Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Experimental Section

Materials

Cobaltous nitrate ($Co(NO_3)_2·6H_2O$), ferric nitrate ($Fe(NO_3)_3·9H_2O$), ferric chloride hexahydrate ($FeCl_3·6H_2O$), sodium sulfate (Na_2SO_4) and hexamethylenetetramine (HMT) were purchased from Beijing Chemical Corporation. Sodium hypophosphite (NaH_2PO_2), Nafion, butylated hydroxytoluene (BHT), α-tocopherol and 1,1-diphenyl-2-picrylhydrazyl (DPPH) were purchased from Aladdin Ltd. (Shanghai, China). RuO_2 particles were purchased from Sigma-Aldrich. Potassium hydroxide (KOH), ethanol and Hydrochloric Acid (HCl) were purchased from Tianjin Chemical Corporation. Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Aloe vera was collected from local nursery in Chengdu. All the chemicals in the experiment were analytical grade and used without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of Fe-doped CoP nanosheets array on carbon cloth (Fe-CoP/CC)

In a typical synthesis, $Fe(NO_3)_3·9H_2O$ (0.202 g), $Co(NO_3)_2·6H_2O$ (1.311 g) and HMT (1.442 g) were dissolved in 36 mL water under vigorous stirring for 30 min. CC was washed with HCl, ethanol, and water several times to remove the surface impurities. Then the solution was transferred into a Teflon-lined stainless autoclave (40 mL) and a piece of CC (3 cm × 2 cm) was immersed into the solution. The autoclave was sealed and maintained at 100 °C for 10 h in an electric oven. After the autoclave cooled down slowly at room temperature, the resulting Fe-Co-hydroxide precursor on CC was taken out and washed with water thoroughly before vacuum dried. To obtain Fe-CoP/CC, Fe-Co-hydroxide precursor and NaH_2PO_2 were put at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the furnace. Subsequently, the samples were heated at 300 °C for 120 min in a static Ar atmosphere, and then naturally cooled to ambient temperature under Ar. $Fe_{1/15}$-CoP/CC and $Fe_{1/5}$-CoP/CC were made by varying the atomic ratio of Fe:Co in solutions to 1:15 and 1:5, respectively, under otherwise identical experimental conditions used for preparing Fe-CoP/CC. The actual Fe:Co ratios in the products were determined by ICP-MS. CoP was made by using Co only.

Preparation of FeP nanosheets array on carbon cloth (FeP/CC)

In a typical synthesis, $FeCl_3·6H_2O$ (0.404 g) and Na_2SO_4 (0.284 g) were dissolved in 35 mL of deionized water and stirred for 10 min to form a clear solution. Then the above pellucid solution and a piece of cleaned CC (3 cm × 2 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h, and then cooled down to room temperature. The samples were rinsed several times with deionized water and ethanol with the assistance of ultrasonication, and dried at 60 °C. The FeP/CC nanosheets array was similarly converted using NaH_2PO_2 as precursor.

Preparation of commercial RuO_2 loading on CC (RuO_2/CC)

The commercial RuO_2/CC electrode was prepared by making a suspension with a proportion of 50 mg RuO_2 particles (the average size of the commercial RuO_2

particles was estimated to be about 50 nm[1]), 1.2 mL of deionized water, 1.2 mL of ethanol and 20 μL of Nafion solution. The suspension was sonicated to achieve a homogeneous dispersion. The resulting suspension was then uniformly coated onto CC until a catalyst loading of 1.2 mg cm^{-2} was achieved.

Preparation of aloe extracts (AE)

Fresh succulent leaves of Aloe vera were collected then their inner gel and outer leafy coat were manually separated. Fresh Aloe vera leaf skin (1 kg) was washed with distilled water and was extracted with ethanol by maceration at room temperature for 48 hours. After filtration, the ethanol was evaporated under reduced pressure to yield the ethanolic extract (26.3 g). The extracts were dissolved in water, kept at 4°C for 12 hours and filtered again, then titrated with KOH to pH = 14 thus obtaining the aqueous extracts (100 mL).

