Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Tracking the In Situ Generation of Hetero-Metal−Metal Bonds in Phosphide Electrocatalyst for Electrocatalytic Hydrogen Evolution

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METHODS

1.1 Chemical reagents

Ruthenium (III) chloride hydrate (35-40%, ACROS), cobalt (II) nitrate hexahydrate (99%, SHOWA), urea (99.5%, ACROS), sodium hypophosphite (> 99%, SEEDCHEM), potassium hydroxide (85%, SHOWA), sulfuric acid (96%, AENCORE), acetone (95%, ECHO Chemical) and ethanol (95%, ECHO Chemical). Ultrapure water (18.2 MΩ-cm, type I) was produced by PURELAB Classic system (ELGA).

1.2 Fabrication of Ru_x@CoP on carbon paper.

1.2.1 Pretreatment of carbon paper substrate

Piranha solution composed of 3 parts of sulfuric acid and 1 part of hydrogen peroxide solution was first prepared for hydrophobic treatments. Pristine carbon cloth was washed by acetone, ethanol and deionized water for 1 hour ultrasonically, followed by treatment with piranha solution at room temperature for 24 hours. Then the carbon paper was rinsed with deionized water until it returned neutral, which was monitored by pH test strips. The obtained hydrophilic carbon cloth was stored in fresh DI water.

1.2.2 Fabrication of ruthenium-substituted cobalt hydroxide precursors on carbon paper substrate.

Kapton tape with moderate size was stuck onto the pretreated hydrophilic carbon paper (CP, 2.0 cm × 2.5 cm) to allow only 1.0 cm × 1.0 cm of area for further reaction. In the case of synthesis for pure cobalt-based catalyst, the carbon cloth was immersed into the aqueous reactant solution (6mL) composed of 100 mM cobalt(III) nitrate hydrate, 1.5 M urea, 300 mM potassium hydroxide which was well-mixed in a 20 mL sample vial. The container was then heated at 85 °C through a hot air circulation oven for 6 hours. The obtained precursor film on CP was carefully rinsed with DI water and acetone 3 times as well as preventing the demolition of the as-grown hydroxide film. After rinsing the precursor film, Kapton tapes were removed and followed by dehumidification with nitrogen gas. In the case of synthesis of cobalt precursor with metallic ruthenium, various concentrations of ruthenium(III) chloride hydrate, which were 0mM, 60 mM, 120 mM, 180 mM, and 240 mM, were included in CoP, $Ru_{0.6}$@CoP, $Ru_{1.2}$@CoP, $Ru_{1.8}$@CoP, and $Ru_{2.4}$@CoP, respectively.

1.2.3 Fabrication of Ru_x@CoP on carbon paper

The second step was phosphorization combining reduction through decomposition of sodium hypophosphite in tube furnace. The as-prepared precursor film and 0.52 g of sodium hypophosphite were placed in a customized glass tube, and the precursor was kept 6 cm away from the sodium hypophosphite powder in the glass tube (the length of that is 10 cm). The glass tube was set to the center of furnace tube and remained at 30 °C for 5 minutes to achieve thermal equilibrium. After isothermal treatment which ensuring initial temperature to be 30 °C, the target temperature was set to be 200 °C for 6 hours with 5 °C min^{-1} of heating rate then cooled to room temperature naturally. Finally, the obtained catalyst was rinsed by DI water for several time to make sure that the impurities which might exist on the surface had been removed.

1.3 Physical and chemical characterizations

The morphology of samples was studied by JEOL JSM-7600F field emission scanning electron microscope (SEM). Element mapping was conducted through Oxford Instruments INCA x-act silicon drift detector energy-dispersive X-ray spectroscope (EDS). The low resolution XRD patterns were obtained from Bruker AXS D2 PHASER. *In situ* XRD and XAS were performed using synchrotron radiation at room temperature within customized electrochemical cell. The *in situ* XAS and XRD data were collected in TLS-01C1 and TLS-17C1 at NSRRC, Taiwan. The XAS experiments were performed in total-fluorescence-yield mode at the scan range of 21867-22917 eV for Ru K-edge and 7600-8300 eV for Co K-edge.

1.4 Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 760E electrochemical workstation (CH Instruments, Inc., Shanghai) with a configured three-electrode system, in which a graphite rod served as the counter electrode, a Ag/AgCl (saturated KCl solution) electrode worked as the reference electrode and the as-prepared electrocatalyst as the working electrode. HER performance of all as prepared catalysts were evaluated by linear sweep voltammetry (LSV) measurements, which were conducted in 0.5 M H_2SO_4 electrolyte with a scan rate of 1 mV s^{-1}. Notably, 10 cycles cyclic voltammetry (CV) were conducted at scan rate of 25 mV s^{-1} to make the catalyst stabilize before LSV tests. The saturated Ag/AgCl electrode converted to reverse hydrogen electrode (RHE) has been calibrated. All the measured polarization curve potentials in this work were converted to RHE by following equations: $E_{RHE} = E_{Ag/AgCl} + 1.014$ V (1.0 M KOH solution), where the ERHE is the potential referred to reversible hydrogen electrode (RHE) and $E_{Ag/AgCl}$ is measured with the Ag/AgCl reference electrode.

