Supporting Information

Metal-Free 3D Porous Electrode for Full Water Splitting at All pH Values

Jianping Lai,[a,b] Suping Li,[a] Fengxia Wu,[a,b] Muhammad Saqib,[a,b] Rafael Luque,*[,a,c] and Guobao Xu*[,a]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, PR China;

[b] University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, PR China.

[c] Departamento de Química Orgánica, Universidad de Córdoba Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV, Km 396, Córdoba (Spain), E-14014.

Experimental Section

Chemicals and materials.

Ammonium persulfate (APS) was purchased from Beijing Chemical Corp. Aniline and phytic acid were purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Nafion (10%) and commercial Pt/C were purchased from Sigma-Aldrich. All chemicals were analytical-reagent grade and used without further purification. CC is provided by Tsukuba Materials Information Laboratory (*TMIL*) Ltd.

Apparatus.

Scanning electron microscopy (SEM) images were recorded in a FEI XL30 ESEM FEG Scanning Electron Microscope operated at 25 kV. TEM images were all obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. Energy dispersive spectrometer (EDS) spectrums were collected in a Hitachi S-4800 Scanning Electron Microscope operated at 20.9 KV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Cu Kα radiation) in the 30 to 80º 2theta range. The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded from KBr disks using a Perkin-Elmer GX instrument in the wavenumber range of 4000-400 cm^{-1}. Tapping-mode AFM imaging was performed on a Digital Instruments multimode AFM controlled by a Nanoscope IIIa apparatus (Digital Instruments, Santa Barbara, CA) equipped with an E scanner. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Nitrogen sorption isotherms were measured with an ASAP 2020 Physisorption Analyzer (Micrometrics Instrument Corporation).

Preoxidation of CC.

CC was washed repeatedly with aqueous solutions of HCl (19 wt.%) and HNO_3 (10 wt.%), followed by washing with water. After drying, the purified CC was functionalized by oxidation treatment with concentrated HNO_3 (65 wt.%) at room temperature for 40 min to generate oxygen-containing functional groups (e.g. carboxylic groups) on its surface. Then the resulting CC was subjected to repeated water washing and drying at 120 °C.

Preparation of ONPPGC/OCC.

The preoxidized CC (2 cm × 2 cm) was immersed into the 2 ml water solution containing 0.458 ml aniline monomer (5 mmol) under stirring, and then 0.921 mL phytic acid solution (1 mmol) was added into the mixture under stirring. 0.286 g of ammonium persulfate (APS) (1.25 mmol) was dissolved into the 1 mL water under stirring. After cooling down to about 4 °C, both solutions were mixed together and stirred for 2h. The mixture was transferred into a Teflon-lined autoclave, which was sealed and aged statically at 100 ºC for 5 h under autogenous pressure. The resultant precipitation was washed with a large amount of water and dried at 60 °C, followed by annealling at 1000 °C for 2h under N_2. The obtained sample was named ONPPGC/OCC. The weight increment of OCC was directly weighted after the growth of ONPPGC. For ONPPGC/OCC electrode, the loading mass of ONPPGC is 0.1 $mgcm^{-2}$.

Electrochemical measurements.

The test solutions were performed with a CHI 660C electrochemistry workstation (Shanghai CHI Instruments Company, China) in a standard three-electrode system using ONPPGC/OCC as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. To prepare the Pt/C loaded electrode, The Pt/C catalysts were resuspended in a mixture containing water, isopropanol, and Nafion (10%) (v:v:v 4:1:0.05) to form a 0.5 mg/mL catalyst ink. 2 μL catalyst inks was deposited on glassy carbon electrodes (0.07 cm^{-2}) that were polished prior to catalyst deposition by 0.3 μm and 0.05 μm alumina powder and rinsed by sonication in ethanol and in deionized water. The Pt/C catalysts modified electrode was dried at ambient condition. For Pt/C loaded electrode, the loading mass of Pt/C is 0.14 $mgcm^{-2}$. All potentials measured were calibrated to RHE using the following Equation: E(RHE)=E(Ag/AgCl)+0.197 V+0.059×pH. Polarization curves were obtained using LSV with a scan rate of 2 mVs^{-1} and no activation was used before recording the polarization curves. The long-term durability test was performed using chronoamperometry and chronopotentiometric measurements. All currents presented are corrected against ohmic potential drop. The electrochemical impedance spectroscopy (EIS) measurement was carried out in a frequency range from 100 kHz to 5 Hz with an AC voltage amplitude of 10 mV at a open circuit potential in 0.5 M H_2SO_4 solution.

Table S1. Comparison of the electrocatalytic activity of ONPPGC/OCC via some representative solid-state water electrolysis catalysts recently reported for basic solutions.

Catalyst	Catalyst amount ($mgcm^{-2}$)	Current Density j	potential (vs. RHE) at the corresponding j	Reference
NiFe LDH/NF	N	$10mAcm^{-2}$	1.7	21
NiSe/NF	2.8	$10mAcm^{-2}$	1.63	15
Ni_2P	5	$10mAcm^{-2}$	1.63	14
$NiFeO_X$	3	$10mAcm^{-2}$	1.51	20
Pt/C	0.14	$10mAcm^{-2}$	1.69	This work
ONPPGC/OCC	0.1	$10mAcm^{-2}$	1.66	This work

Table S2. Element compositions of ONPPGC/OCC samples.

