Supporting Information for

A sea anemone-like CuO/Co$_3$O$_4$ composite: an effective catalyst for electrochemical water splitting

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Experimental details

Chemicals: Cobalt nitrate (Wako, Japan) and copper nitrate (Wako, Japan) with analytical grade are used as chemicals for the preparation of pure CuO, Co$_3$O$_4$ and CuO/Co$_3$O$_4$ composite catalysts. Potassium hydroxide (Sigma-Aldrich, Japan) is dissolved in deionized water as electrolyte solution for electrochemical characterization of electrodes. Carbon rods (CR, φ 5mm) are provided by C-task company, Japan.

Preparation of CuO, Co$_3$O$_4$ and CuO/Co$_3$O$_4$ electrodes: Potentiostat (Princeton Applied Research, VersaSTAT 4, USA) operated with VersaStudio software is applied to controllably deposit Cu/Co(OH)$_2$ composite and characterize the electrochemical properties of the as-fabricated electrodes. Three electrodes of platinum wire (ALS, Japan), Ag/AgCl/saturated KCl electrode (ALS, Japan) and CR substrate are used as counter electrode, reference electrode and working electrode, respectively. Carbon rods are pretreated in ethanol to facilitate their hydrophilicity at first. Electrolyte solution for Cu/Co(OH)$_2$ composite precursor is freshly prepared with a composition of Co(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ (concentrations varied as a parameter in this study). For comparison Cu and Co(OH)$_2$ precursors for pure CuO and Co$_3$O$_4$ electrode are also prepared in 0.05 M

$Cu(NO_3)_2$ and 0.1 M $Co(NO_3)_2$ electrolyte solutions, respectively. In this work, the unipolar pulse electrodeposition (UPED) method is used to prepare single as well as composite electrodes. In particular, the potentials applied during the on-time operation range from -0.2 to -1.2 V. On-times of 0.2, 0.5, 1.0, 1.5 and 2.0 s are used, while the off-time is fixed at 1.0 s. The number of pulse cycles to generate the film is varied from 100 to 600. Temperature programmed drying and calcination in air are used in the final preparation step. With a heating rate of 0.5 °C/min, the electrochemically-prepared electrodes are heated to 65 °C and held at this temperature for 5 h and then heated to 110 °C and held at this temperature for another 5 h. Finally, it is heated at a rate of 5 °C/min to 350°C, and held there for 3 h.

Characterizations: The electrolysis performance test is carried out using the linear sweep voltammetry (LSV, scan rate: 2 mV/s) in a solution of 1 M KOH. Electrochemical impedance spectroscopy (EIS) is performed within a frequency range of 0.01 Hz–0.1 MHz in 1 M KOH solution. The morphology and element composition are investigated by scanning electron microscopy (SEM, Hitachi, Japan) with an Energy Dispersive X-ray Detector (EDX). TEM images are obtained using a JEM-2100F transmission electron microscope JEOL operating at 200 kV. The crystal structures of the catalyst before and after the calcination are determined by X-ray diffraction (XRD 610, Shimadzu, Japan) with Cu-Kα radiation. The Brunauer–Emmett–Teller (BET) surface area is analyzed using adsorption data in a relative pressure range from 0.05 to 0.2 and the pore size distributions of the materials are determined by using the Barrett–Joyner–Halenda (BJH) algorithm according to the desorption data of the N_2 isotherm

Optimization of preparation parameters

In order to prepare CuO/Co_3O_4 composite electrodes with high catalytic performance, the preparation parameters of $Cu/Co(OH)_2$ precursor on the electrode are optimized based on linear sweep voltammetry. Revealed by Fig S1, the concentration of solution for the electro-deposition process has great influence on catalytic performance of composite, and the composite electrode with the highest catalytic performance is obtained in the solution of 0.1 M $Co(NO_3)_2$ and 0.05 M $Cu(NO_3)_2$.

