## **Supporting Information**

## Ultrathin PdTe Nanowires Anchoring Reduced Graphene Oxide

## **Cathodes for Efficient Hydrogen Evolution Reaction**

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## **Experimental section**

**Materials:** Na<sub>2</sub>TeO<sub>3</sub>, poly(vinyl pyrrolidone) (PVP, K = 30) and PdCl<sub>2</sub> were purchased from Shanghai Chemical Reagent Co. Ltd., hydrazine hydrate (85% w/w%), aqueous ammonia solution (25 - 28% w/w%), ethanol, ethylene glycol (EG) and isopropanol were purchased from Tianjin Guangfu Chemical Co. Ltd., Nafion (5 wt.%) was purchased from Sigma-Aldrich, natural graphite (SP - 1) was purchased from Bay Carbon (Bay City, MI, USA) for the synthesis of graphene oxide (GO). All the chemical reagents used as received without further purification. Deionized water (DIW) was used in all experiments.

**Synthesis of Te nanowires:** High quality Te nanowires (NWs) were prepared by a reported hydrothermal method.<sup>1</sup> Briefly, 1.0 g PVP and 92.2 mg Na<sub>2</sub>TeO<sub>3</sub> were dissolved in 35 mL DIW which previously added 1.65 mL hydrazine hydrate (85%, w/w %) and 3.35 mL aqueous ammonia under vigorous magnetic stirring. Then, the mixed solution was transferred into a 50 mL Teflon vessel held in a stainless steel vessel and heated in an oven at 180 °C for 3 h.

**Synthesis of PdTe nanowires:** In a typical synthesis,<sup>2</sup> about 0.2 mmol Te NWs were dispersed in 30 mL ethylene glycol (EG) firstly. Then, 0.2 mmol PdCl<sub>2</sub> were added into the previous solution and shaken in a shaking bath at 50 °C for 13 h. Finally, the products were collected by centrifugation and washed with ethanol for three times. According to the molar ratio of Pd and Te in the resulting product, we named the catalyst as  $Pd_{1.82}$ Te, in which the number means the molar ratio of Pd and Te is 1.82:1. By turning the molar quantities of PdCl<sub>2</sub>, we prepared  $Pd_{0.93}$ Te,  $Pd_{1.82}$ Te,  $Pd_{3.02}$ Te NWs,  $Pd_{3.17}$ Te NWs and  $Pd_{5.09}$ Te NWs, subsequently.

Synthesis of reduced graphene oxide (rGO): Graphene oxide (GO) was prepared from natural graphite according to the modified Hummer's method.<sup>3</sup> rGO was obtained from the reduction of GO.<sup>4</sup> First of all, 12.5 mg as-prepared GO were dispersed in 50 mL DIW by ultrasonic. Then, the suspension was transferred into a 250 mL flask and adjusted pH to 10 by adding aqueous ammonia. Finally, after adding 10  $\mu$ L hydrazine hydrate, the suspension was refluxed at 95 °C for 1 h and the products was washed with DIW for three times.

**Synthesis of PdTe NWs / rGO hybrid:** The PdTe NWs/rGO hybrid was prepared by 30 min ultrasonic treatment of a mixture solution of PdTe NWs and rGO (the mass ratio of the PdTe NWs and the rGO is 1:1.5). The resulting products were collected by centrifugation and washed with DIW. The PdTe NWs/rGO products were dried in a vacuum oven at 30 °C for further use.

**Characterizations:** Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were obtained using a FEI Tecnai  $G^2$  transmission electron microscope operating at 200 kV (FEI Company). Except the shape and structure, the composition and chemical state of PdTe NWs/rGO are recognized by energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS). EDX was performed on a Tecnai  $G^2$  microscope and XPS analysis was

conducted using a PHI-5702 X-ray photoelectron spectrometer. Raman spectra was obtained using an inVia Renishaw confocal spectrometer with 633 nm laser excitation. XRD spectra was conducted at room temperature and performed using a Rigaku D/max-2400 diffractometer employing Cu-K $\alpha$  radiation as the X-ray source in the 2 $\theta$  range of 10–90°. Inductive coupled plasma atomic emission spectroscopy (ICP-AES) analysis was conducted using a PerkinElmer (Optima 4300DV) instrument.

