Two-Dimensional TaC Nanosheets on Reduced Graphene Oxide Hybrid as Efficient and Stable Electrocatalyst for Water Splitting

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Experimental

Chemicals and Reagents

Concentrated sulfuric acid (H_2SO_4, 98 wt%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide solution (30 wt%), potassium flurotantalate (K_2TaF_7) and graphite powders (325 mesh, XFNANO Material Technologic Co. Ltd., Nanjing, China). Platinum on an XC-72 support (Pt/C, 20 wt%) was purchased and used as received (TKK, Japan). The bulk TaC （≤3 μm, AR） and Ta_2O_5（AR）powders were purchased from Guangzhou Dongzheng Chemical□Glass Instrument Co. LTD.

Synthesis of graphite oxide (GO)

GO powders were synthesized via a modified Hummers method. In a typical process, 2.0 g natural graphite powders were gradually added into the concentrated H_2SO_4 (46 mL, 98 wt%) under stirring in an ice bath and the stirring continued for 15 min after mixing. Then 10.0 g $KMnO_4$ and 5.0 g $NaNO_3$ were slowly added in under vigorous agitation to keep the suspension temperature lower than 20 ^{o}C, before the temperature was raised to 40 ^{o}C and retained for 35 min. Afterwards, 50 ml of deionized water was added to the mixture slowly and the suspension temperature kept at 95 ^{o}C for 30 min. Finally 200 mL deionized water and 10 ml of 30% H_2O_2 were added into the suspension. At the end of the reaction, solution color changed from dark brown to yellow. The mixture was filtered and washed with 1 mol L^{-1} HCl aqueous solution (250 mL) and deionized water to remove metal ions.

Growth of two-dimensional TaC nanosheets on reduced graphene oxide (RGO)

Typical procedure for preparing two-dimensional TaC nanosheets on RGO (2D TaC-RGO) is as follows. 0.1 g GO powder was first dissolved in 200 mL deionized water in a beaker then sonicated for 2 h to form chemically exfoliated GO dispersion (~0.5 mg ml^{-1}). 2D TaC-RGO hybrid was prepared by mixing 0.05 g K_2TaF_7 with 200 ml of thus obtained GO dispersion; the mixture was sonicated for 30 min, then stirring continuously at 90 ^{o}C, until almost the moisture has evaporated and turning into hydrogel-like mixture and further freeze dried. The collected final mixture was then annealed under argon atmosphere at 1200 °C for 2 h at a heating rate of 5 °C min^{-1}.

Characterizations

X-ray diffraction (XRD) was performed on a Rigaku D/Max-III using Cu Kα radiation operating at 30 kV and 30 mA. 2θ angular regions between 15° and 80° were measured at a scan rate of 6° min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an XPS apparatus (ESCALAB 250, Thermo-VG Scientific Ltd.). Raman spectrum was collected on a Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser of 514.5 nm wavelength. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed on a field emission transmission electron microscope (FETEM, FEI Tecnai G2 F30) operating at 300 kV. Ta L_3 edge

X-ray absorption spectroscopy (XAS) of a Ta foil standard and catalyst samples were measured in total electron yield transmission mode at the beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China.

Electrochemical measurements.

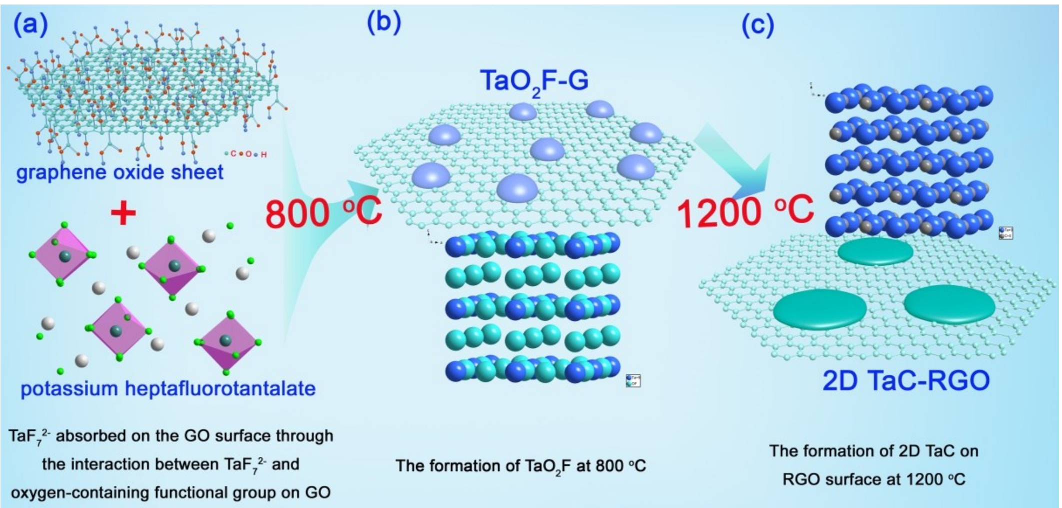
All electrochemical measurements were conducted in a standard three-electrode cell using 0.5 mol L^{-1} H_2SO_4 as the electrolyte solution, a piece of graphite (10×1 cm^{-2}) as the counter electrode, a reversible hydrogen electrode (RHE) as the reference electrode, and a glassy carbon disk (A=0.2825 cm^2) as the working electrode. Electrocatalytic HER activities of TaC-RGO hybrids were investigated by depositing samples at a mass loading of ~0.64 mg cm^{-2} prepared as follows: 5.0 mg catalyst was first dispersed in 0.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt %, DuPont, USA), the mixture ultrasonicated for an hour to form a well-dispersed ink; a certain amount of the ink was then transferred onto the glass carbon electrode surface and dried under infrared lamp for 5 min to obtain a catalyst thin film.