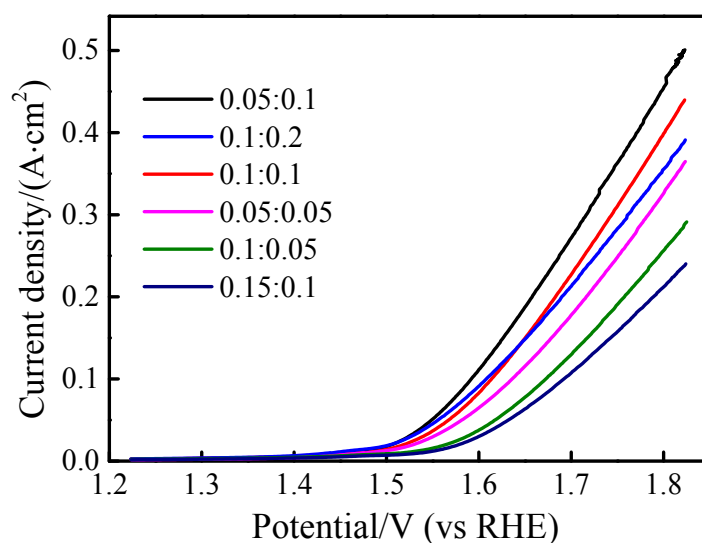Fig. S1. Polarization curves of CuO/Co$_3$O$_4$ composite catalysts prepared at different concentration ratios (M:M) of Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$

Fig. S2 shows the morphology of composite catalysts prepared at different concentration ratios of Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$. One can see that CuO pillar@Co$_3$O$_4$ nanosheets core/shell array can be obtained in solution of 0.05 M Cu(NO$_3$)$_2$ and 0.1 M Co(NO$_3$)$_2$ (Fig. S2 A). Benefiting from this smart hybridization structure, the obtained composite electrode showed remarkably enhanced catalytic performances for OER. However when the concentration ratio of Co(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ increases to 0.1 M:0.2 M (Fig S2 B), the surface of electrode is completely covered by Co$_3$O$_4$ nanosheets, and this accumulational structure is not benefit for the electrolyte circulation. Fig. S2 C and D shows the morphologies of composites obtained at concentration ratios of 0.1 M: 0.05M and 0.15 M: 0.1M, due to the high concentration and fast reduction rate of Cu^{2+}, the electrode is almost covered by pine needle-like CuO material completely. Moreover, the composite obtained at 0.15 M: 0.1 M has larger particle-size than that from 0.1 M: 0.05M. Because of the low activity of CuO, catalytic performances of composites prepared at these concentration ratios are not good. In contrast, the composite prepared at 0.1M: 0.1M is accumulated by porous ball formed by Co$_3$O$_4$ nanosheet (Fig. S2 E), and shows relatively high catalytic activity due to the enough Co$_3$O$_4$ component per geometric area. As the concentration ratio is decreased to 0.05M: 0.05M, an interesting hybridization structure with a tree-like morphology is obtained (Fig. S2 F), but its catalytic activity is also low due to the accumulational structure.

The formation of CuO/Co$_3$O$_4$ composite with such hierarchical core/shell arrays