1.5 Electrochemical hydrogen evolution mechanism:

HER in alkaline solution:

$M + H^+ + e^- \rightarrow M\text{-}H_{ads}$ Volmer step (Tafel slope ≥118 mV dec^{-1})

$M + M\text{-}H_{ads} + H^+ + e^- \rightarrow M + H_2$ Heyrovsky step (Tafel slope ≈ 39 mV dec^{-1})

$M\text{-}H_{ads} + M\text{-}H_{ads} \rightarrow 2M + H_2$ Tafel step (Tafel slope ≤ 29 mV dec^{-1})

Where M denotes an active site on the surface of catalyst.

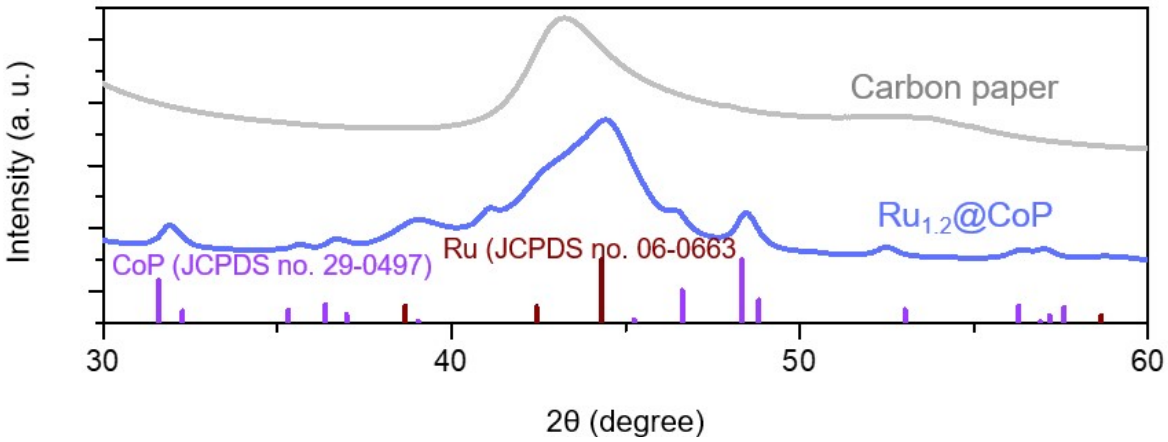

Figure S1. XRD patterns of the as-prepared $Ru_{1.2}$@CoP and substrate of carbon paper.