Characterizations

X-ray diffraction (XRD) data were collected on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) measurements were performed on a HITCHI S-4800 with scanning electron microscope with an accelerating voltage of 25 kV. X-ray photoelectron spectrometer (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the excitation source. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on ThermoScientific iCAP6300. Brunauer-Emmett-Teller specific surface area and pore size were analyzed using a Quantachrome NOVA 1000 system at liquid N_2 temperature. Transmission electron microscopy (TEM) measurements were made on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Fe-CoP/CC as working electrode, a graphite rod as the counter electrode, and a Ag/AgCl electrode used as the reference electrode. Working and reference electrodes are in the one cell which contains 50 mL KOH solution containing AE, and counter electrode is in the other with KOH only. All electrolytes were titrated with KOH to pH = 14. All potentials measured were calibrated to RHE using the following equation: E (RHE) = E (Ag/AgCl) + 1.0244 V. All experiments were carried out at room temperature (~25 °C).

Assay of DPPH radical scavenging activity

The electrolyte containing 5 mL AE before and after chronopotentiometry test at 25 mA cm^{-2} was titrated with CH_3COOH to pH = 5. Then the 1 mL ethanol was added into 1 mL treated electrolyte to obtain the solution before and after electrochemical test for next estimate. The antioxidant activities of solution before and after electrochemical test, BHT, α-tocopherol (100 mg L^{-1}) were measured in terms of their hydrogen donating or radical scavenging ability, using the stable radical DPPH. A total of 2 mL of 100 μg mL^{-1} BHT or α-tocopherol, or as-prepared solution before and after electrochemical test was placed in a cuvette, respectively, and 2 mL of a 2×10^{-4} mol L^{-1} ethanol solution of $DPPH^{\cdot}$ was added. Absorbance measurements commenced immediately. The decrease in absorbance at 517 nm was determined continuously at every 15-min intervals using a spectrophotometer until the absorbance reached a steady state (after nearly 120 min). The inhibition of the DPPH radical by the samples was calculated according to the reported formula.[1] The contents of polysaccharide and flavonoid in the solution before and after electrochemical test, which are the strong antioxidant in AE, were determined by reported method.[2]

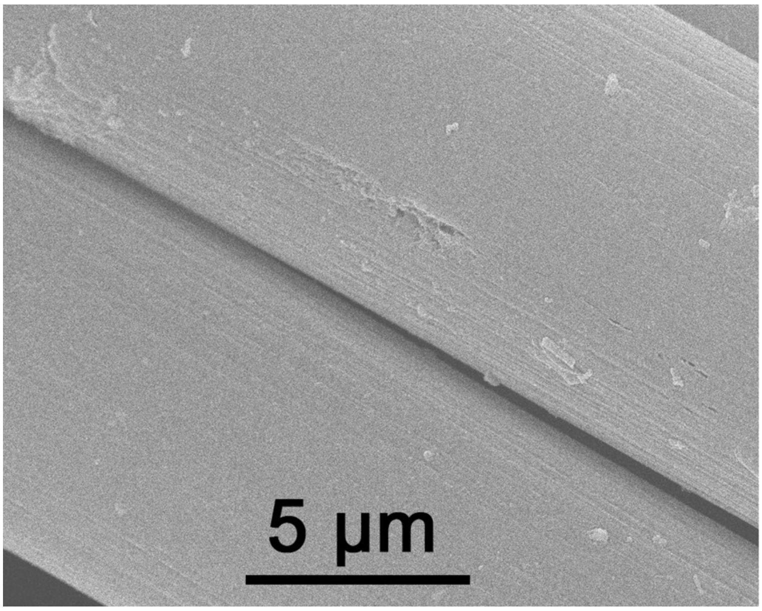

Fig. S1. SEM image for bare CC.

