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碳点增强的 Ru 纳米颗粒复合材料用于碱性条件下高效电解水析氢

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Carbon Dots Enhance Ruthenium Nanoparticles for the Efficient Hydrogen Production in Alkaline

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Experimental Section

Preparation of electrocatalysts

Synthesis of Ru@Molecule： Citric Acid (2.1014 g), Melamine (1.2612 g) and $RuCl_3 \cdot xH_2O$ (300 mg) was dissolved in deionized water (200 mL). Then the solution was transferred to a Teflon autoclave (250 mL) and heated at 200 °C for 8 h. The resulting solution was concentrated by evaporation and freeze-dried. The solid was annealed in a tube furnace at 500 °C, 600 °C and 700 °C for 6 h under Ar atmosphere with a heating rate of 2 °C·min^{-1}.

Synthesis of Ru-MOF： $[Ru_2(OOCCH_3)_4Cl]$ was first synthesized. $RuCl_3 \cdot xH_2O$ (0.5 g) and $LiCl \cdot H_2O$ (0.5 g) were dissolved in glacial acetic acid (17.5 mL) and acetic anhydride (3.5 mL). Subsequently, the mixture was refluxed for 24 h at 140 °C. The resulting powder was filtered and washed with acetone several times and dried under dynamic vacuum. To synthesize the Ru-MOF, 0.17 g of the resulting $[Ru_2(OOCCH_3)_4Cl]$ and 0.101 g of 1,3,5-benzenetricarboxylic acid were mixed with 4 ml of deionized water and 0.7 ml of acetic acid in a 20 ml Teflon vessel. The vessel was then sealed in an autoclave and heated at 160 °C for 3 days. The final product was washed with water and ethanol for several times and dried at 160 °C for 8 h under dynamic vacuum. The Ru-MOF was annealed in a tube furnace at 500 °C, 600 °C and 700 °C for 2 hours under Ar atmosphere with a heating rate of 2 °C·min^{-1}.

Synthesis of Ru@CNTs： Ultrasonically disperse 200 mg carboxylated CNTs in 50 mL of ethanol, then dissolve 30 mg $RuCl_3 \cdot xH_2O$ in 150 mL of deionized water, and pour into ethanol-dispersed CNTs with stirring. Then the solution was transferred to a Teflon autoclave (250 mL) and heated at 200 °C for 8 h. The resulting solution was concentrated by evaporation and vacuum drying. The solid was annealed in a tube furnace at 500 °C, 600 °C and 700 °C for 6 h under Ar atmosphere with a heating rate of 2 °C·min^{-1}.

Synthesis of Ru@GO： After dissolving 200 mg of graphene oxide with ultrasonic stirring to dissolve and disperse it uniformly in 200 mL of deionized water, add 30 mg of $RuCl_3 \cdot xH_2O$, and after homogenizing again, hydrothermal at 200 °C for 8 h to obtain graphene aerogel. After cooling the supernatant was precipitated and freeze-dried. The solid was annealed in a tube furnace at 500 °C, 600 °C and 700 °C for 6 h under Ar atmosphere with a heating rate of 2 °C·min^{-1}.

Characterizations

Transmission electron microscope (TEM) images and energy-dispersive X-ray spectroscopy (EDS) maps were obtained on a FEI Talos, F200S instrument with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was acquired on a PHI quantera SXM spectrometer using Al as the excitation source. X-ray diffraction (XRD) patterns were collected on a PANalytcal X'Pert PRO instrument with scan range from 10° to 90° at 3 (°)·min^{-1}. (Cu K_α radiation, 40 kV, 40 mA, λ = 0.15418 nm). Infrared spectra were obtained using an IR Spectrometer NEXUS 470. UV-Vis was acquired on a TU-1810PC. PL emission, and PL excitation spectra were acquired on an RF-6000 instrument (Shimadzu, Japan).

Supporting Data

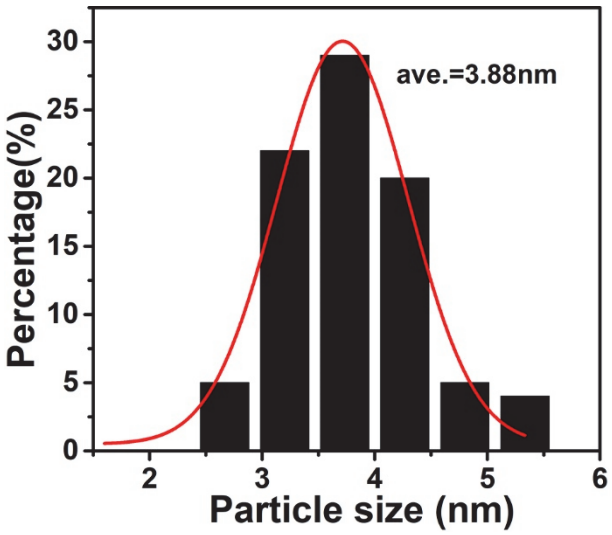

Fig. S1 Particle size distribution of CDs.