should be attributed to the faster reaction rate of Cu^{2+} reduction than Co^{2+}, Cu nuclei could be formed at first and then grows as nanopillar during the electrodeposition process of Cu/Co(OH)$_2$ precursor. Generally, the charge applied on the substrate will concentrate on the embossment parts with higher curvature (refer website: http://library.automationdirect.com/corona-discharge-and-high-voltage-leaks-issue-12-2008/; refer paper: H S Fricker, Physics Education. 1989, 24, 157, doi:10.1088/0031-9120/24/3/309). Thus, there should have higher partial voltage on the first-formed Cu pillar on the substrate in the following deposition process, as a result, Co(OH)$_2$ nanosheets become easier to deposit around Cu pillars at higher potential, which will hinder the lateral growth of Cu pillars. Consequently, with the deposition proceeded, Co(OH)$_2$ nanosheet shell is gradually formed on the Cu pillars and finally a novel hierarchical core/shell structure is obtained.
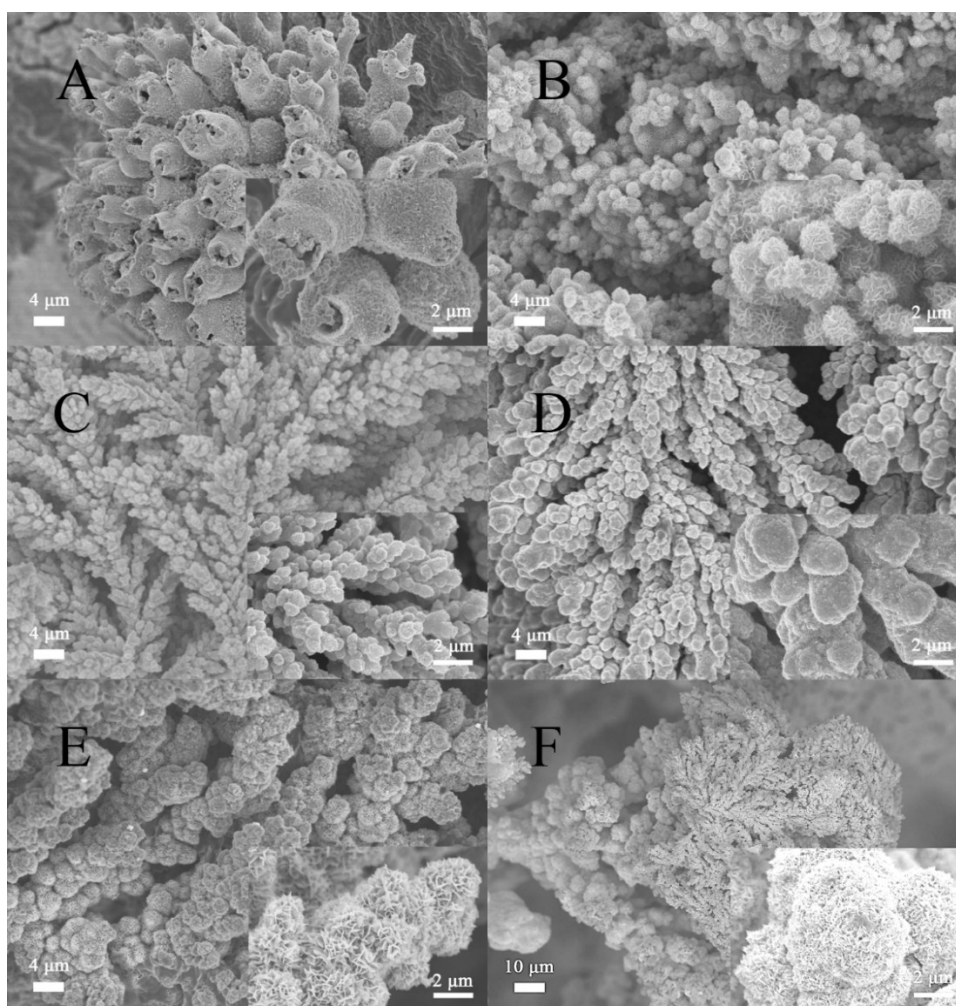

Fig. S2 SEM images of CuO/Co$_3$O$_4$ composite catalysts obtained at different concentration ratios (M:M) of Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$ (A: 0.05 :0.1, B: 0.1 :0.2, C: 0.1 :0.1, D: 0.05 :0.05 , G: 0.1 :0.05, H: 0.15 :0.1). Insets show enlarged images.