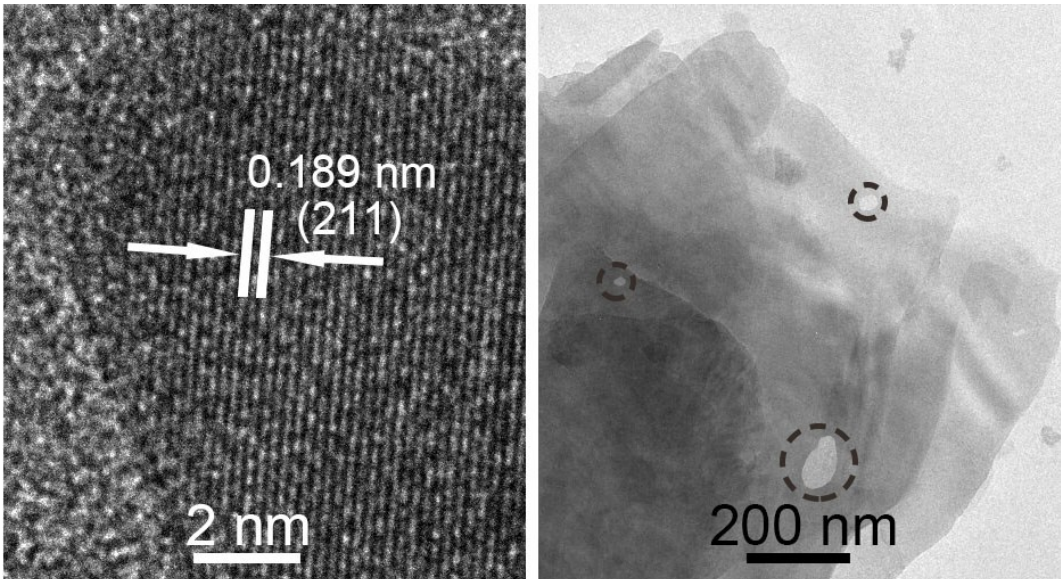

Fig. S2. TEM and HRTEM images of Fe-CoP nanosheets.

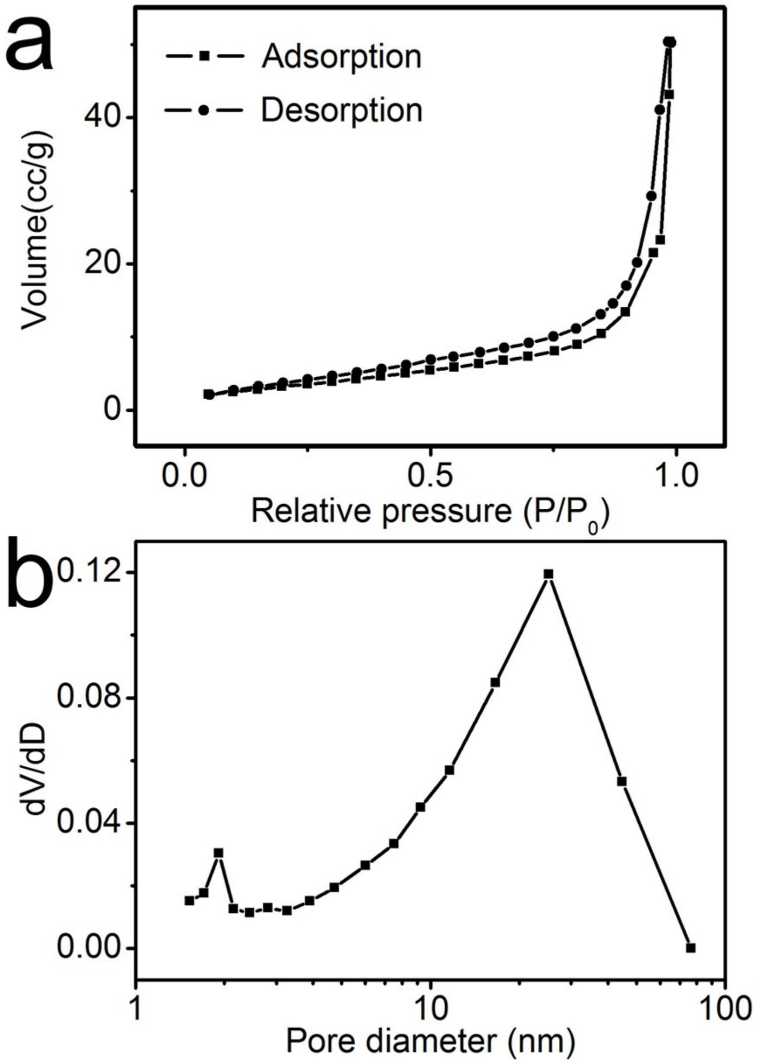

Fig. S3. (a) Nitrogen adsorption/desorption isotherm plot and (b) the Barrett-Joyner-Halenda pore-size distribution curve of Fe-CoP nanosheets.