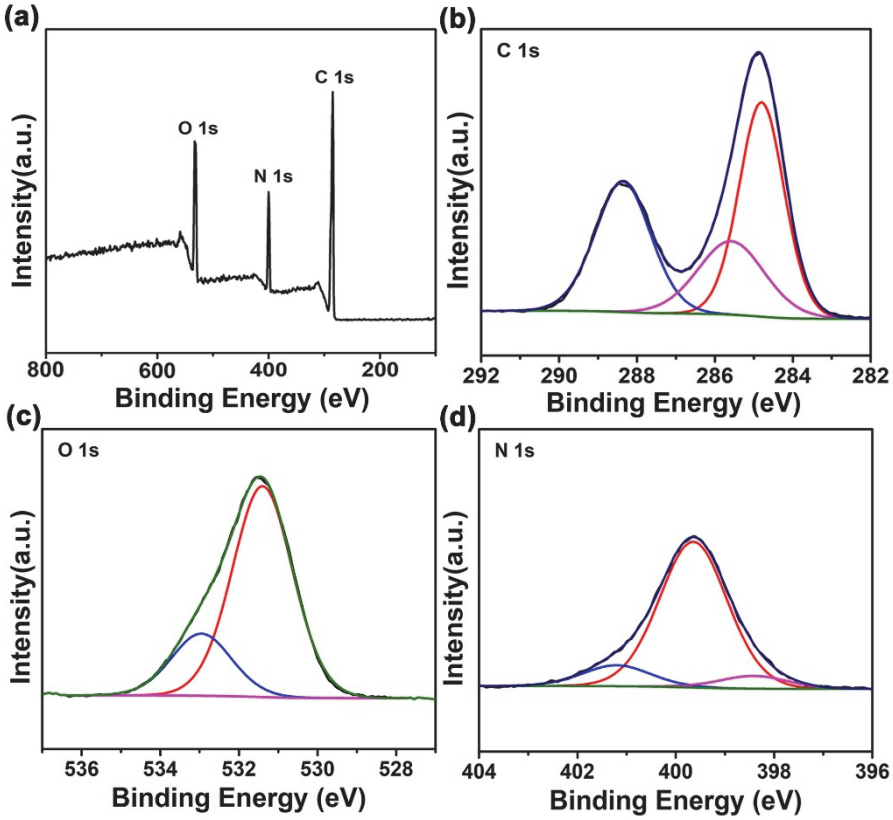

Fig. S2 XPS spectra of CDs: (a) survey; (b) C 1*s*; (c) O 1*s* and (d) N 1*s*.

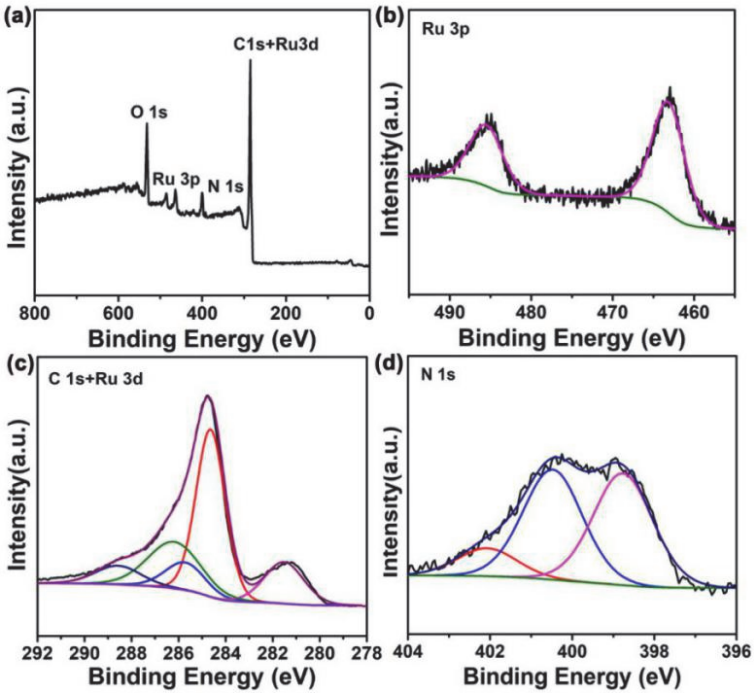

Fig. S3 XPS spectra of Ru@CDs 600: (a) survey; (b) Ru 3*p*; (c) C 1*s* + Ru 3*d* and (d) N 1*s*.