	Molar ratio	C at.%	O at.%	N at.%	P at.%
Aniline: phytic acid	3:1	82.7	16.5	0.39	0.38
Aniline: phytic acid	5:1	82.8	16.4	0.46	0.32
Aniline: phytic acid	7:1	83.0	16.2	0.57	0.18

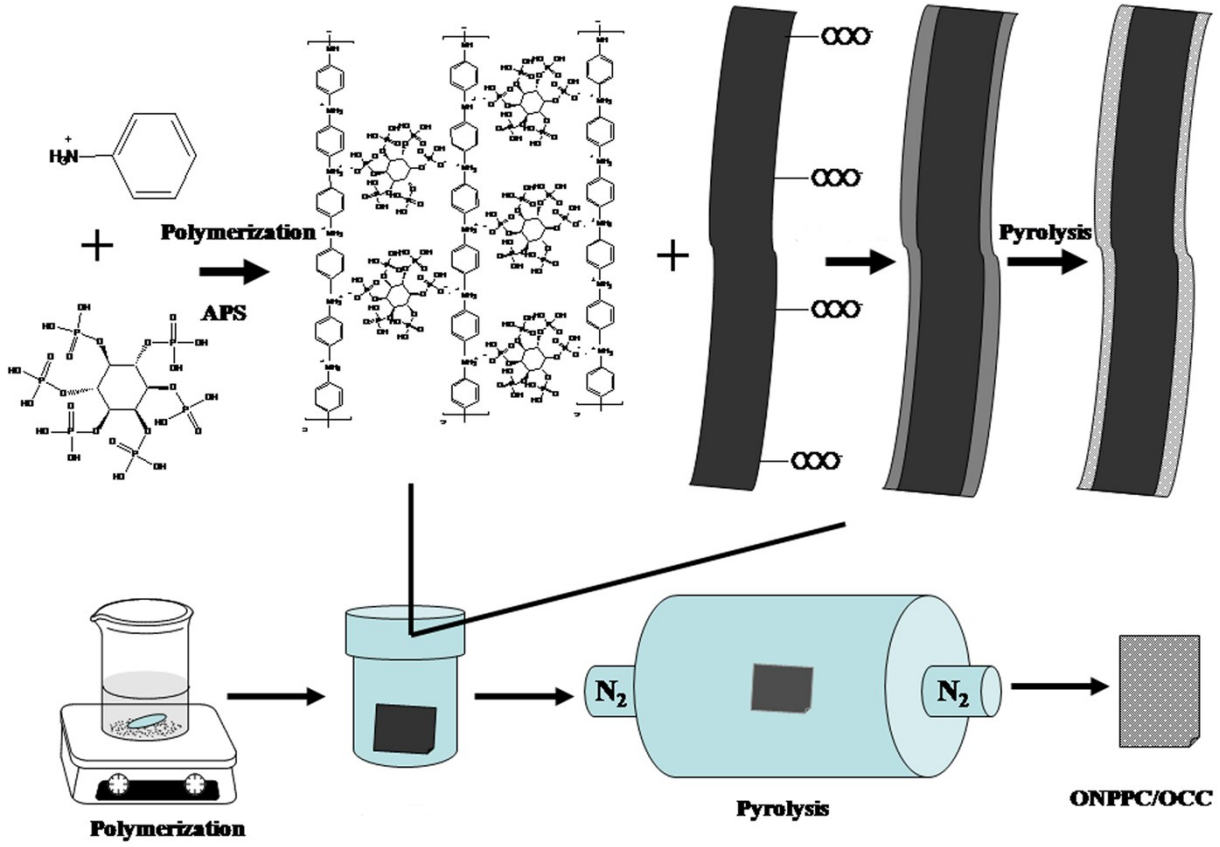

Figure S1. Fabrication of O, N and P tri-doped mesoporous graphite nanocarbon foams directly grown on oxidized carbon cloth.

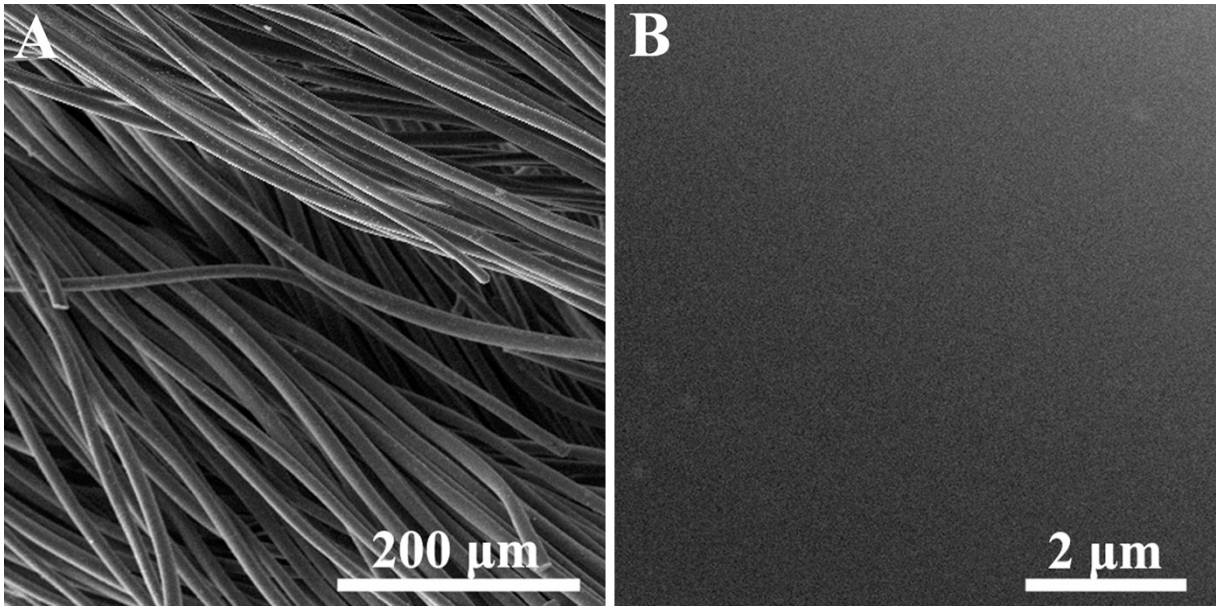

Figure S2. SEM image of OCC.

