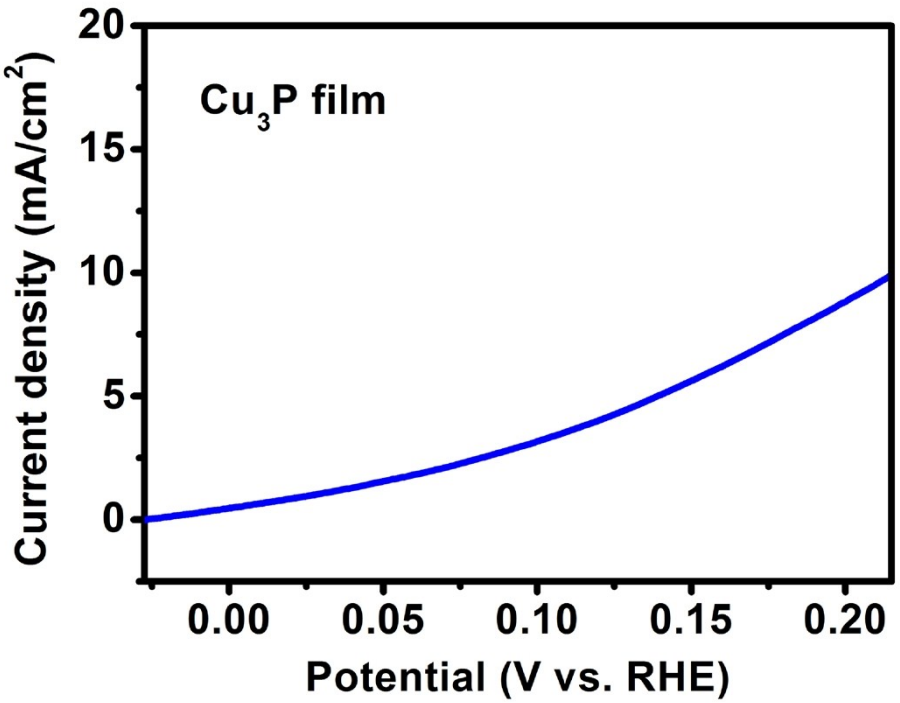

Fig S1. Polarization curve for Cu_3P film towards 0.5 M hydrazine for HzOR in 1.0 M KOH with a scan rate of 5 mV s^{-1}.

Movie S1. This movie shows cathodic (black) hydrogen evolution and anodic (red) HzOR on a Cu_3P/CF catalyst couple.