

Supporting Information

for

Poly(3,4-dinitrothiophene-)-/SWCNT Composite as Low Overpotential Hydrogen Evolution Metal-Free Catalyst

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Experimental details

All the chemicals are purchased from J&K Scientific Ltd. without further purification and the SWCNT are purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences.

Materials preparation. PDNT/SWCNT composites or pure PDNT are prepared by one-step in-situ Yamamoto polymerization of 2,5-dibromo-3,4-dinitrothiophene with or without SWCNT.^[1] The synthesis was carried out under nitrogen atmosphere. In a typical procedure, SWCNT was dispersed in 15 mL DMF by an ultrasonic bath. Into the suspension Bis(1,5-cyclooctadiene)nickel(0) (0.41 g, 1.5 mmol), 1,5-cyclooctadiene (0.18 g, 1.7 mmol), 2,2'-Bipyridine (0.26 g, 1.7 mmol) were added. The mixture was then stirred for 30 min at room temperature, after which the mixture was heated to 70 °C and then 2,5-dibromo-3,4-dinitrothiophene (0.5 g, 1.5 mmol) dissolved in 15 mL DMF was added dropwise into the mixture during 30 min. The reaction mixture was stirred at 70 °C for 16 hours (dark brown precipitate was yielded without SWCNT). The resultant mixture was poured into 100 mL 1:1 hydrochloric acid – methanol solution and stirred for 1 hour. The precipitate was collected by centrifugation at relative centrifuge force (RCF) of 2569×g (6578×g if no SWCNT) for 5 min, repeatedly washed in the order of methanol, DI water, saturated EDTA aqueous solution and DI water, and recollected by centrifugation. Finally the product was frozen by liquid nitrogen and lyophilized overnight. The little residual weight of pure PDNT at 800 °C presented in Fig. S1, and the EDX spectrum in Fig. S2c indicate that the metal impurity was effectively removed after such process. FT-IR spectrum in Fig. S3 confirmed the chemical structure of PDNT. According to the SWCNT used in the procedure, the products are denoted as PDNT0 (0 mg), PDNT1 (400 mg), PDNT2 (100 mg) and PDNT3 (50 mg).

Electrochemical measurement. Modified glassy carbon electrode for each sample was prepared as follows:^[2] 20 mg catalyst was sonicated in 5 mL mixture of water, ethanol and Nafion (Dupont, 5 wt%) with the volume ratio of 1.8:3.0:0.2 for 60~120 min to obtain a suspension. 50 μL of the suspension was gradually dropped onto the glassy carbon disk with a diameter of 3 mm (loading ~2.86 mg cm⁻²) and dried under reduced pressure at room temperature for 3 hours. Modified glassy carbon, platinum plate and saturated calomel electrode (SCE) were connected to a potential static electrochemical workstation (VMP3, Bio-Logic) and served as work, counter and reference electrodes, respectively. Cyclic voltammetry (CV) and electrochemical impedances spectra (EIS) measurements were performed in a 1 mol L⁻¹, nitrogen saturated H₂SO₄ aqueous solution.

The SCE was calibrated with respect to reversible hydrogen electrode (RHE) as reported.^[3] Briefly, two Pt plates and the SCE that used in the above measurement were placed in 1 mol L⁻¹, high purity hydrogen saturated H₂SO₄ electrolyte, serving as work, counter and reference electrodes. During this measurement, 1 atm H₂ was continuously flowing above the electrolyte, and massive bubbles were observed on the surface of Pt working electrode. The average value of two potentials where the current crossed zero (background current deducted) in the CV (1 mV s⁻¹) was used as the thermodynamic potential. Accordingly, in our condition, E (RHE) = E (SCE) + 0.223 V.

Hydrogen evolution and I-t curve measurement. Prepared following similar procedure as the electrodes above, a glassy carbon plate electrode with 1.4 mg catalyst and 0.5 cm² electrode area (2.8 mg cm⁻²) was used as the work electrode in this measurement. The measurement was carried out in a gas-tight, three-electrode electrochemical cell with stirring. The system was connected to a CHI1232b workstation (CH Instrument, Inc.) to perform potential static I-t test, and the produced hydrogen gas was pumped by a photocatalytic activity evaluation system (Cel-SPH2N, AuLight) into a gas chromatograph (GC 7890, Techcomp Ltd.) every half an hour. 10 cycles of CV was performed before the data was recorded.

Characterization. The morphology of the samples was characterized by scanning electron microscope (Hitachi S-4800) and transmission electron microscope (Tecnai G2 20 S-TWIN). The thermo gravimetric analysis (TGA) were carried out with the thermal analyzer (Diamond TG/DTA, Perkin Elmer) from room temperature to 800 °C in nitrogen at a heating rate of 10 °C min⁻¹. The structure of PDNT was confirmed by FTIR spectroscopy (Spectrum One).