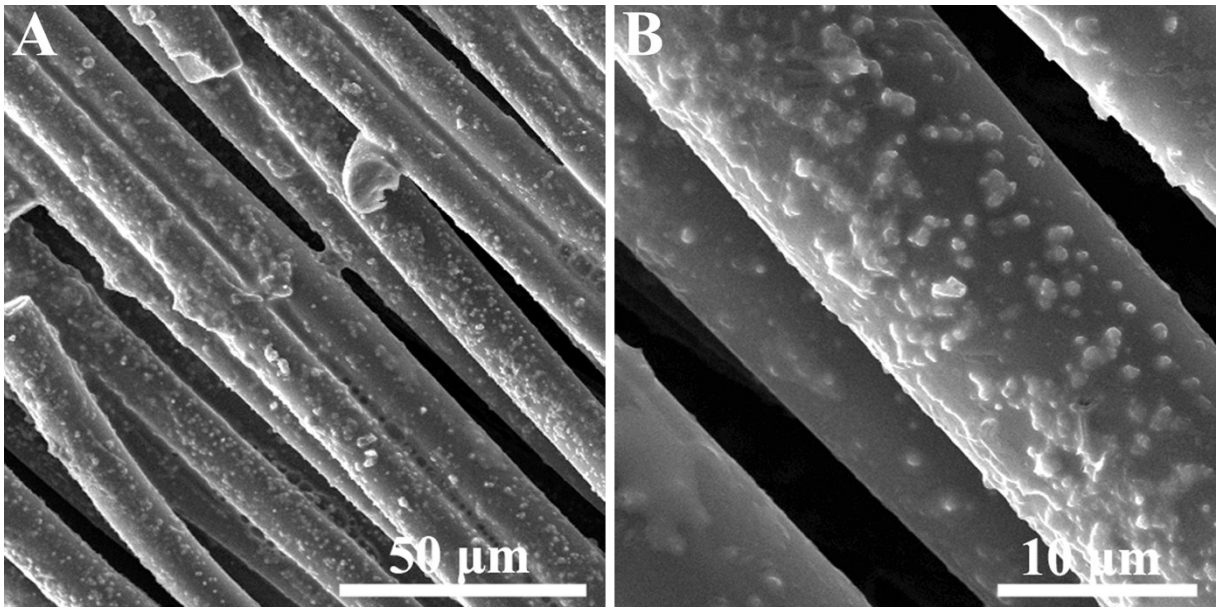

Figure S3. SEM image of polyaniline hydrogel on OCC surfaces.

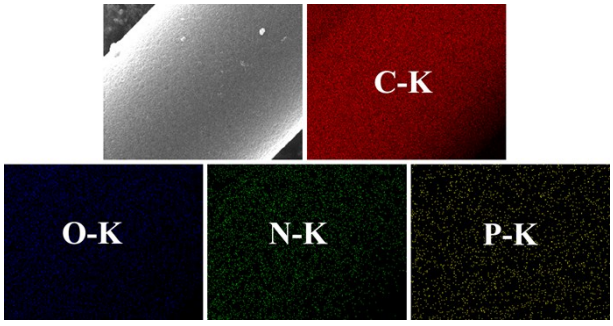

Figure S4. SEM images of the ONPPGC/OCC and corresponding EDX elemental mapping images.

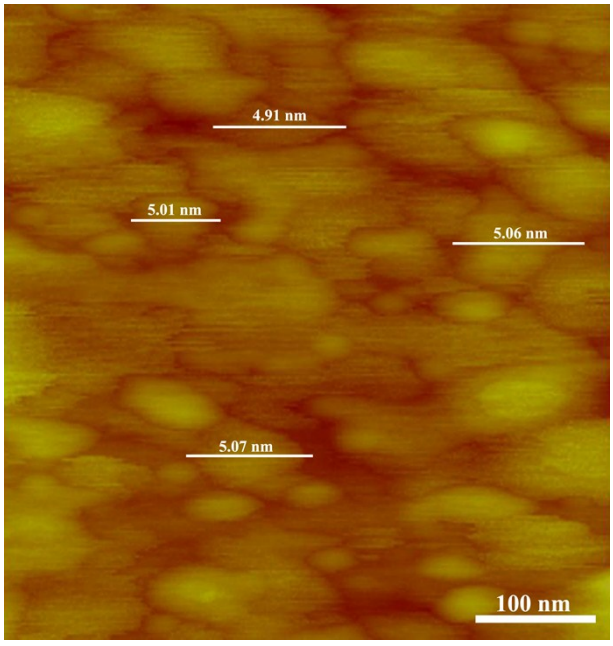

Figure S5. AFM images of ONPPGC.

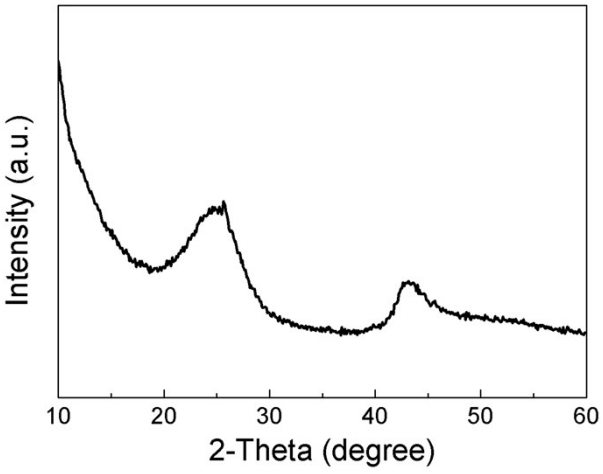

Figure S6. XRD pattern of ONPPGC/OCC.