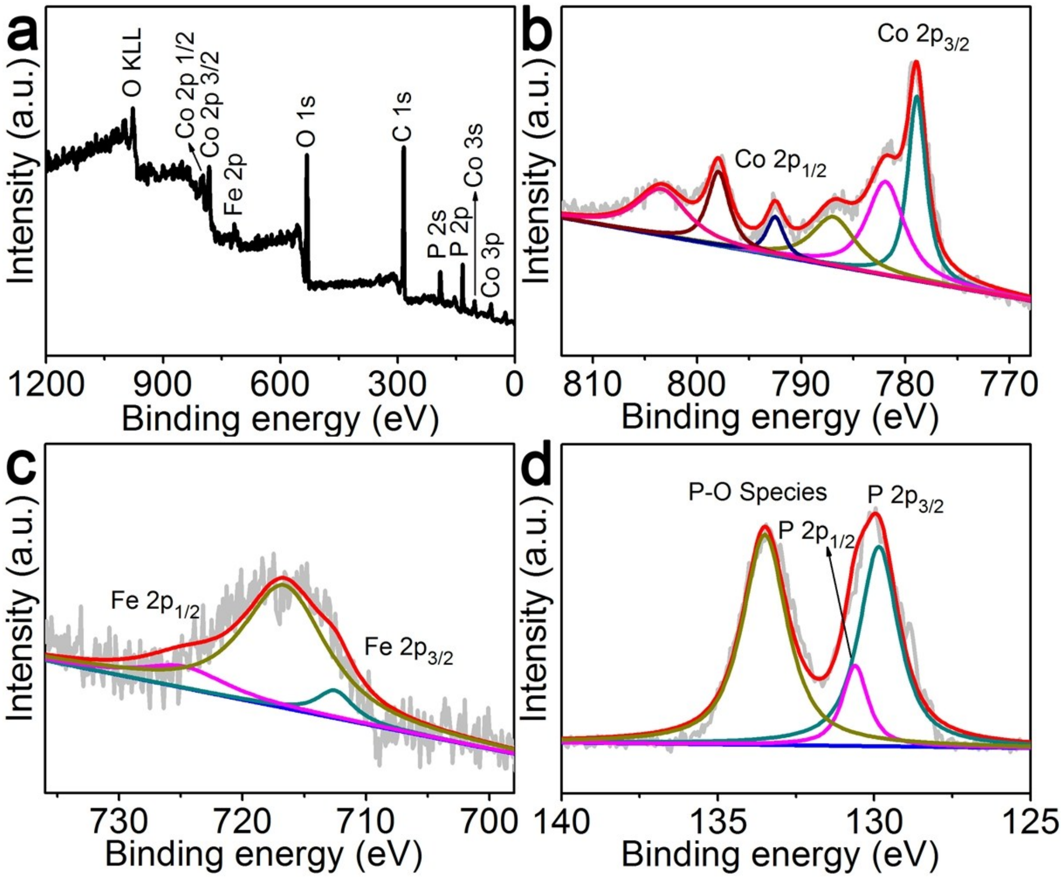

Fig. S4. (a) XPS survey spectrum of the Fe-CoP/CC. High-resolution XPS spectra in the (b) Co 2p, (c) Fe 2p and (d) P 2p regions.