**Electrochemical measurements:** To prepare the working electrode: (1) 4 mg of catalyst and 30  $\mu$ L Nafion solutions were successively dispersed in 1 mL water-isopropanol solution with volume ratio of 3:1 to form a homogeneous mixture by sonicating. (2) 5  $\mu$ L of the dispersion (containing 20  $\mu$ g of catalyst) was loaded onto a glassy carbon electrode (GCE) with 3 mm diameter (loading 0.285 mg cm<sup>-2</sup>). For the preparation of Pt/C catalyst electrode, 1 mg commercial Pt/C catalyst (20 wt. %, Johnson Matthey) was dispersed in 1 ml DIW water. After a rigorous sonication of 30 min, 70  $\mu$ l of the suspension was deposited onto a glassy carbon electrode (0.07 cm<sup>2</sup>) and was dried in air to form a uniform thin film for electrochemical characterizations. Therefore, the actual loading amount of noble metal from Pd<sub>3.02</sub>Te NWs/rGO and Pt/C was approximately the same (Pd form the Pd<sub>3.02</sub>Te NWs/rGO is 71.2  $\mu$ g cm<sup>-2</sup>).

Electrochemical tests were performed with a model CH Instrument 660 electrochemical workstation (Shanghai Chenhua Equipment, China). Linear sweep voltammetry (LSV) with scan rate of 5 mV s<sup>-1</sup> was conducted in 1 M KOH (or 0.5 M H<sub>2</sub>SO<sub>4</sub>) solution using Ag/AgCl as the reference electrode and a Pt wire as the counter electrode, which yields the relation E (V vs. RHE) = E (V vs. SCE) +0.209 V. The electrochemical impandance spectroscopy (EIS) measurements were carried out in the same configuration at  $\eta = 200$  mV from 100 KHz to 10 mHz.

The Tafel slopes were determined by fitting the linear regions of the Tafel plots to the Tafel equation:  $\eta = b \log(j) + a$ 



Figure S1. XRD patterns of graphite oxide and reduced graphite oxide.



**Figure S2.** CV profiles of  $Pd_{3.02}$ Te NWs/rGO recorded in (a) 1 M KOH and (b) 0.5 M  $H_2SO_4$  solution at a sweep rate of 100 mV s<sup>-1</sup>.



**Figure S3.** HRTEM image of the  $Pd_{3.02}$ Te NWs/rGO after the electrochemical dealloying procedure. The SCSs is still retained along the NWs and the majority lattice parameter of the SCSs is 0.225 nm.



**Figure S4.** The HER activity of  $Pd_{3.02}$ Te NWs/rGO in (a) 1 M KOH and (b) 0.5 M H<sub>2</sub>SO<sub>4</sub>, without and with CV electrochemical treatment before the electrocatalytic measurements.



**Figure S5.** HER activities of PdTe NWs with different composition in 1M KOH at room temperature. The polarization curves were recorded at a sweep rate of 5 mV s<sup>-1</sup>.



**Figure S6.** HER activities of different PdTe NWs anchored on rGO with the same loading amount in 1M KOH at room temperature. The polarization curves were recorded at a sweep rate of 5 mV s<sup>-1</sup>.



**Figure S7.** Polarization curves obtained on glassy carbon electrodes coated with different  $Pd_{3.02}$ Te NWs loading amount loading on rGO sheets.



**Figure S8.** Nyquist plot of  $Pd_{3.02}$ Te NWs and  $Pd_{3.02}$ Te NWs/rGO. The DC bias used for the impedance studies is 200 mV with 5 mV ac amplitude. The frequency range used for the studies is from 100 kHz to 10 mHz.



Figure S9. (a-b) TEM images of Pd<sub>3.02</sub>Te NWs/rGO after the stability tests.

Table S1. (	Dneset overpotentials,	Tafel slopes,	exchange c	urrent den	sities j <sub>0</sub> col	lected in bo	th 1 M K	OH
and 0.5 M H	$H_2SO_4$ solution							

Catalyst	pН	Oneset potential (mV)	Tafel slope [mV / decade]	Exchange current density j <sub>0</sub> [mA cm <sup>-2</sup> ]
Pd <sub>3.02</sub> Te NWs	14	111	125	0.701
Pd <sub>3.02</sub> Te NWs/rGO	14	7	90	1.848
Pt/C	14	23	65	0.594
Pd <sub>3.02</sub> Te NWs/rGO	0	6	63	1.807
Pt/C	0	3	34	0.999

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