The HER experiments were conducted on an Autolab PGSTAT 302 (ECO Chemie, Netherlands) at 25 ^{o}C in a thermostatic water bath. Linear sweep voltammetry (LSV) tests were performed at 2 mV s^{-1} scan rate. Before the HER measurements, the electrodes were pre-treated by cycling the potential between -0.4 and +0.4 V at a sweep rate of 50 mV s^{-1} for 30 cycles to activate the catalysts, remove surface contamination and stabilize electrochemical current. Electrochemical impedance spectroscopy (EIS) measurements were recorded at frequency range of 100 kHz to

100 mHz with modulation amplitude of 10 mV. Stability of the catalysts was studied by cycling the potential between -0.3 and 0.2 V at a sweep rate of 50 mV s^{-1} for 10,000 cycles. To ensure the calalyst layer stick on the glassy carbon electrode during the long time stable performance, before the test, we drop 10 μL 0.05 wt% Nafion solution on the electrode, after dried under infrared lamp for 5 min, than set it overnight. Stability of the catalysts was studied by potentiodynamic test between -0.3 and 0.2 V at a sweep rate of 50 mV s^{-1} for 10,000 cycles. Long-term (50 h) stability was also tested at controlled potentials.

For comparison, 20 wt% Pt/C was measured under identical conditions, the loading is 12.5 μg cm^{-2} for Pt metal. And the HER performance of physical mixture of commercial bulk TaC and RGO (bulk TaC/RGO) with an equivalent TaC loading was also test.

Additional experimental data



Scheme S1. Schematic illustration of the 2D TaC-RGO synthetic process. (a) the GO absorb TaF^{2-} on the surface through physisorption/chemical coordination between the oxygen-containing functional group on GO and TaF^{2-}, (b) heat-treatment in N_2 atmosphere, forming TaO_2F intermediates at temperatures above 800 °C and (c) GO reduction and formation of 2D TaC-RGO simultaneously at 1200 °C.

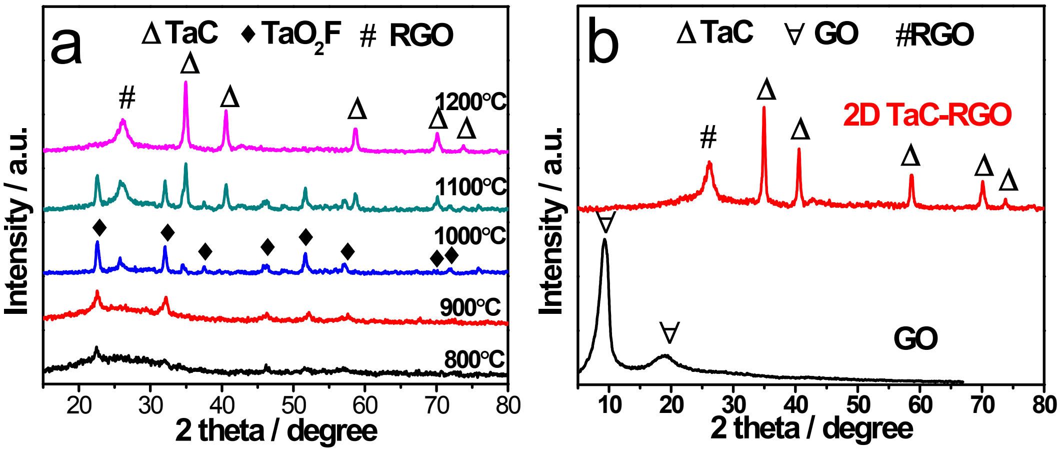


Figure S1. (a) XRD patterns of the products sintered at different temperatures from 800 °C to 1200 °C under pure N_2. The symbol for TaO_2F is appeared at 800 °C, and he TaO_2F phase transferred into TaC phase with the temperature increase to 1200 °C. (b) the comparison of the XRD patterns of the GO and 2D TaC-RGO. The XRD pattern of GO displays typical characteristic diffraction peaks of GO at 9.32° and 19.0°. And the diffraction peaks of GO at 9.32° and 19.0° were disappeared completely in the 2D TaC-RGO, indicating that the GO was reduced completely after annealing.