Pulse cycle times are correlated with the effective component amount and the pulse duration will influence microstructure of electrodes. In this study, with the increase in pulse cycle times, more active component can be deposited on the surface of carbon rod; however if too many pulse cycle times are used, an accumulational structure will be formed. Here, CuO/Co_3O_4 composite catalyst prepared at pulse cycles, pulse duration of 500, 1.0 s respectively shows the highest catalytic activity (Fig. S3), which should be owed to the smaller particles which can provide more active components in this material.
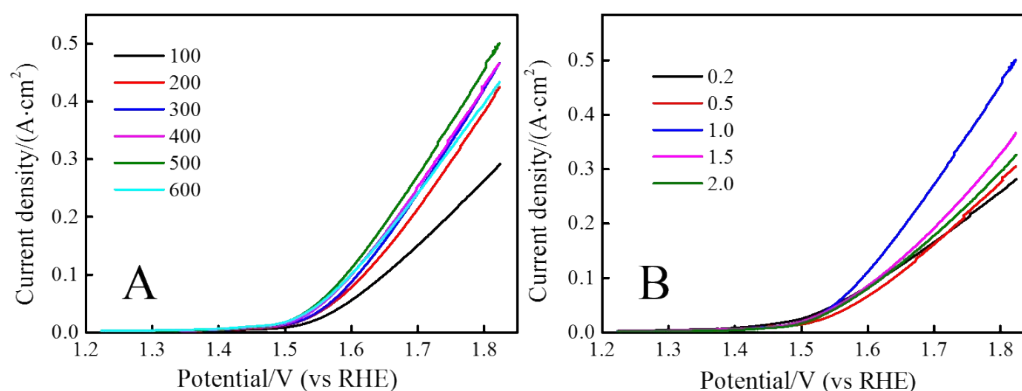

Fig. S3 Polarization curves of CuO/Co_3O_4 composite catalyst prepared at different pulse cycle times (A) and pulse duration (B).
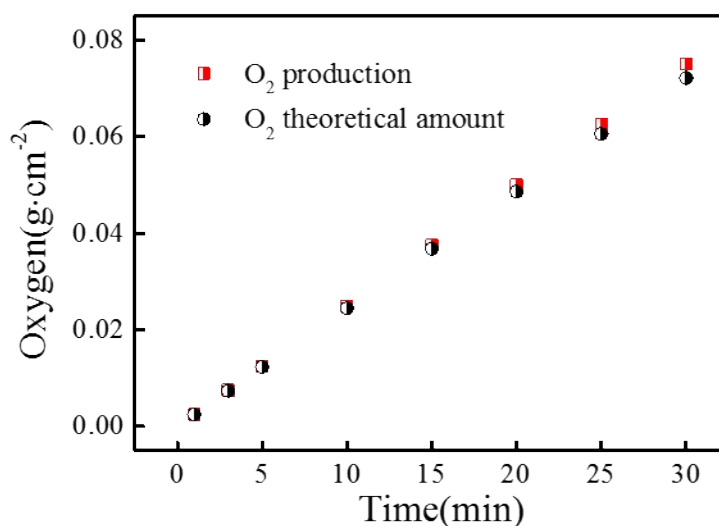

Fig. S4. Theoretical amount of oxygen produced and real oxygen production during the course of electrolysis by CuO/Co_3O_4 composite electrode. Applied potential is 0.8V vs Ag/AgCl.