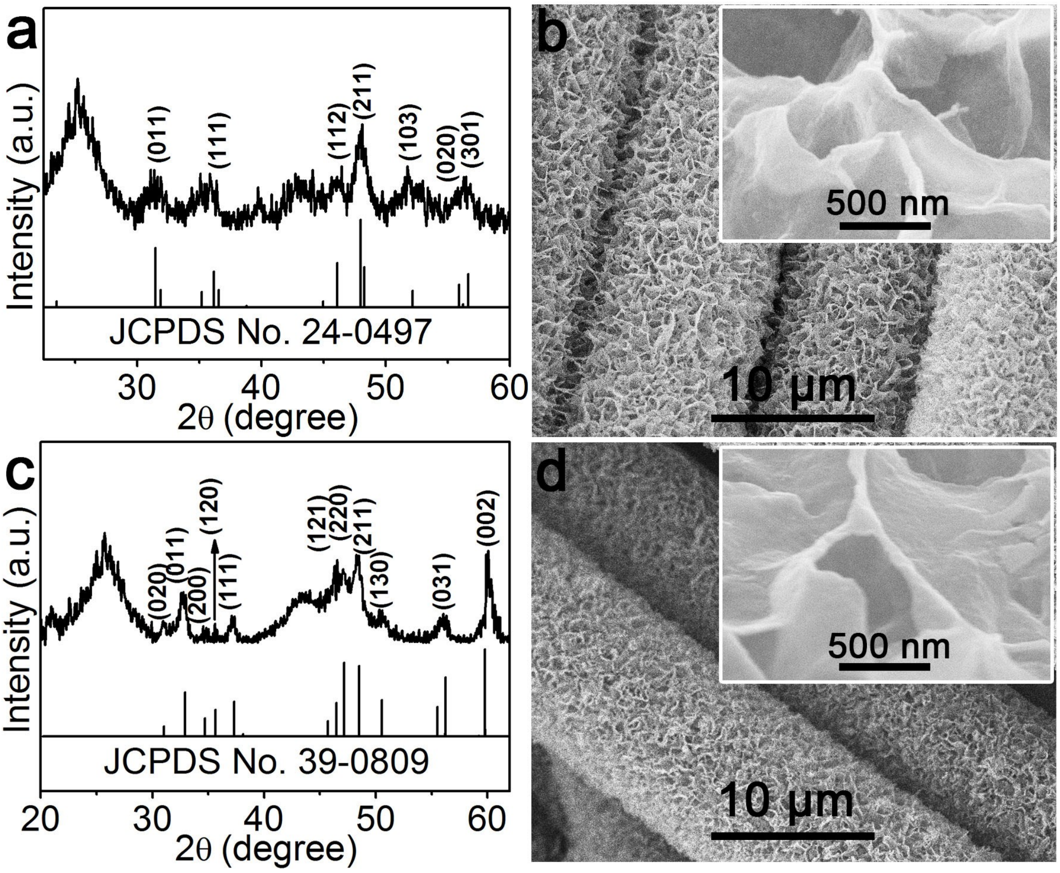

Fig. S5. (a) XRD pattern for CoP/CC. (b) SEM images for CoP/CC. (c) XRD pattern for FeP/CC. (d) SEM images for FeP/CC.

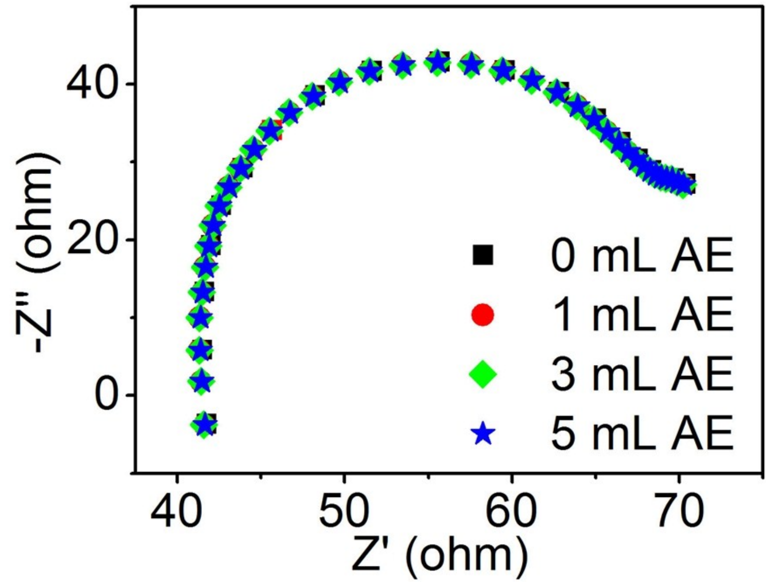

Fig. S6. Nyquist plots for Fe-CoP/CC with the addition of different amount of AE.