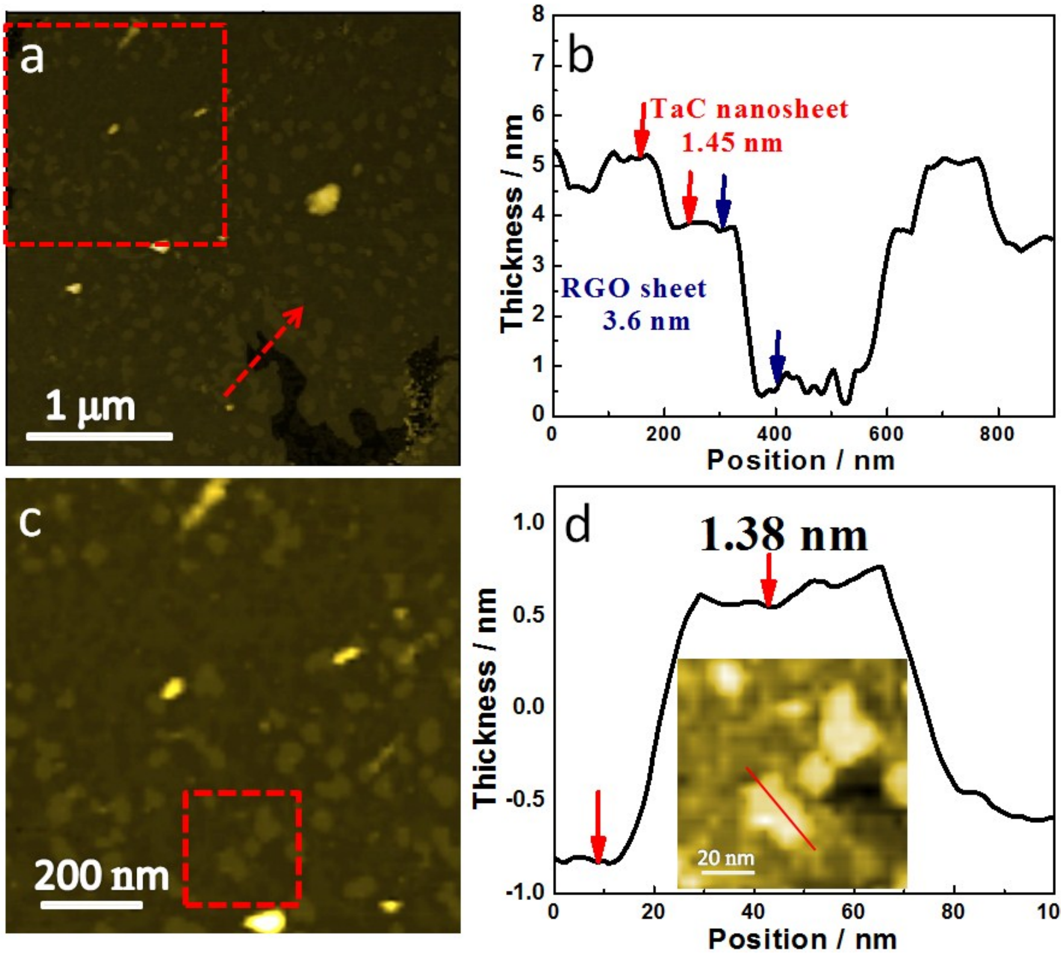


Figure S2. (a) Tapping mode AFM image of 2D TaC-RGO on newly-delaminated mica, showing the TaC nanosheets dispersed homogeneously on RGO sheets, (b) the height profile along the red arrows in the inset in (a), showing that the RGO is 3.6 nm and TaC nanosheet 1.45 nm, (c) a close-up of the dotted red square in (a), (d) the height profile along the red line in the inset, a close-up of the dotted red square in (c).

