Electronic Supplementary Information

Controllable fabrication of uniform ruthenium phosphide nanocrystals for hydrogen evolution reaction

Yutong Li, a Fuqiang Chu, a Yunfei Bu, a,b Yong Kong, a Yongxin Tao, a Xiao Zhou, a Haoran Yu, a Junjie Yu, a Lin Tang, a and Yong Qin a

a Jiangsu Key laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu, China
b Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, Jiangsu, 210044, China

*Corresponding authors:
E-mail: jpu441@yahoo.com
E-mail: qinyong@cczu.edu.cn
Experimental Section

Preparation of NG

For the preparation of graphene oxide (GO), graphite flakes (1.0 g) and KMnO$_4$ (6.0 g) were added into a mixture of 120 mL concentrated H$_2$SO$_4$ and 13.3 mL H$_3$PO$_4$, producing a slight exotherm to 35°C. The mixture was then heated to 50 °C and kept there under stirring for 12 h. The reaction was cooled to room temperature and poured into ice water (150 mL) with 30% H$_2$O$_2$ (10 mL). The mixture was sifted through a polyester fiber. The filtrate was centrifuged (4000 rpm for 4 h), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The eventual solution was centrifuged (4000 rpm for 4 h) and the supernatant was decanted away. The solid was vacuum-dried overnight at room temperature, resulting 1.8 g GO. For the fabrication of NG, 150 mg GO was dispersed in 15 mL water to form a concentrated GO suspension, which was mixed with 1 mL formaldehyde solution (37 wt.%.) and 0.35 g melamine. The mixture was then transferred into an autoclave and hydrothermally treated at 180 °C for 12 h. The obtained composite hydrogel was dried at 80 °C for 24 h in an oven. The dry aerogel was subsequently calcined at 750 °C for 5 h in N$_2$ atmosphere, resulting in the final NG product.

Preparation of ruthenium phosphide (Ru$_2$P and RuP) on NPG

20 mg NG was firstly dispersed in 1.0 mL N,N-dimethyl formaldehyde (DMF). 30 mg TPP-Ru and the necessary PA solution (50 wt.% in water) was added and dissolved in the above dispersion. For the fabrication of Ru$_2$P and RuP, 0.075 mL and 1.25 mL PA solution were required respectively. The mixture was placed in an open Teflon vessel and dried at 60 °C slowly. After annealing at 700 °C for 3h, the resulting Ru$_2$P and RuP on NPG were obtained.
Preparation of RuNC

20 mg graphene was dispersed in 10 mL phosphate buffer solution (pH 8.5) followed by addition of 2.6 mL RuCl$_3$:3H$_2$O water solution (4 mg mL$^{-1}$), 40 mg dopamine hydrochloride, and 300 mg cetyl trimethyl ammonium bromide (CTAB). The mixture was treated at 140 °C for 6 hours. Afterwards, it was centrifuged at 3000 rpm. The obtained solid was washed by water and ethanol, subsequently dried and annealed at various temperatures for 3 hours under Ar atmosphere.

Determination of Ru loading

The determination of Ru on NPG is employed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. Briefly, the ruthenium phosphide/NPG composites were first digested in concentrated aqua regia (mixture of 6.6 M HCl and 2.1 M HNO$_3$) at 60 °C overnight. The digestion solution was then pipetted and diluted to obtain a working solution. The weight loadings of Ru were averaged from twice measurements.

Electrochemical measurements

The electrochemical measurements were conducted on an electrochemical cell with conventional three-electrode system. The commercial glass carbon electrode (GCE) with the diameter of 5 mm was used as the working electrode. The current densities were normalized by the geometric surface area of the GCE. The graphite rod electrode and the saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The working electrodes were fabricated by the following procedure: the suspensions of the as-prepared materials were drop coated onto a glassy carbon disk with the diameter of 3 mm (mass-loading ~0.06 mgRu cm$^{-2}$) and dried at room temperature in air for 6 h. Then 5 μL Nafion
solution (0.02 wt.%) were cast on the electrode surface to adhere the materials on electrodes. The potential versus saturated calomel electrode were converted into the potential versus reversible hydrogen electrode (RHE) according $E_{\text{vs RHE}} = E_{\text{vs SCE}} + E_{\text{SCE}}^0 + 0.059 \text{ pH}$.

The calibration test was conducted in a 0.25 M H$_2$SO$_4$ solution containing 10 mM CuSO$_4$ with saturated N$_2$ during the whole test. The electrode was first cycled between 0.23 and 0.7 V in 0.25 M H$_2$SO$_4$ with scan speed of 10mV s$^{-1}$ for many scans as the background. Then the solution was changed into 0.25 M H$_2$SO$_4$ and 10 mM CuSO$_4$ with scan speed of 10mV s$^{-1}$. And the ECSA was calculated after 20 times CV scan. The ECSA was calculated by the following formula:

$$ECSA_{(cm^2/mg\text{ metal})} = \frac{Q_{\text{Cu}}}{M_{\text{metal}} \times 420 \mu C \ cm^2}$$

The $M_{\text{metal}}$ is the numerous loading of Ru nanoparticles on the working electrode. And $Q_{\text{Cu}}$ is the average charge calculated from area under the voltragram of the Cu-upd CV curve.

Afterwards, the HER turnover frequency (TOF) is defined as:

$$TOF = \frac{\text{total hydrogen turnovers/cm}^2\ \text{geo}}{\text{total active sites/cm}^2\ \text{geo}}$$

The upper hydrogen turnovers per geometric electrode area can be calculated by the hydrogen evolution current density under a certain overpotential:

$$H_2 = \left( \frac{j \text{ mA}}{cm^2 \text{ geo}} \right) \times \left( \frac{1 C/s}{1000 mA} \right) \times \left( \frac{1 \text{ mol e}^-}{96485 C} \right) \times \left( \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} \right) \times 6.02 \times 10^{23} = j \times 3.12 \times 10^5 \text{ H}_2/\text{s/cm}^2_{\text{geo}}$$

The total active sites per geometric electrode area can be calculated through the pre-calculated ECSA above.
Fig. S1 XRD pattern of the ruthenium phosphide using TPP-Ru as the Ru and P precursors

Fig. S2 XRD pattern of the ruthenium phosphide using RuCl$_3$ and PA as the Ru and P precursors, respectively
Fig. S3 XRD patterns of the obtained ruthenium phosphides as the molar ration of PA to TPP-Ru varied from 1 to 40 without NG.

Fig. S4 TEM images of Ru$_2$P (a, b) and RuP (c, d) observed under the low-resolution.
Fig. S5 XPS survey of Ru$_2$P and RuP supported on NG

Fig. S6 N1s XPS of Ru$_2$P and RuP on NPG.
Fig. S7 The ECSA of the catalysts estimated by a double layer capacitance ($C_{dl}$) measurement

Fig. S8 TEM images of Ru$_2$P and RuP after 20,000 cycles.
Fig. S9 The LSV curve of Ru$_2$P/RuP in alkaline medium (1.0 M KOH).
Fig. S10 The electrocatalytic performance of Ru₂P and RuP for HER in acid medium (0.5 M H₂SO₄) (a), LSV; (b) Tafel curves; (c, d) CV in H₂SO₄ (0.25 M H₂SO₄) or the mixture of H₂SO₄ (0.25 M H₂SO₄) and CuSO₄ (10 mM CuSO₄) (Cu-upd method); (e) TOF; (f) the ECSA calculated by Cu-upd method.
Fig. S11 LSV curves of Ru$_2$P and RuP in a neutral medium (1.0 M PBS)