As shown in Fig. S4, the oxygen concentration increases linearly along with the proceeding of electrolysis. Theoretical amount of oxygen can be calculated according to the recorded passed charge using Faraday's law:

$$m = \frac{MQ}{nF}.$$

Where "m" is the mass of reactant, "M/n" is chemical equivalent, "Q" is electric quantity applied on electrode, "F" is faraday constant. Divided the experimental recorded oxygen amount by theoretical calculated oxygen amount, Faraday efficiency of CuO/Co_3O_4 composite electrocatalyst is calculated to be about 95%. It suggests that the electrical energy can be efficiently utilized and converted to chemical energy with the as-prepared electrocatalyst.
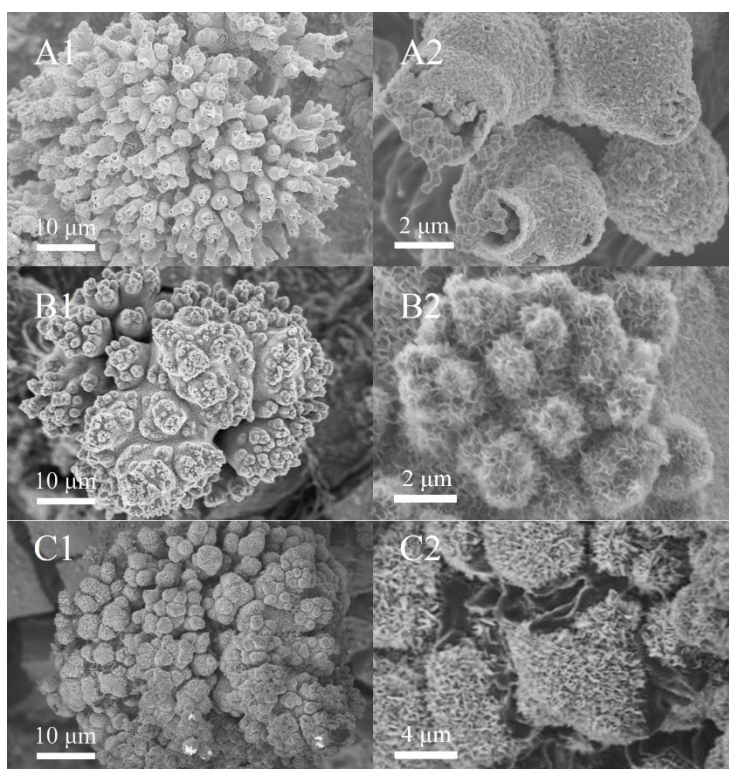

Fig. S5 SEM images of CuO/Co_3O_4 composite catalysts obtained at different potentials (A1: -0.8V, B1: -1.0V, C1: -1.2V). A2, B2, C2 show the corresponding enlarged images.
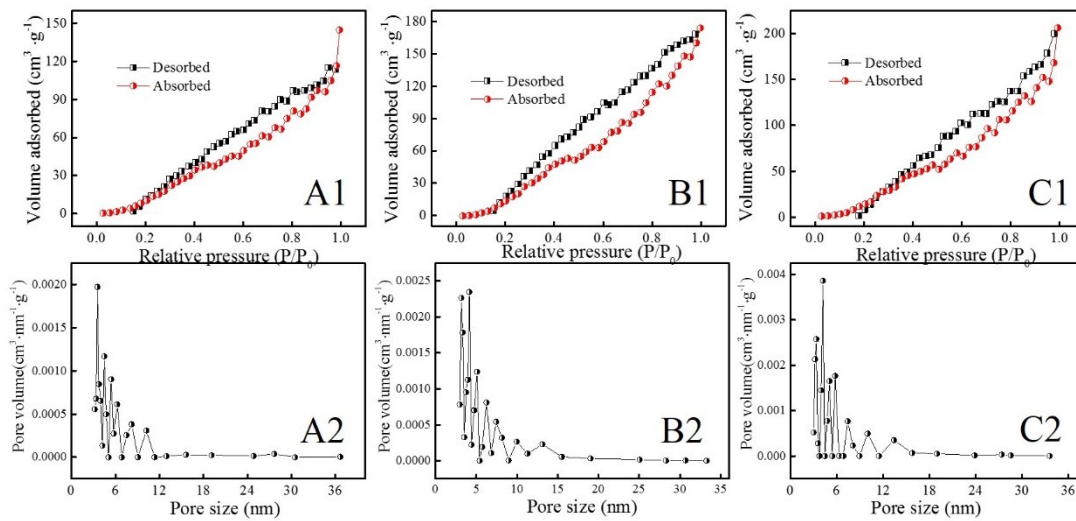
Fig. S6. Nitrogen adsorption/desorption isotherms of pure CuO (A1), Co_3O_4(B1) and CuO/Co_3O_4(C1) composite catalysts, A2-C2 show the corresponding pore size distributions curves