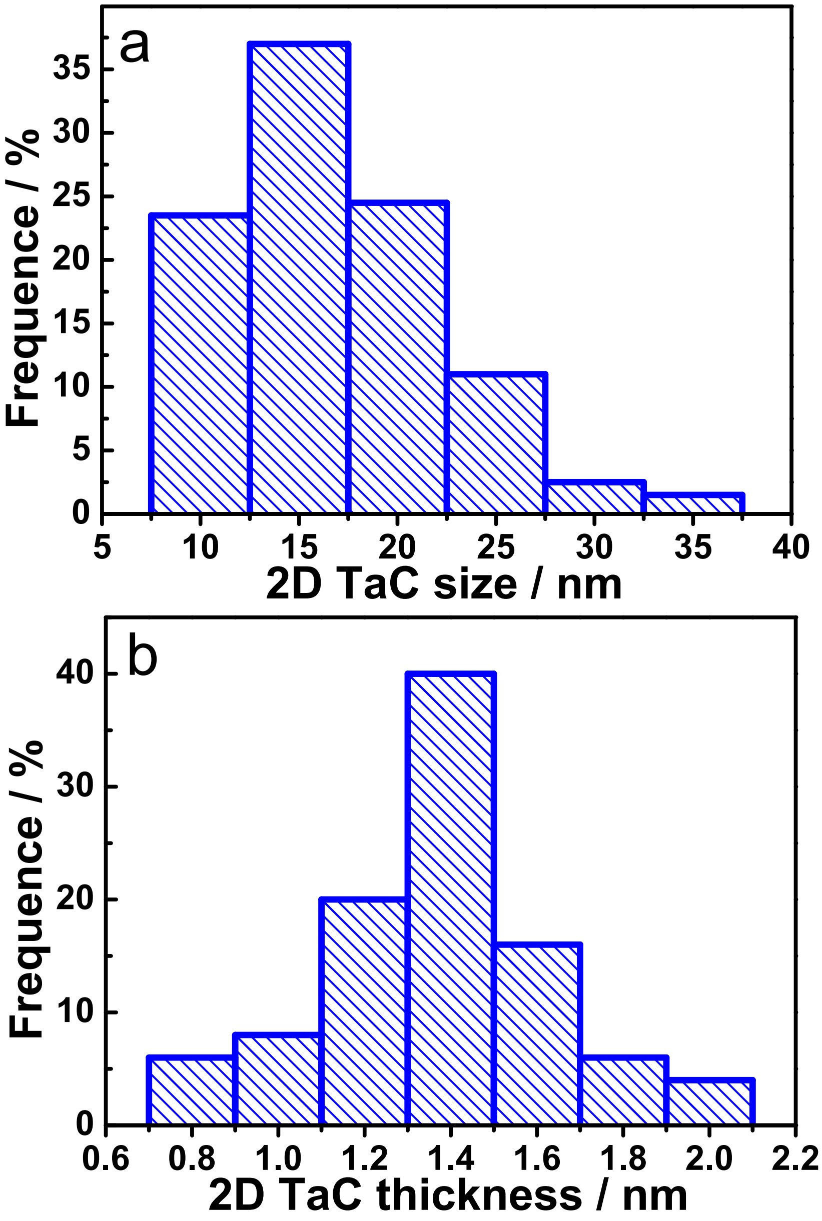


Figure S3. (a) Size-distribution histograms of the 2D TaC nanosheets, (b) the corresponding thickess-distribution histograms of the 2D TaC nanosheets.