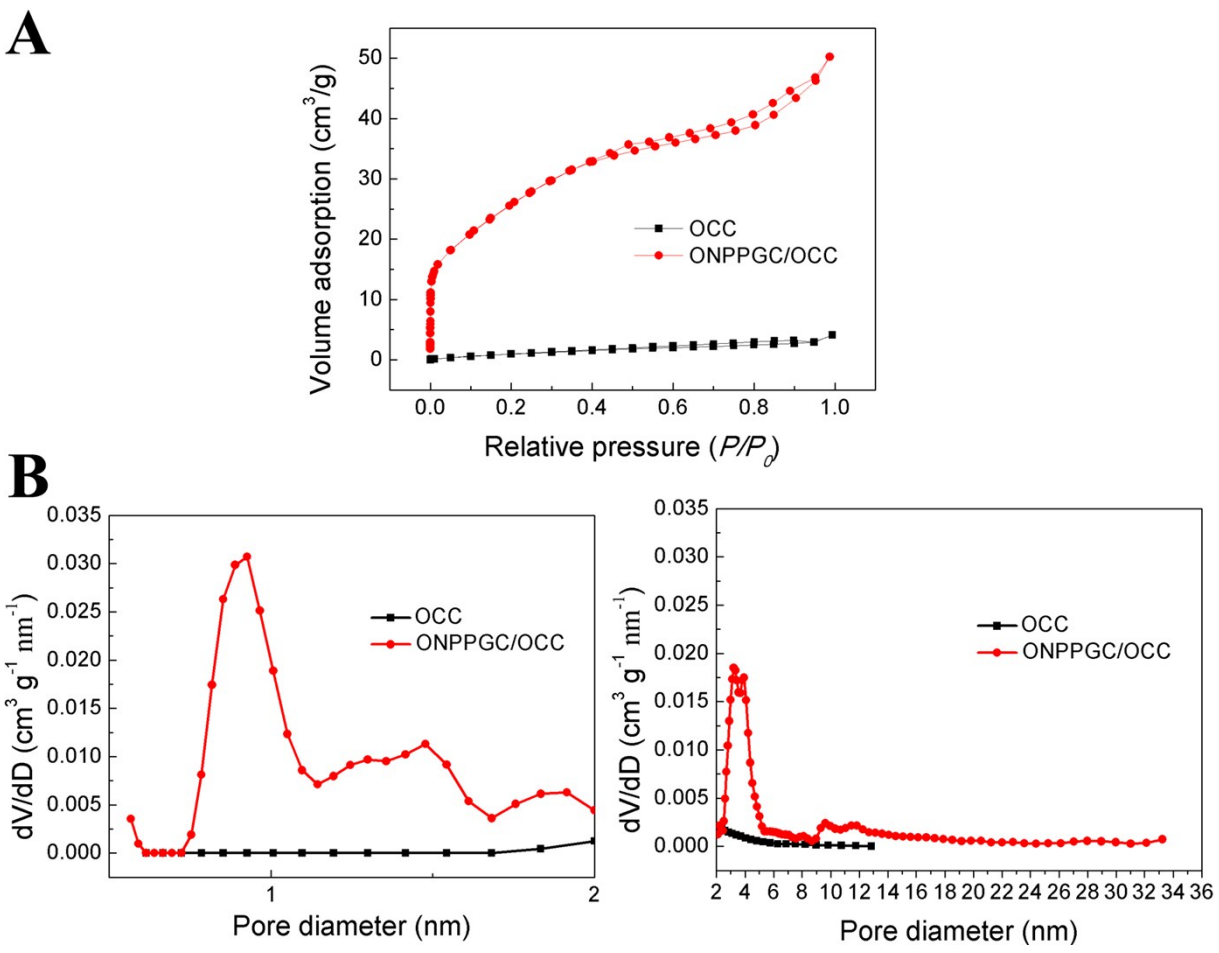

Figure S7. (A) N_2 adsorption–desorption isotherms (B) and corresponding DFT pore size distribution curves for OCC and ONPPGC/OCC.

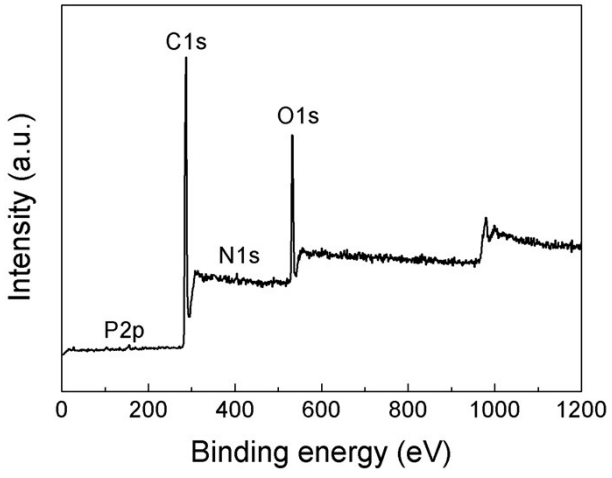

Figure S8. XPS survey spectrum of ONPPGC/OCC.

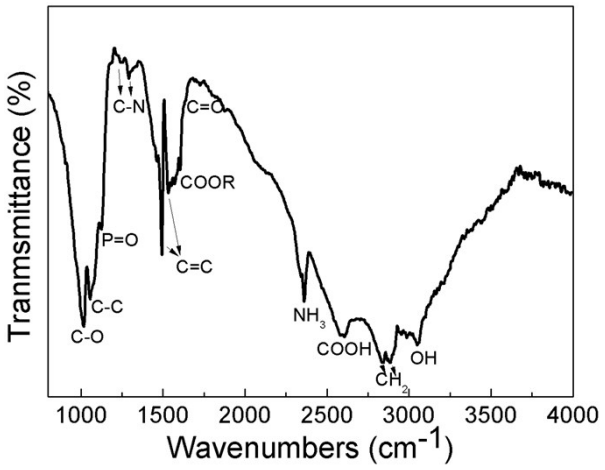

Figure S9. FTIR of ONPPGC/OCC.