The Brunauer–Emmett–Teller (BET) method with N_2 adsorption is applied to investigate the surface areas of the as-prepared pure CuO, Co_3O_4 and CuO/Co_3O_4 composite electrodes. Their BET surface-area are about 114.4 m^2/g 153.6 m^2/g and 168.5 m^2/g, respectively. The pore size distribution curves revealed in Fig. S6 indicate that the pore sizes of CuO catalyst range in 3–12 nm and those of Co_3O_4 and CuO/Co_3O_4 catalysts range in 3–16 nm.
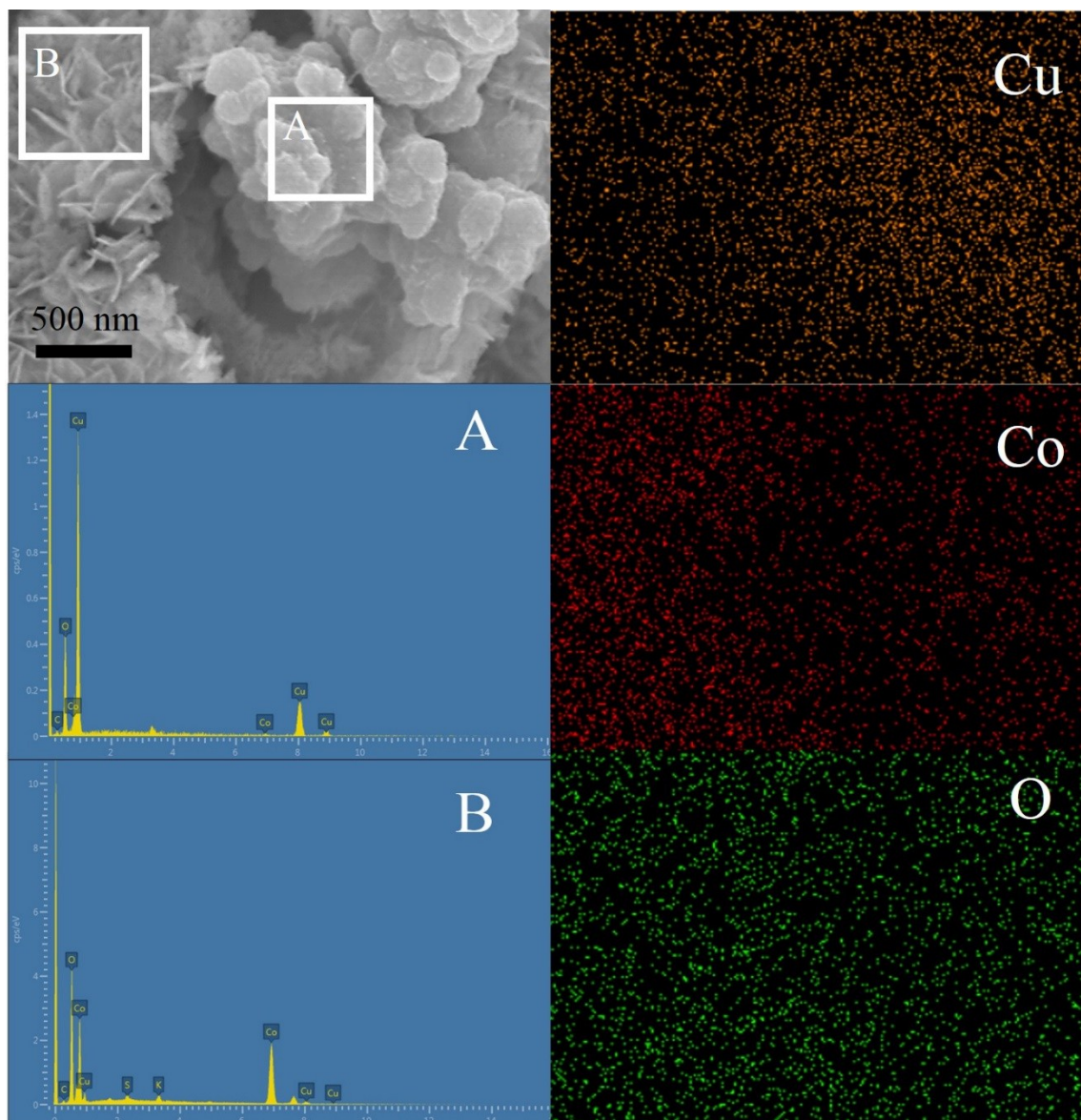
Fig. S7 EDS elemental mapping and spectra of CuO pillar in the core (A) and Co_3O_4 nanosheets shell (B), and corresponding SEM image.
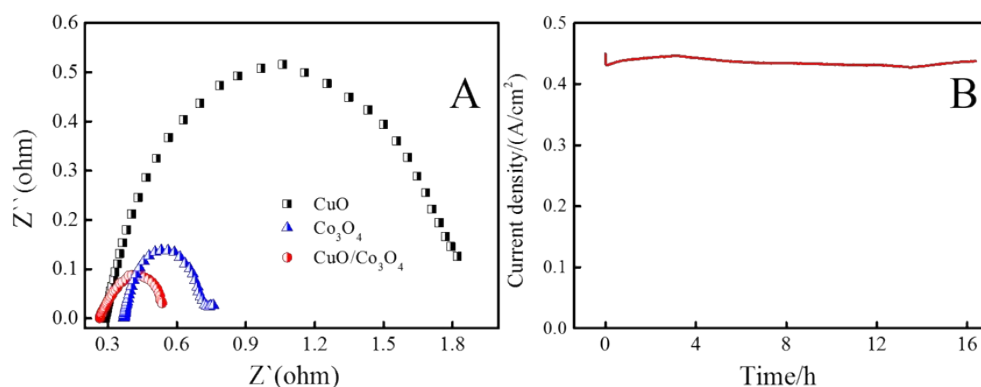
Fig.S8. (A) Nyquist plots of pure CuO (black), Co_3O_4 (blue) and CuO/Co_3O_4 composite catalyst (red) prepared at -0.8V, overpotential is 0.4V. (B) Time dependence of current density for CuO/Co_3O_4 composite catalyst in 1 M KOH electrolytes over 60,000 s.

Fig. S8 A shows the electrochemical impedance spectroscopy (EIS) of CuO/Co_3O_4 composite and pure CuO, Co_3O_4 electrodes. The values of R_{ct} (referred as the charge transfer resistance) can be calculated from the arc radius of the Nyquist plot. Obviously, the CuO/Co_3O_4 electrode exhibits the lowest R_{ct} of 0.29 Ω, while the R_{ct} of CuO and Co_3O_4 are 1.57 and 0.35 Ω respectively, implying that CuO/Co_3O_4 has lower charge transfer resistance through a mutual reinforcement and/or modification of CuO and Co_3O_4. Fig. S8 B shows the durability of $CuO/Co_3O_4/CR$ electrode, the time-dependent current density curve is collected at 1.8 V where the cell shows a high hydrogen evolution rate. One can see that only a slight fluctuation of the current is observed during 16 h, indicating that such a composite electrode is capable of maintaining its catalytic activity for a long time. Therefore, this material has great potential to replace noble metals for hydrogen evolution from water electrolysis.