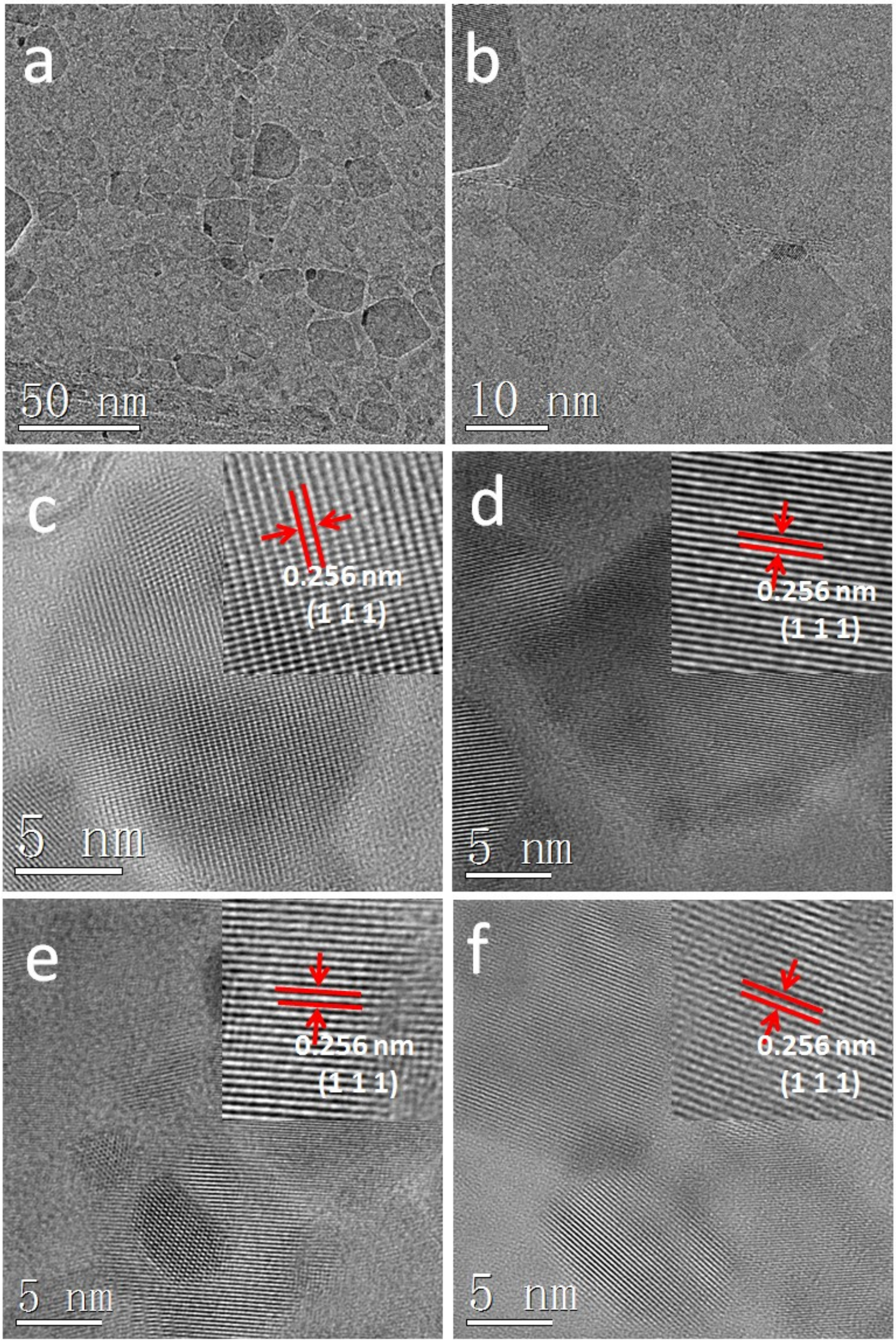


Figure S4. (a, b) (a,b) TEM (c-f) HRTEM images of 2D TaC-RGO hybrid at different magnifications; inset shows enlarged lattice fringes images.

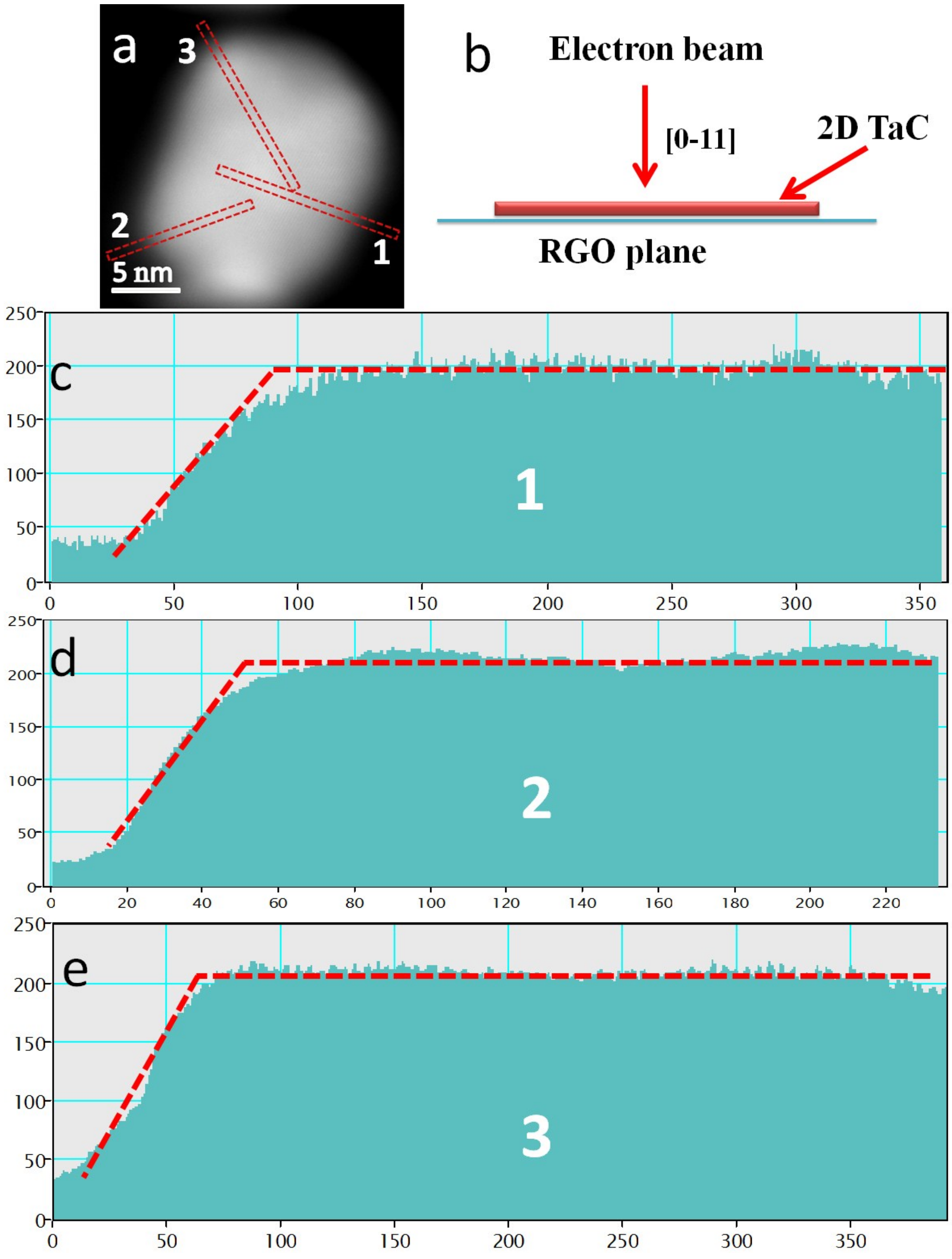


Figure S5. (a) high-resolution HAADF-STEM image of an individual 2D TaC nanocrystal oriented along [0-11], (b) a vertical section model of 2D TaC nanocrystal on RGO plane surface, (c-e) the intensity profiles acquired from the projection of the 2D TaC nanocrystal from different directions.