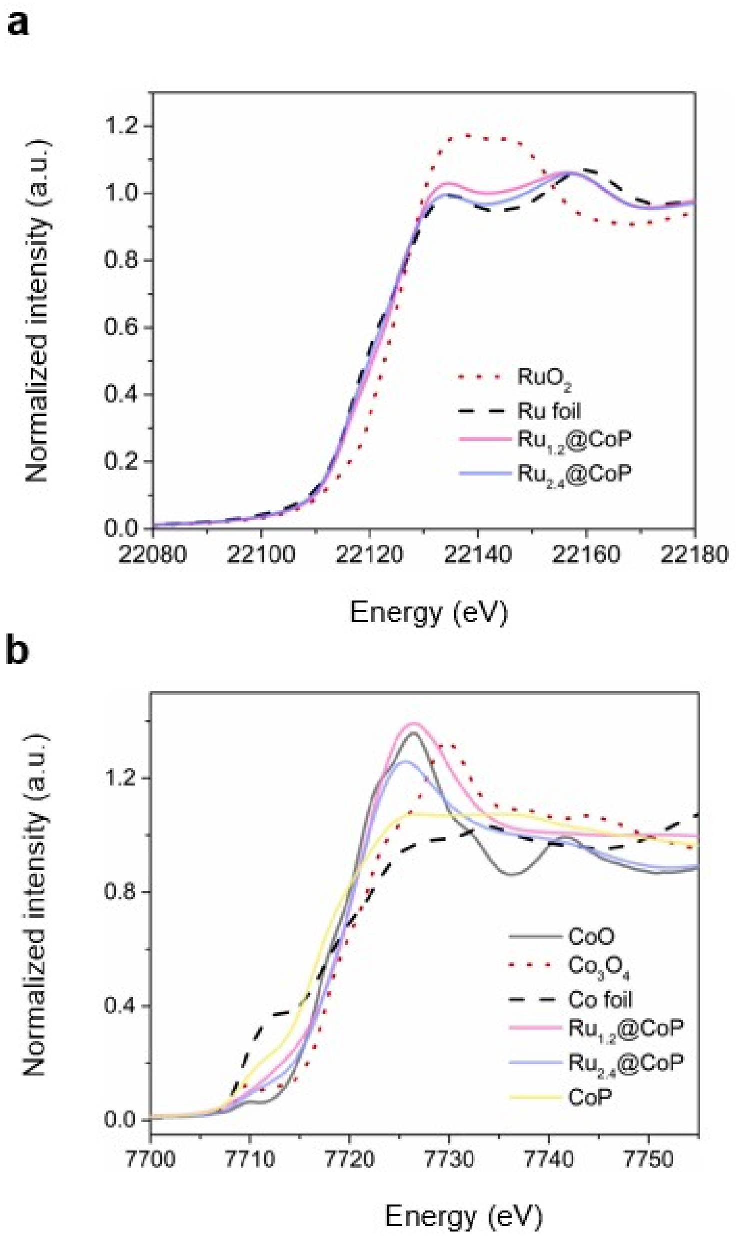

Figure S2. (a) Ru and (b) Co K-edge XANES spectra of the as-prepared Ru$_{1.2}$@CoP, Ru$_{2.4}$@CoP, CoP and references.

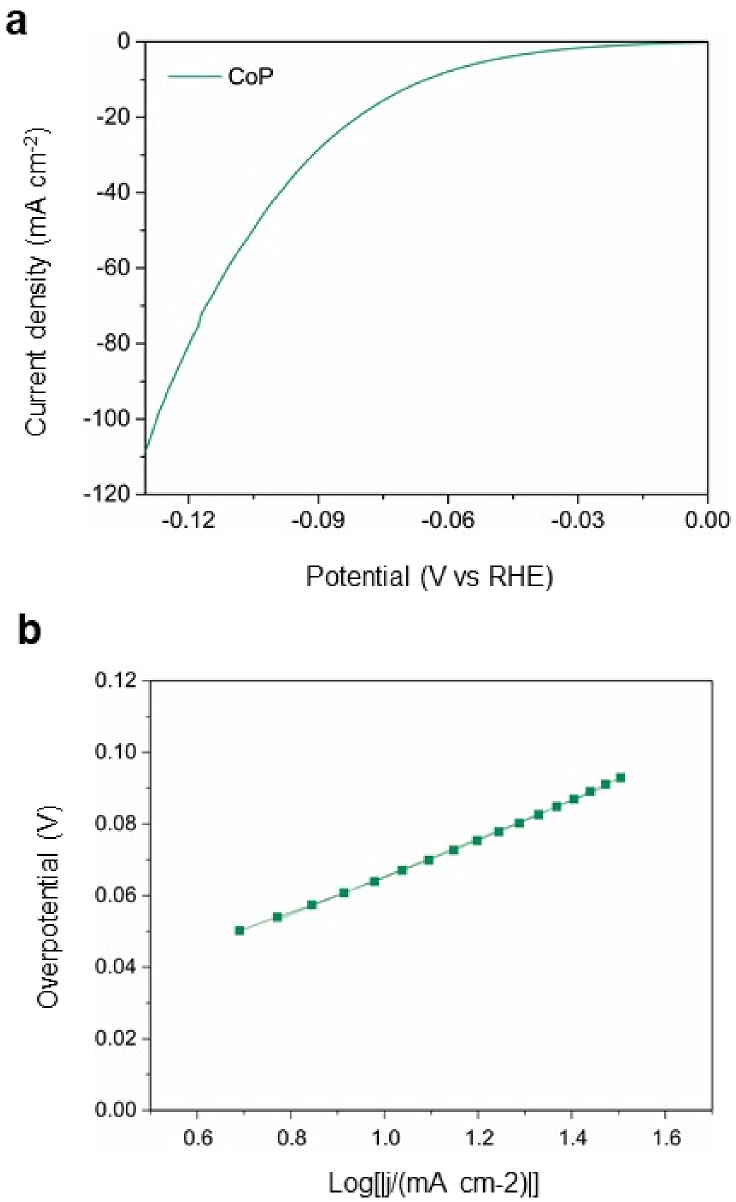

Figure S3. (a) LSV polarization curves and (b) corresponding Tafel plots of the CoP.