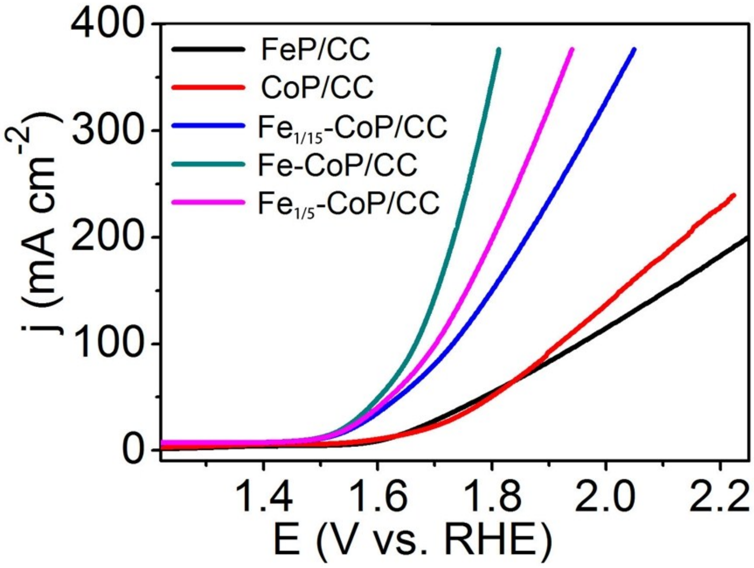

Fig. S7. LSV curves for CoP/CC, FeP/CC, Fe-CoP/CC, $Fe_{1/15}$-CoP/CC and $Fe_{1/5}$-CoP/CC with a scan rate of 5 mV s^{-1} for AE oxidation reaction.

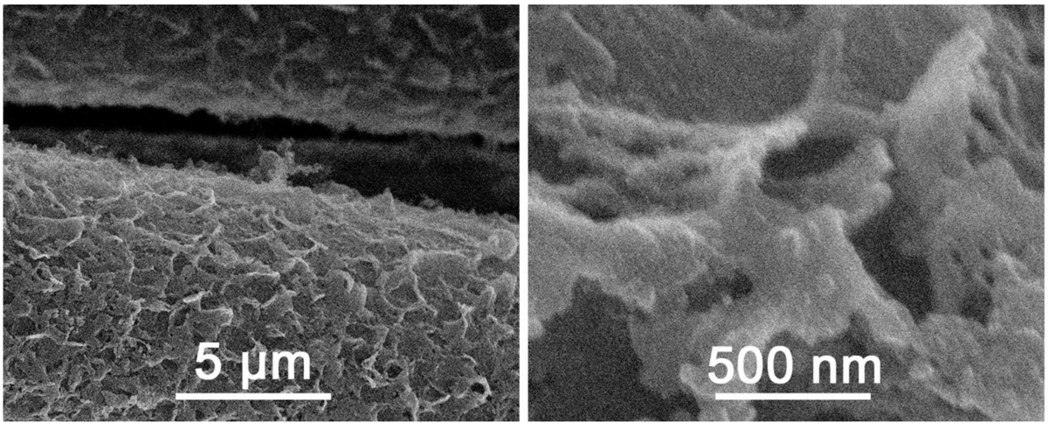

Fig. S8. SEM images of anodic catalyst after 6 h electrolysis in 50 mL 1.0 M KOH containing 5 mL AE.