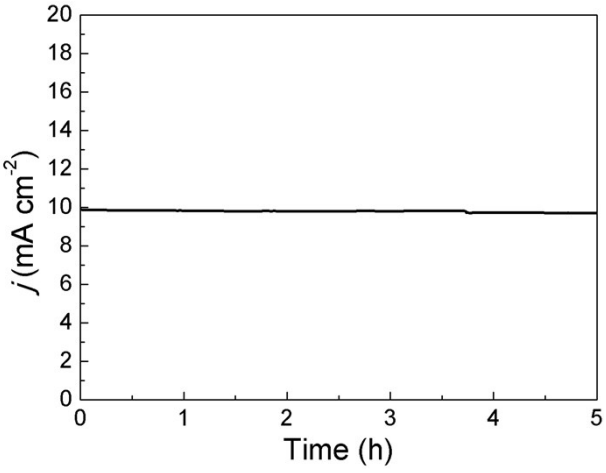

Figure S10. A current density-time (*j*-t) curve obtained for OER with ONPPGC/OCC at 1.65 V (vs. RHE) in an alkaline solution (1 M KOH, pH = 14).

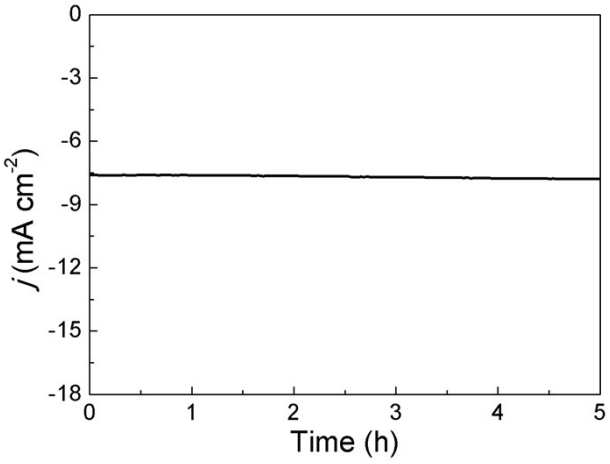

Figure S11. A current density-time (*j*-t) curve obtained for HER with ONPPGC/OCC at -0.4 V (vs. RHE) in an alkaline solution (1 M KOH, pH = 14).

Figure S12. Photograph of the system showing the hydrogen (left) and oxygen (right) generation during water electrolysis.

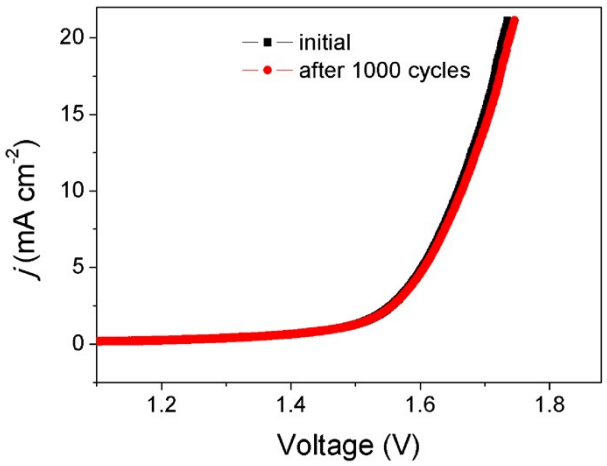

Figure S13. LSV curves for ONPPGC/OCC before and after 1000 CV cycles in 1.0 M KOH.

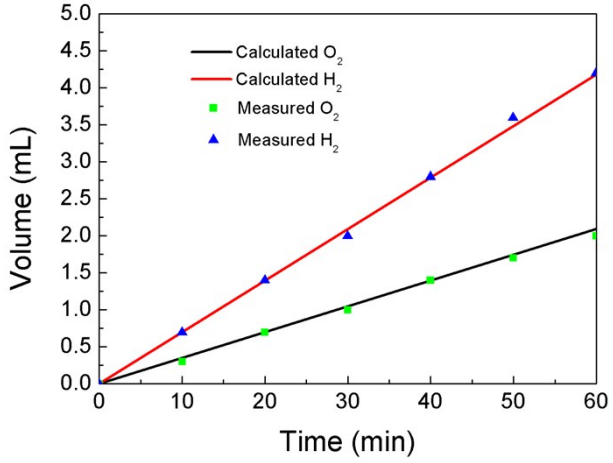

Figure S14. The amount of gas theoretically calculated and experimentally measured versus time for overall water splitting of ONPPGC/OCC.

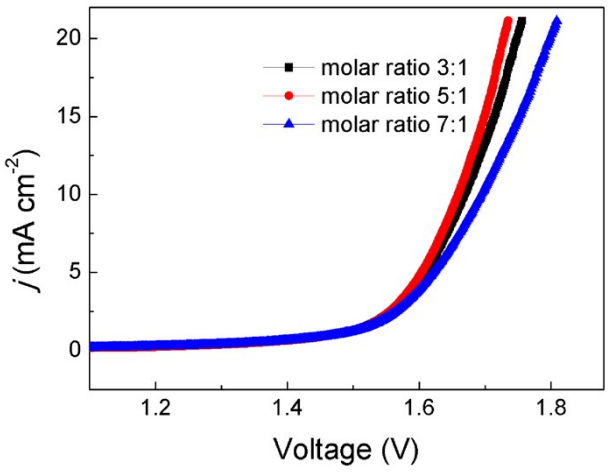

Figure S15. LSV curves of water electrolysis for ONPPGC/OCC (ONPPGC prepared with various molar ratios of aniline to phytic acid) in a two-electrode configuration with a scan rate of 2 mVs^{-1} in 1.0 M KOH.