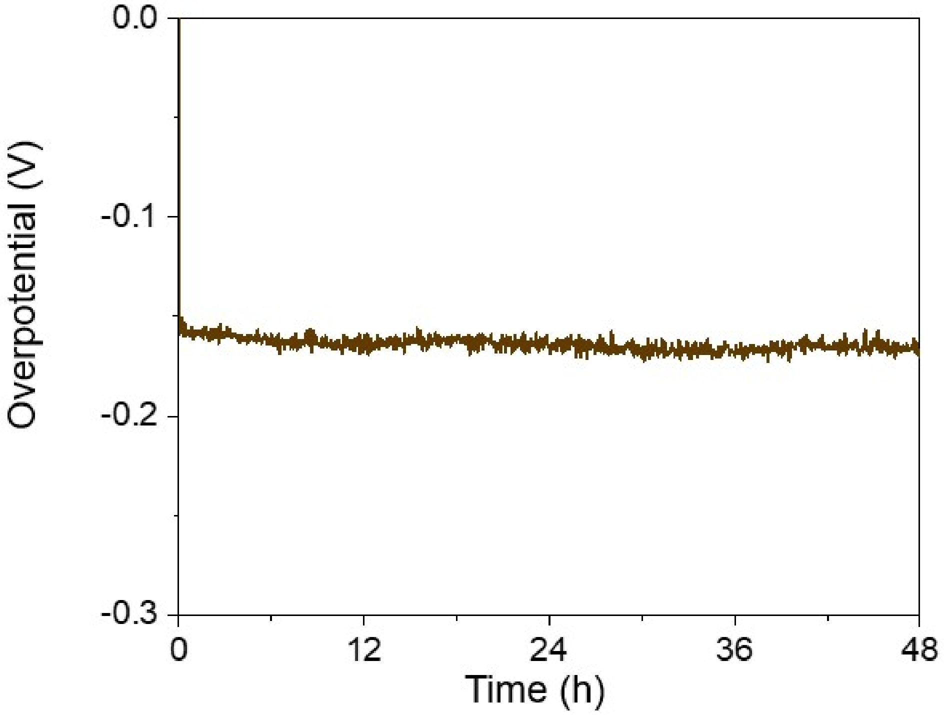

Figure S4. The chronopotentiometric curve of $Ru_{1.2}$@CoP recorded at a constant cathodic current density of 10 mA cm^{-2} for the HER

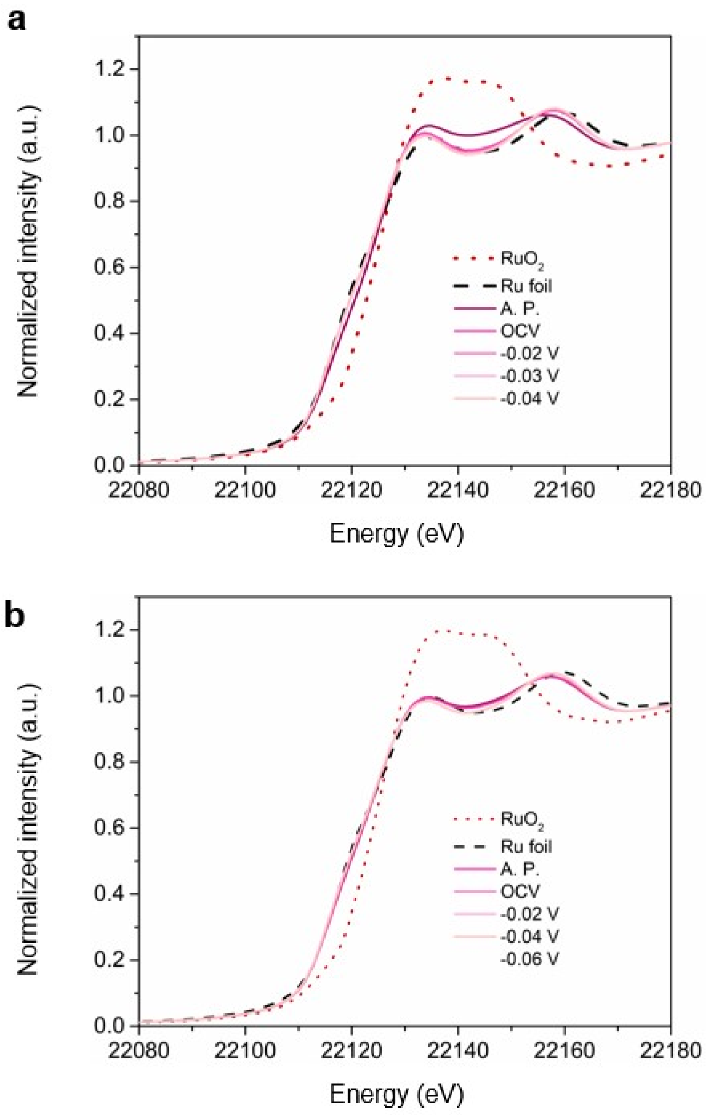

Figure S5. In situ Ru K-edge XANES spectra of the (a) $Ru_{1.2}$@CoP and (b)$Ru_{2.4}$@CoP.