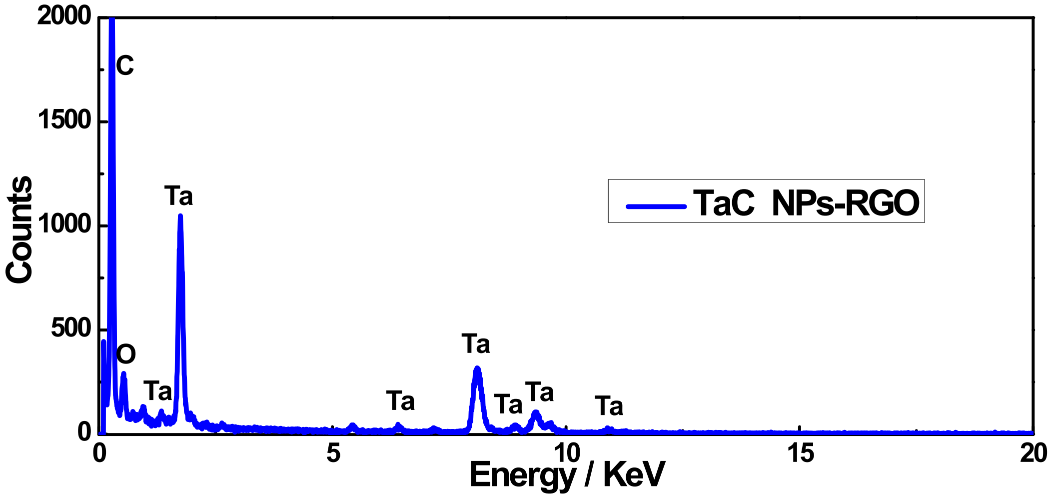


Figure S6. EDS pattern of 2D TaC-RGO.

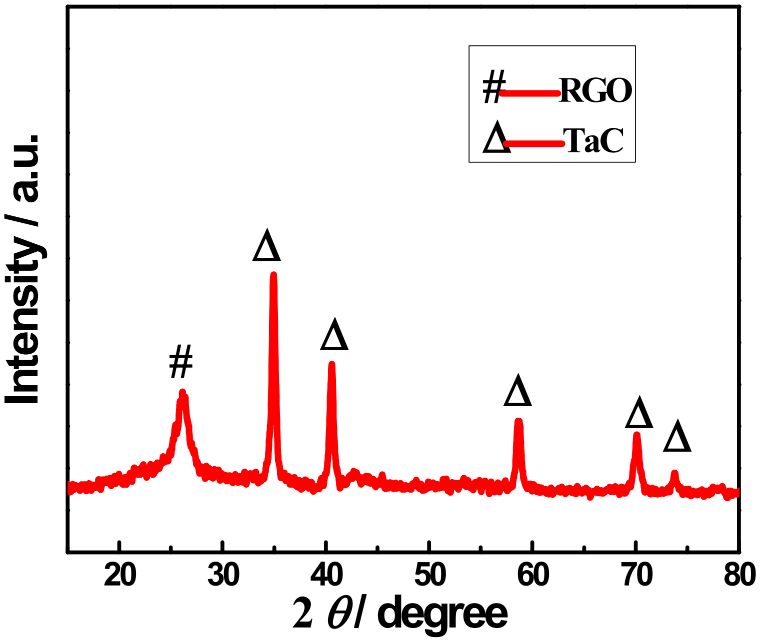


Figure S7. XRD pattern of 2D TaC-RGO.

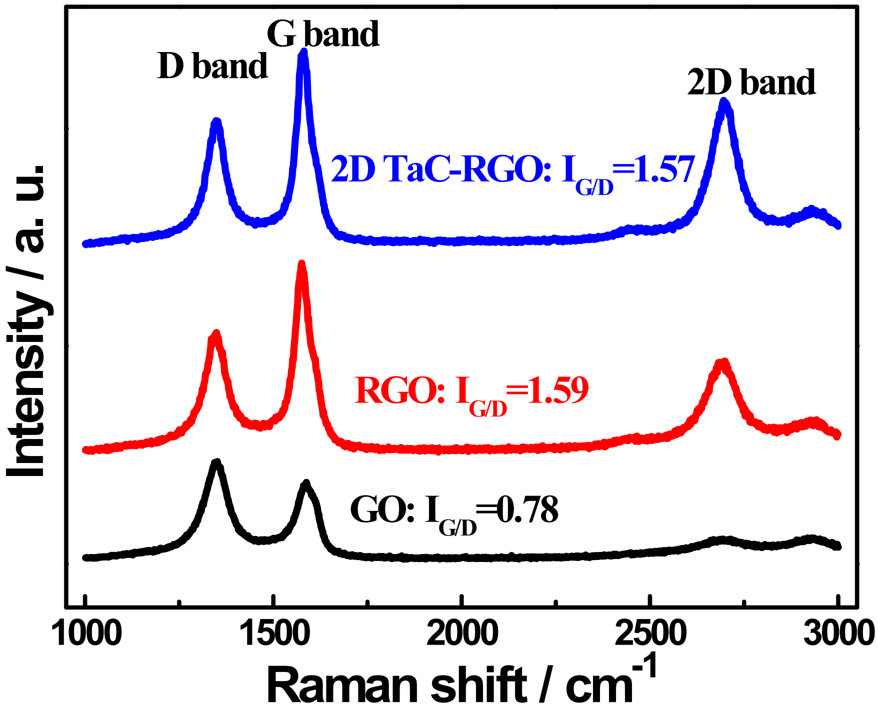


Figure S8. Comparison of Raman spectra of the GO, RGO and 2D TaC-RGO.