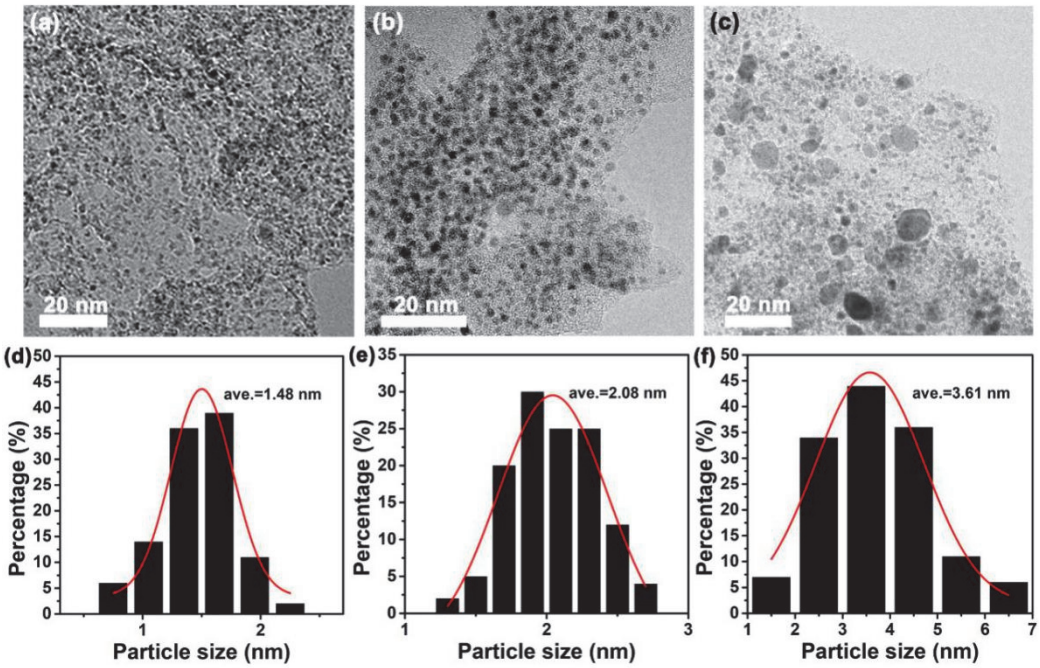

Fig. S4 (a–c) TEM images of Ru@CDs 500, Ru@CDs 600 and Ru@CDs 700; (d–f) particle size distribution of Ru@CDs 500, Ru@CDs 600 and Ru@CDs 700.

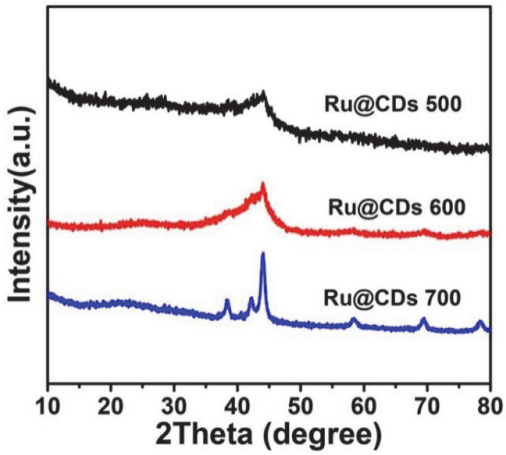

Fig. S5 XRD patterns of Ru@CDs 500, Ru@CDs 600 and Ru@CDs 700.

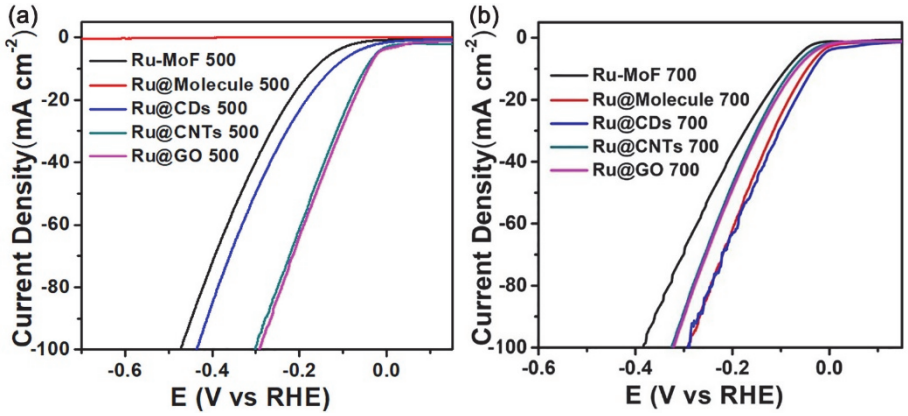

Fig. S6 Polarization curves for the HER on RDE modified with Ru@CDs, Ru-MOF, Ru@Molecule, Ru@CNTs and Ru@GO annealed at (a) 500 °C and (b) 700 °C.