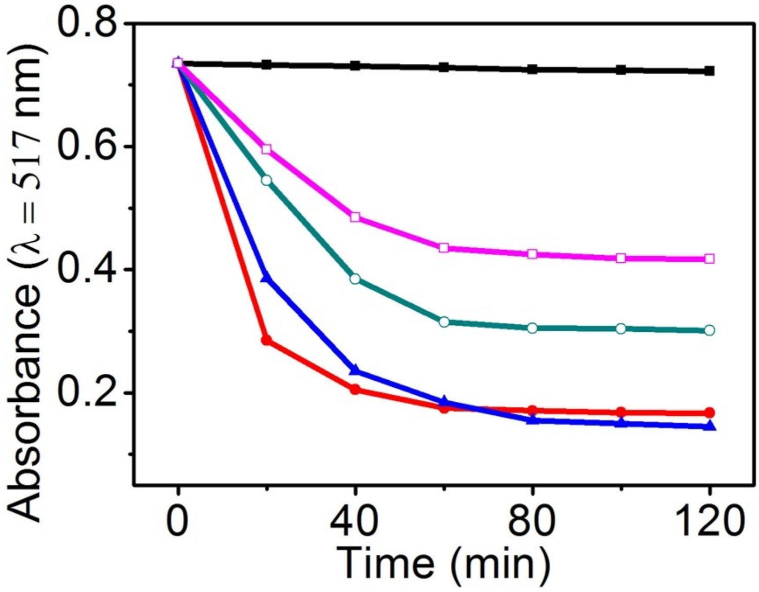

Fig. S9. Kinetics behavior of radical scavenging performance for blank (■),BHT (▲), α-tocopherol (●) and solution before (○) and after (□) electrochemical test.

Table S1. Polysaccharides and flavonoids content in the solution before and after electrochemical test.

solution	**Polysaccharide (g L^{-1})**	**Flavonoids (g L^{-1})**
before	0.71	0.63
after	0.52	0.48

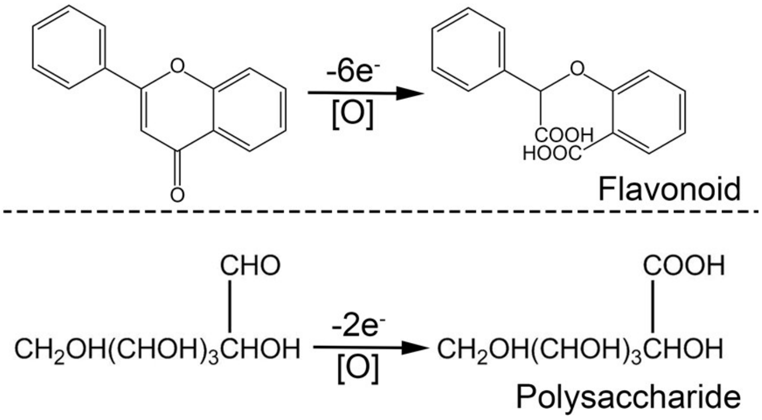

Fig. S10. The electron transfer process of AE oxidation.

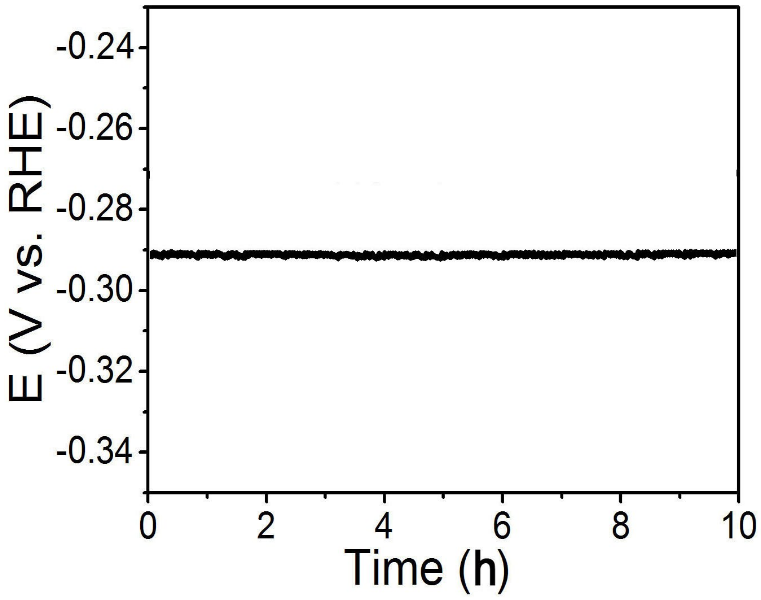

Fig. S11. Chronopotentiometric curve of Fe-CoP/CC with constant current density of -50 mA cm^{-2}.

Movie S1. This movie shows hydrogen generation and AE oxidation catalyzed by Fe-CoP/CC in an H-type cell driven by 1.55 V in 50 mL 1.0 M KOH containing 5 mL AE.

References

1 H. S. Jeon, A. D. C. Permana, J. Kim and B. K. Min. *Int. J. Hydrogen Energy*, 2013, **38**, 6092-6096.

2 Y. Hu, J. Xu and Q. Hu, *J. Agric. Food Chem.,* 2003, **51**, 7788-7791.