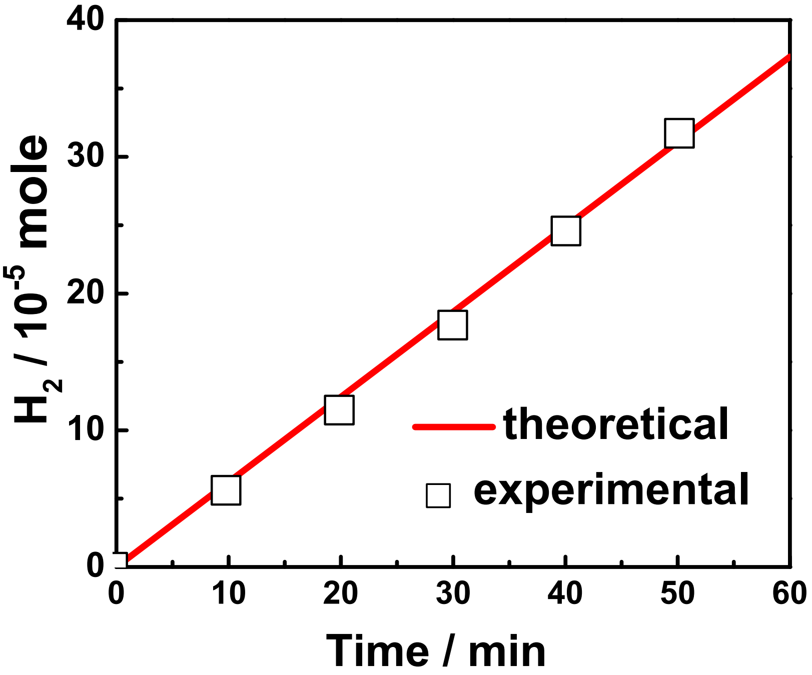


Figure S9. The Faradic efficiency of 2D TaC-RGO for HER under chronopotentiometry at a cathodic current of 10 mA cm^{-2}. The calculated quantity of hydrogen and the experimentally collected hydrogen are compared.

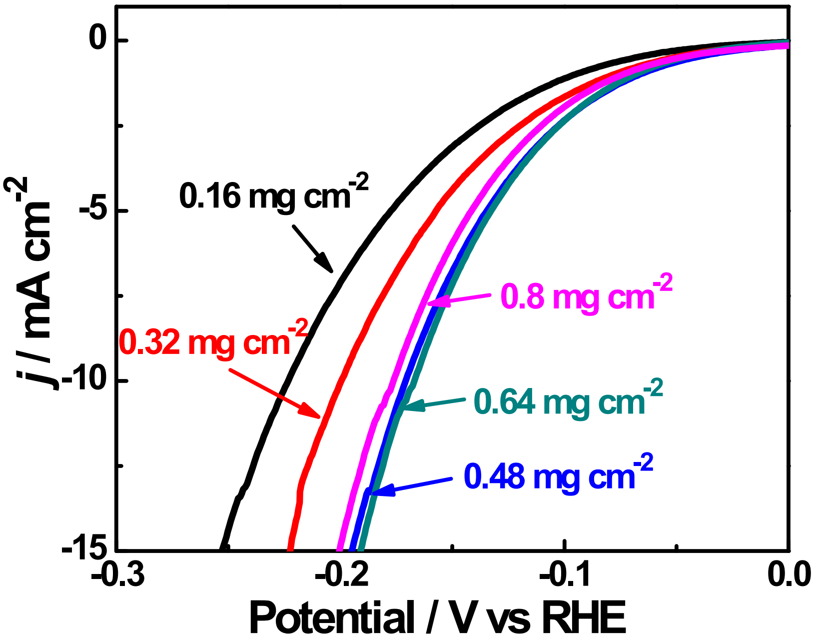


Figure S10. Polarization curves of the 2D TaC-RGO catalyst at different loadings.