Table S1 Electrochemical performance of HER catalysts in acid electrolyte.

Active Material	Onset Overpotential (mV) ^[a]	Electrolyte	Hydrogen Evolution Rate (/umol h ⁻¹ cm ⁻²)	Faradaic Efficiency (%)	Reference
MoS ₂	110	0.5M H ₂ SO ₄	-	-	[3]
MoS _x	150	0.5M H ₂ SO ₄	135	-	[4]
Mo ₃ S ₄	- ^[b]	1M HClO ₄	160	98	[5]
Cu ₂ MoS ₄	140	pH=0	340	98	[6]
WS ₂	130	0.5M H ₂ SO ₄	-	-	[7]
WO ₃	- ^[b]	1M HClO ₄	65	100	[8]
Ni ₂ P	110	0.5M H ₂ SO ₄	-	-	[9]
C ₆₀ (OH) ₈	110	0.5M H ₂ SO ₄	-	-	[10]
C ₃ N ₄	160	0.5M H ₂ SO ₄	-	-	[11]
PEDOT	160	1M H ₂ SO ₄	-	-	[12]
PDNT	40	1M H₂SO₄^[c]	44.2	92.4	This Report

^[a] Sometimes people use the onset potential of Pt (which is very close to 0 V vs. RHE) for comparison. In Table S1, if the authors did not report the electrochemical measurement of Pt at the same condition, we use the onset potential of that catalyst as the overpotential. If there is the electrochemical measurement of Pt in the same report, then we use the gap between the onset potential of Pt and that of catalyst as the overpotential.

^[b] Solar energy assisted electrochemical hydrogen evolution.

^[c] Typically people report the HER performance of the catalyst in electrolyte with 1 mol/L proton. In our study, we use the 1 mol/L H₂SO₄ (2 mol/L proton) as the electrolyte in order to make it comparable to the case of PEDOT (ref. 12). Although the electrolyte in our study was different to those of the other references, the overpotentials are still comparable since the onset potential of Pt indicated the thermodynamic potential of HER in our system.

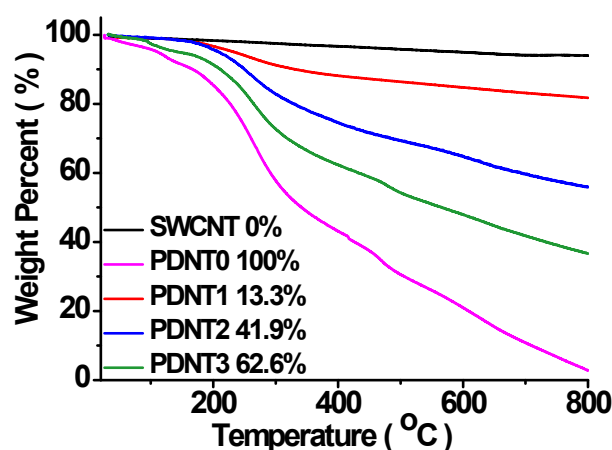


Fig. S1 Thermo gravimetric analysis curves of the PDNT composites as indicated. The weight percentage remained at 800°C are (from up to down) 94.2%, 82.0%, 55.8%, 36.8% and 2.5%, respectively. Based on the residual mass of 94.2% for SWCNT and 2.5% for pure PDNT, the content of the PDNT composite are calculated as: $(94.2 - W_r) / 91.7$ %, where W_r refers to the residual mass percentage of the corresponding sample. The results are marked in the corner of this figure.

