Carbon quantum dots enhanced the activity for the hydrogen

evolution reaction in ruthenium-based electrocatalysts

Weidong Li‡^a, Zhihong Wei‡^a, Boyang Wang^a, Yuan Liu^{a,e}, Haoqiang Song^a, Zhiyong Tang^{b,c}, Bai Yang^d and Siyu Lu^{a,b*}

a. College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China. E-mail: sylu2013@zzu.edu.cn.

b. Henan Institute of Advanced Technology, Zhengzhou University. Zhengzhou, 450001, China.

c. CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, China.

d. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, China.

e. College of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450001, China.

‡ These authors have contributed equally.

Experimental details

Chemicals

The reagents used were of analytical grade and did not require further purification. Porphyra is obtained from the Zhengzhou market in China. RuCl₃·*x*H₂O, ethyl alcohol, (\geq 99%, Sinopharm Chemical Reagent Co. Ltd.), NaHCO₃, KOH, the commercial Ru/C (5%) was bought from Aladdin.

Synthesis of CQDs

The CQDs were synthesized by the typical solvothermal method. First, the porphyra is treated with deionized water for simple washing in order to remove other impurities except laver, dried at 50°C for 12 h under vacuum, and then ground into a powder using a pulverizer. Briefly, 6 g porphyra powder and the mixture of ethanol/water (1:1) were added into a 200 mL Teflon-lined autoclave and heated at 200 °C for 8 hours. After natural cooling, centrifuging and filtering gave a brownish-yellow filtrate. The CQDs were further purified by dialyzing and freeze drying to obtain brownish CQDs powder.

Synthesis of Ru@CQDs

1 g CQDs powder was dissolved in 100ml deionized water, and then 0.5 mmol RuCl₃·*x*H₂O was added, stirred for 30 minutes to get an absolutely homogeneous solution. The resulting black solution was then transferred to a 150 mL Teflon-lined autoclave and heated at 200 °C for 8 hours. After natural cooling to room temperature, a dark brown precipitate was obtained, then, centrifuged and filtered with ethanol and deionized water several times and then dried at 60 °C for 12 h. The collected dark powder was then annealed under argon atmosphere at 600°C, 700°C, 800°C 900°C for 6 h at a heating rate of 10 °C min⁻¹.

Synthesis of Ru@PC

1 g porphyra powder and 0.5 mmol RuCl $_3 \cdot x$ H2O were ground into a powder using a pulverizer, and then annealed under argon atmosphere at 800°C for 6 h at a heating rate of 10 °C min⁻¹.

Synthesis of Ru@P-AC

1 g porphyra residue and 0.5 mmol RuCl₃·xH₂O were ground into a powder using a pulverizer, and then annealed under argon atmosphere at 800°C for 6 h at a heating rate of 10 °C min⁻¹.

Characterization

Powder X-ray diffraction (XRD) studies were performed on a Rigaku Dmax-3C, X-ray diffractometer. (Cu K α radiation, $\lambda = 0.15418$ nm, 40 kV, 40mA). The 2 θ angles were scanned from 5° to 80° at 2° · min⁻¹. Transmission electron microscope (TEM) images and Energy-dispersive X-ray spectroscopy (EDS) mapping were observed on a FEI Talos, F200S instrument with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a PHI quantera SXM spectrometer. Raman spectra were obtained using a LabRAM HR Evolution (HORIBA). Infrared spectroscopy was performed on an IR Spectrometer NEXUS 470. UV-vis was acquired on a TU-1810PC. PL emission, and PL excitation spectra were acquired on a RF-6000 (Shimadzu, Japan).

Electrocatalytic activity

The electrochemical measurements were carried out with an electrochemical work station (CHI760E, Shanghai Chenhua, China) in a conventional three-electrode cell system at room temperature with a graphite rod as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a commercial glassy carbon electrode (GCE, 5 mm diameter, 0.196 cm²) was served as the working electrode. The presented current density referred to the geometric surface area of the GCE. The electrolyte was a 1 M KOH aqueous solution. The working electrodes were prepared as follows: ethanol suspensions containing 500 μ L ethanol, 3 mg of catalyst, and 50 μ L 5 wt % Nafion solutions were obtained by ultrasonic mixing for about 30 min. Then 15 μ L of the catalyst ink suspension thus obtained was coated onto the polished GC electrode, and then it was left to dry in air. this gave a catalyst loading of ~0.42mg cm-2 on the GCE. The overpotential, measured against a saturated calomel electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to E vs RHE = E vs SCE + E θ SCE + E θ SCE + 0.059 pH. The working electrode was polished with Al2O3

powders. Commercial Ru/C catalysts (5%, Aladdin) was used as a reference to evaluate the electrocatalytic performance. Linear sweep voltammetry was conducted with a scan rate of 5 mV s⁻¹. CV was conducted from -1.1V to -1.0V at a sweep rate of 50 mV/s for 2,000 cycles to investigate the cycling stability. The Tafel slope were obtained from the treatment of the polarization curve based on the Tafel equation ($\eta = a + b \log j$, where η is overpotential, a is intercept, b is Tafel slope and j is current density).





Figure S1. Particle size distribution of the CQDs.



Figure S2. XPS spectra of CQDs.



Figure S3. (a) TEM images. (b) HRTEM image. (c) particle size distribution of Ru@CQDs900.

Table S1 The fitting results of electrochemical element parameters for various samples.

Sample	$\operatorname{Rs}\left(\Omega ight)$	CPE	$\operatorname{Ret}\left(\Omega\right)$
Ru@CQDs600	7.9	0.798	98.4
Ru@CQDs700	7.7	0.767	96.2
Ru@CQDs800	6.9	0.704	30.7
Ru@CQDs900	7.1	0.734	40.3

Rs stands the resistance of the electrolyte and intrinsic resistance of the active materials coated on the electrode.

Rct represents for the electron or charge transfer resistance, which determines the interfacial electron.