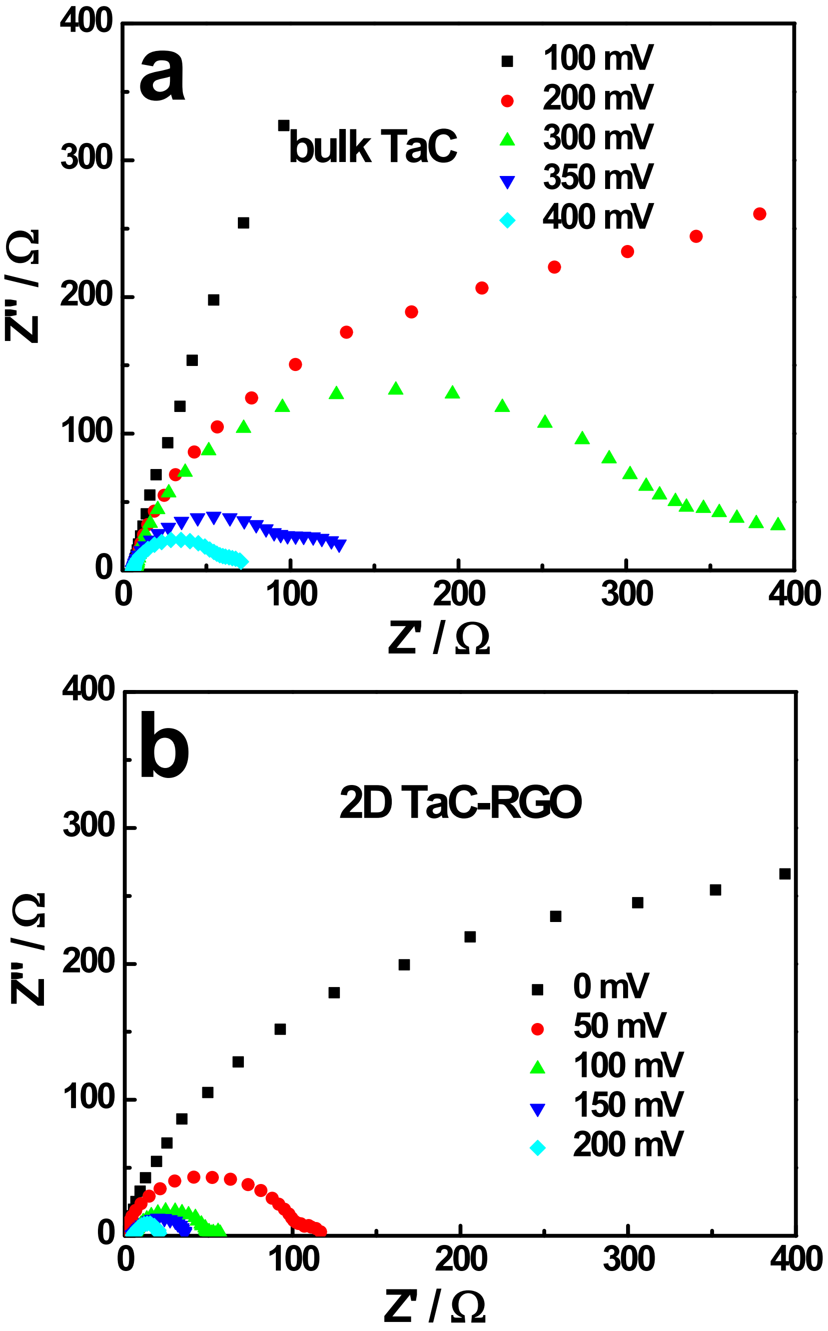


Figure S11 Nyquist plots showing EIS responses of bulk TaC (a) and 2D TaC-RGO (b) electrode at various HER overpotentials.

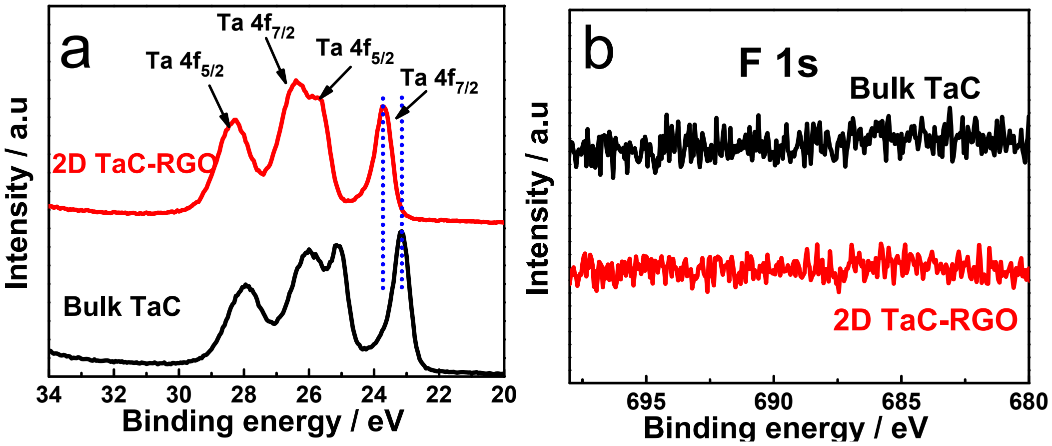


Figure S13. (a) XPS spectra of the Ta 4f region for 2D TaC-RGO and bulk TaC. The Ta 4f peaks of 2D TaC-RGO are shifted significantly compared to those of bulk TaC by about 0.6 eV to a higher binding energy, which mainly stem from the charge-transfer, (b) the F 1s spectra of the 2D TaC-RGO and bulk TaC, suggesting no residual fluorine (F) after the annealing process