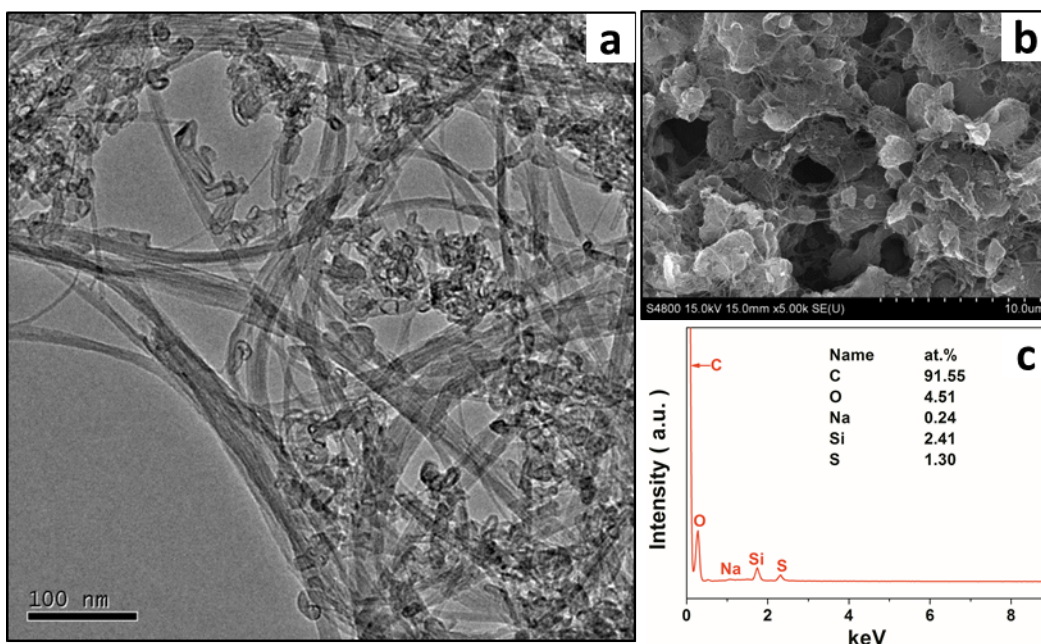


Fig. S2 Additional electron microscopy characterization. (a) TEM image showing the morphology of PDNT2. The PDNT clusters with size of ca. 0.2 μm consist of multiple particles with the size of 20~50 nm. (b) SEM image of PDNT1 on Si wafer and (c) corresponding EDX spectrum of (b). The EDX reported no detectable Ni ($K\alpha$ 7.5 keV) and 0.24 at. % of Na which comes from the EDTA sodium salt in purification procedure.

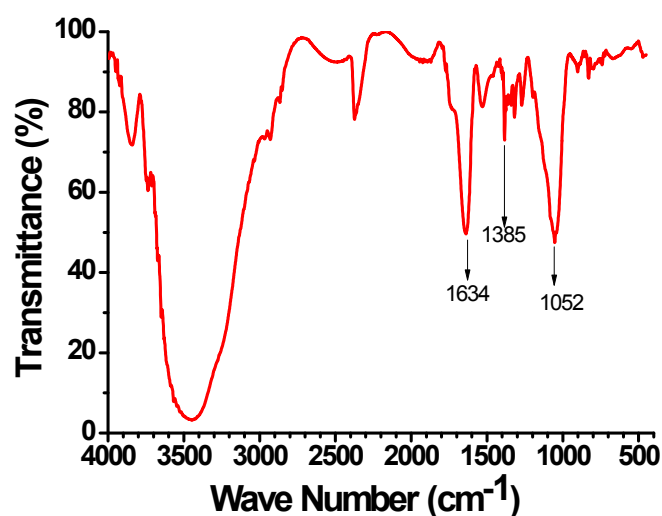


Fig. S3 FT-IR spectrum (KBr) of PDNT0. The sample was dried under reduced pressure at 60 $^{\circ}\text{C}$ for 6 hours before test. The sharp peaks at the wave number of 1385 and 1634 cm^{-1} are ascribed to the nitro groups. The strong peak at 1052 cm^{-1} is contributed by in-plane ring deformation of the thiophene.^[13] Multiple weak peaks within the range of 1267 to 1524 cm^{-1} result from the ring stretching of thiophene.^[14] And the broad peak at ca. 3500 cm^{-1} should be ascribed to water molecular that is strongly binding with nitro groups by hydrogen bonds. This broad peak can also be observed in standard IR spectrum of 2,5-dibromo-3,4-dinitrothiophene.^[15]

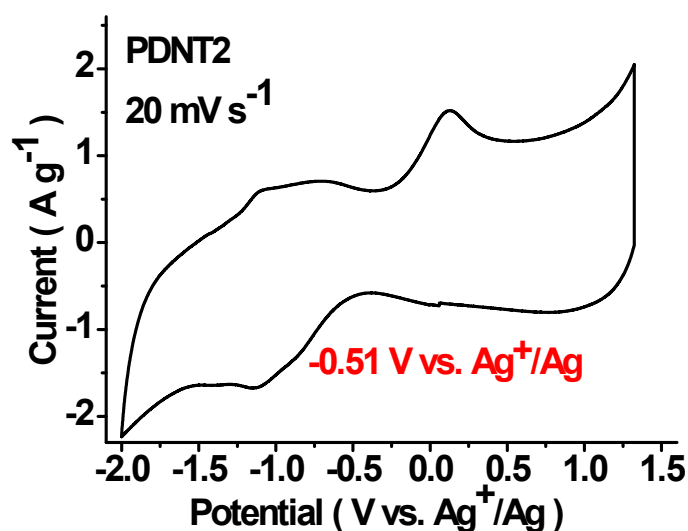


Fig. S4 The CV measurement with scan rate of 20 mV s⁻¹ for PDNT2 in nitrogen saturated 0.5 mol L⁻¹ Et₄N⁺ PF₆⁻/Acetonitrile. PDNT2 electrode (prepared by hot-plate rolling with 10% PTFE, pressed on gold plate), platinum plate and Ag⁺/Ag electrode (silver wire in 0.01 mol L⁻¹ AgNO₃/Acetonitrile) serve as working, counter and reference electrodes.

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