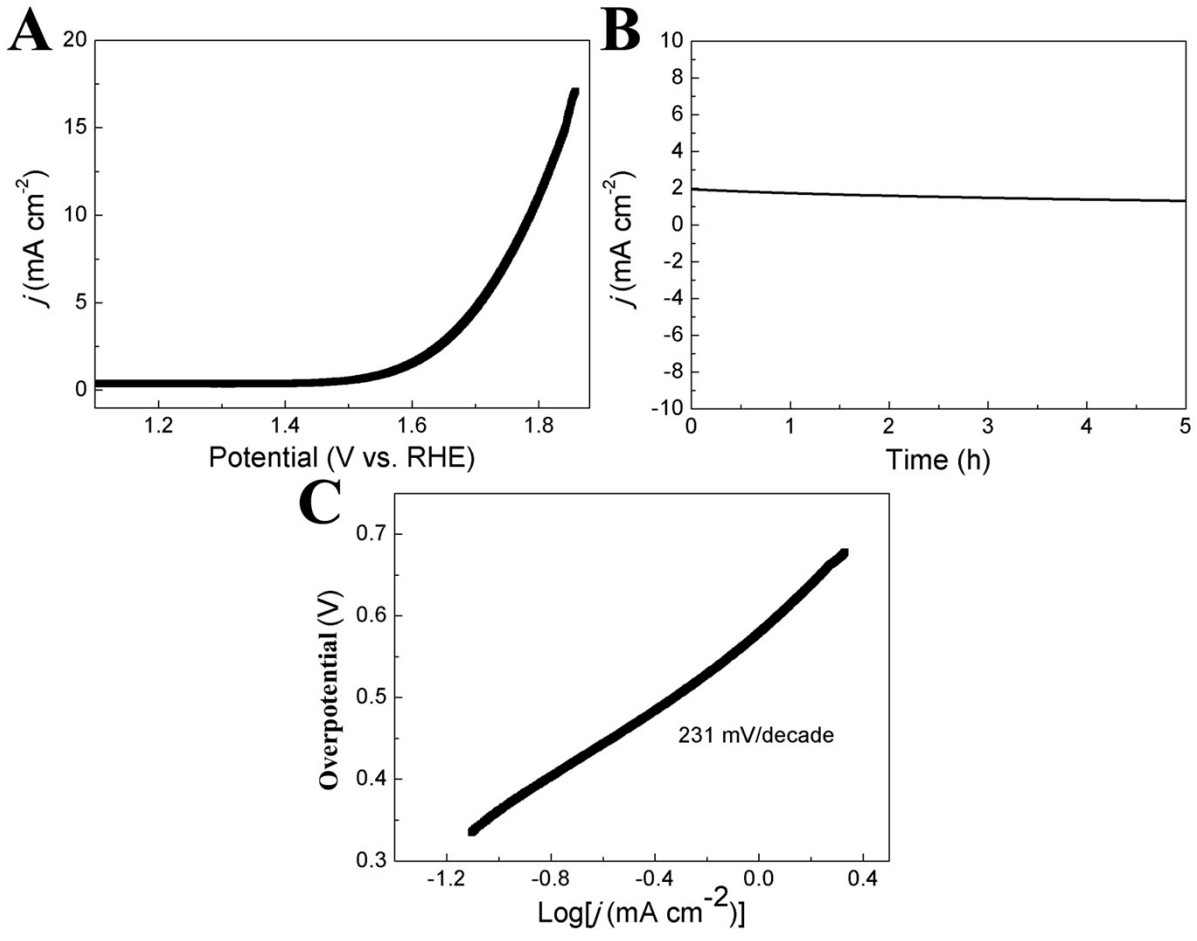

Figure S16. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs^{-1} for OER. (B) A current density-time (*j*-t) curve obtained for OER with ONPPGC/OCC at 1.65 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.2 M PBS.

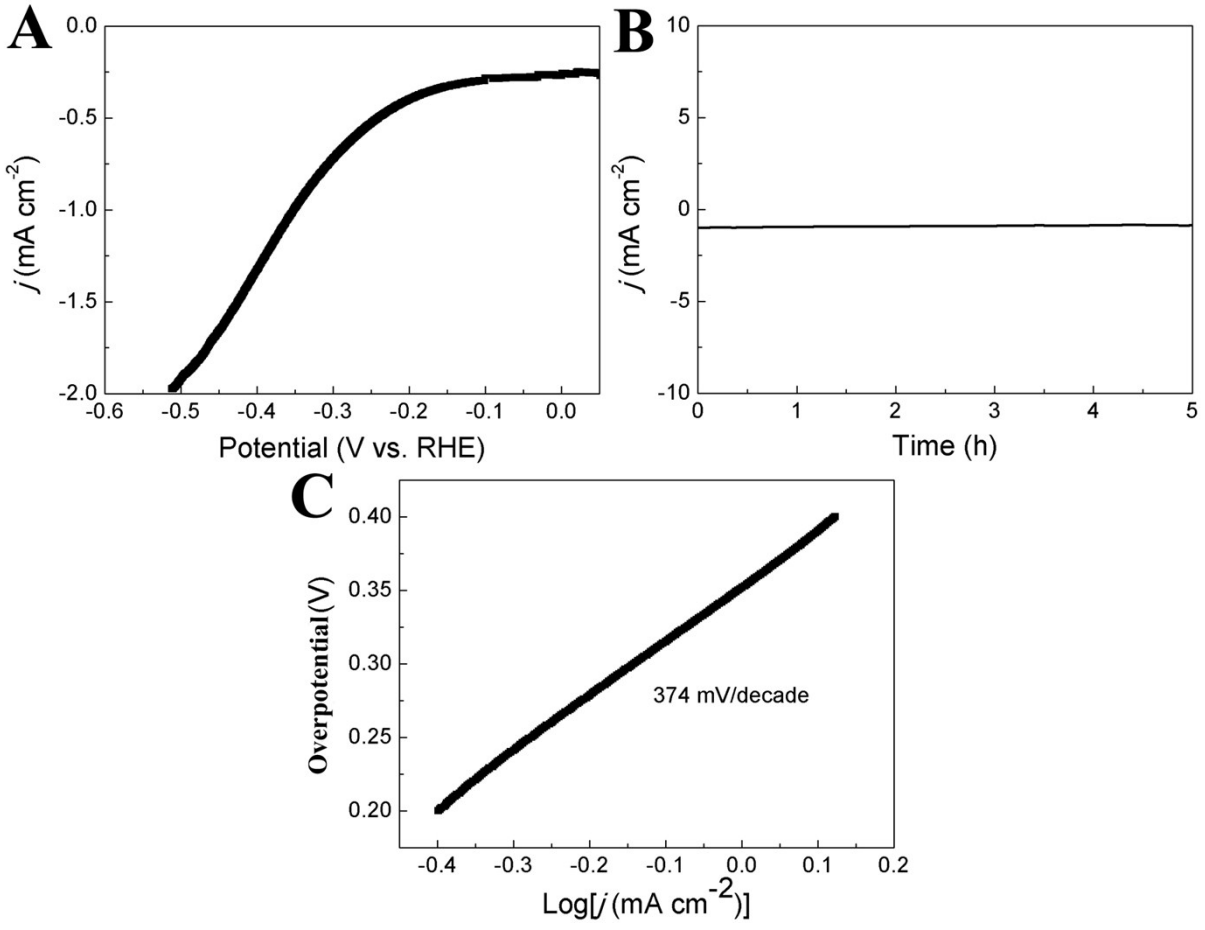

Figure S17. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs^{-1} for HER. (B) A current density-time (*j*-t) curve obtained for HER with ONPPGC/OCC at -0.35 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.2 M PBS.

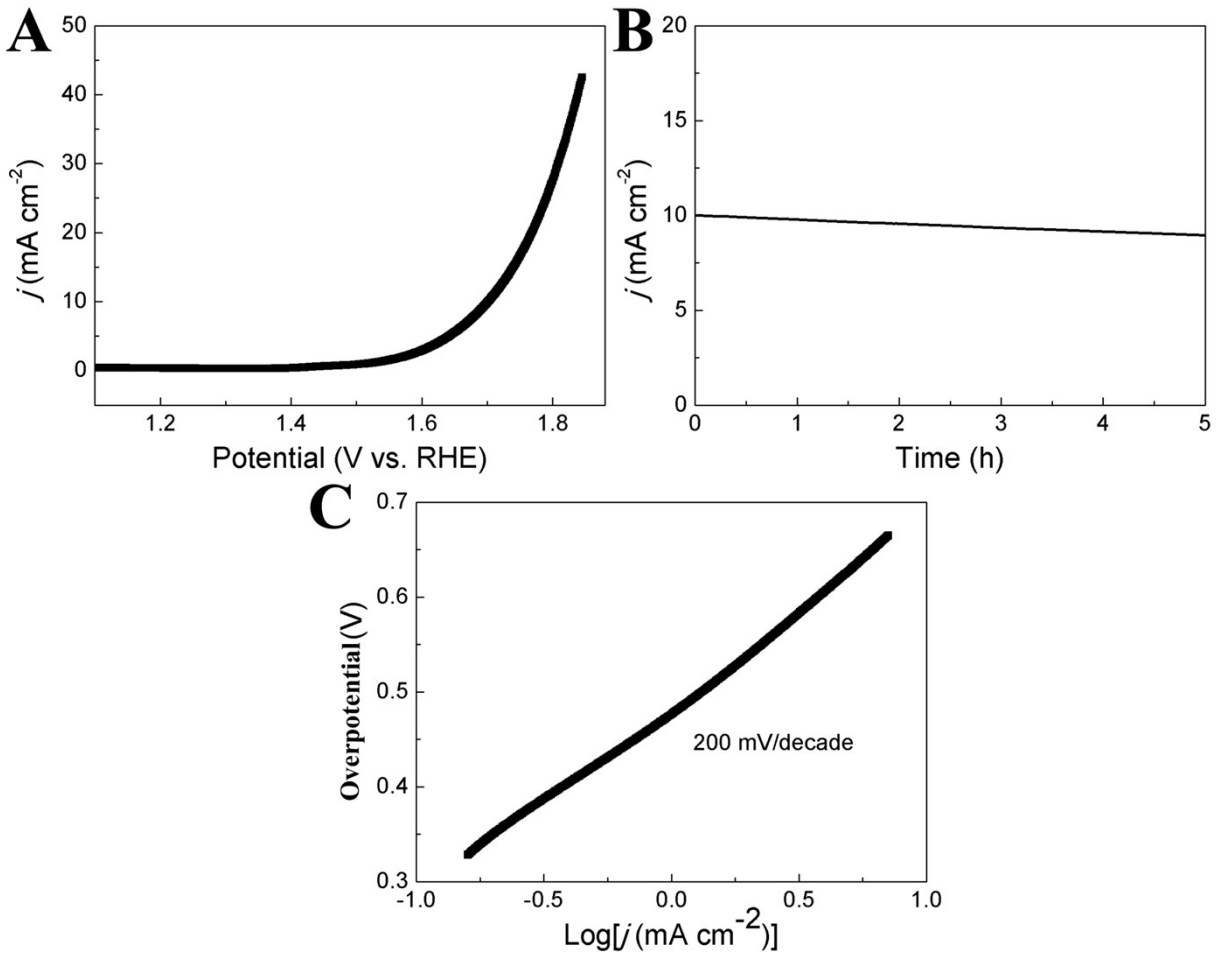

Figure S18. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs^{-1} for OER. (B) A current density-time (*j*-t) curve obtained for OER with ONPPGC/OCC at 1.70 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.5 M H_2SO_4.

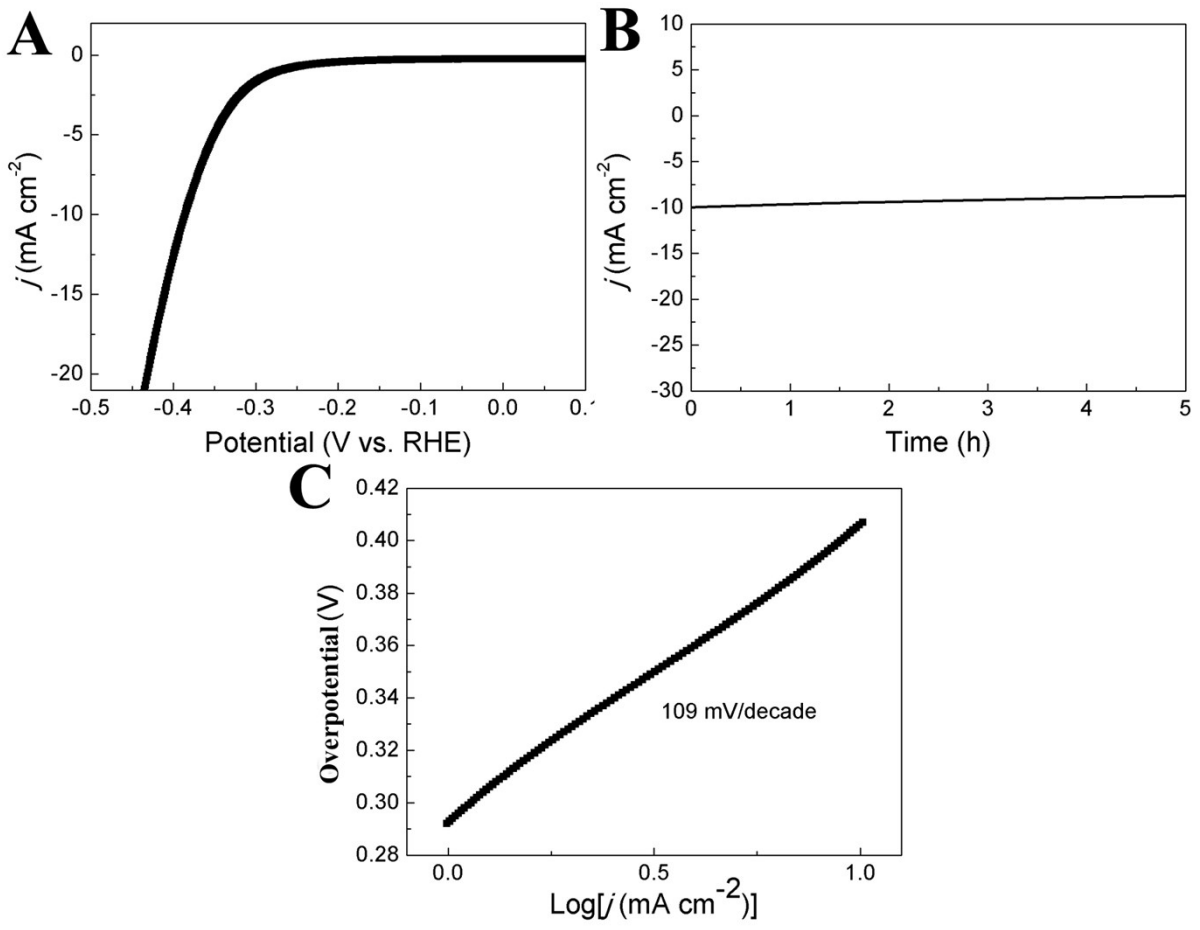

Figure S19. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs^{-1} for HER. (B) A current density-time (j-t) curve obtained for HER with ONPPGC/OCC at -0.39 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.5 M H_2SO_4.

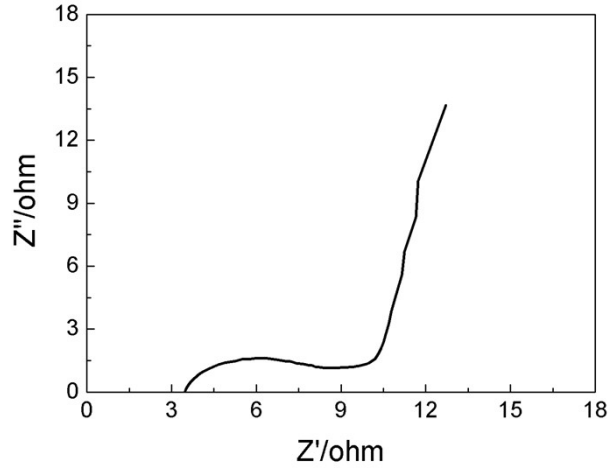

Figure S20. EIS of the ONPPGC/OCC electrodes.

Movie S1. Movie of the system showing the oxygen (left) and hydrogen (right) generation during water electrolysis in 1.0 M KOH.