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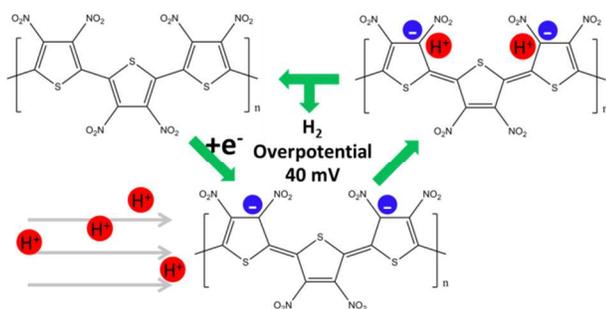
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## 1 Table of Content

2

3 ToC figure:



4 Poly(3,4-dinitrothiophene)/SWCNT composites were prepared and used

5 as electrochemical hydrogen evolution reaction catalyst.

6

## COMMUNICATION

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

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**A novel metal-free hydrogen evolution reaction catalyst Poly(3,4-dinitrothiophene)/SWCNT was developed. This catalyst presents a good hydrogen evolution reaction activity with lower overpotential to metallic catalysts. Its performance was optimized to the overpotential of ca. 0.040 V and hydrogen generation rate of 44.2  $\mu\text{mol h}^{-1} \text{cm}^{-2}$ .**

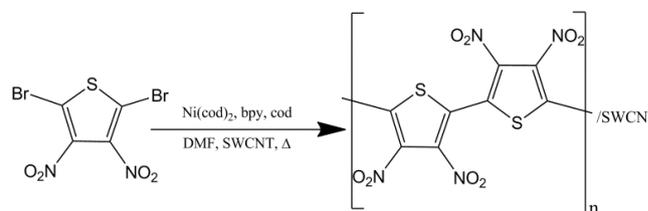
The global climate change and the rapidly diminishing reservation of fossil fuels drive people to seek sustainable energy resources. As a consequence, solar and wind energies, coupled with the corresponding energy storage technics, which are used to deal with the temporal and spatial variability of these types of energy, are attracting increasing world-wide interests.<sup>1</sup> Electrochemically splitting water into hydrogen and oxygen to store the energy in chemical bonds is a particularly promising way among various of energy storage technics, because the energy density stored in chemical bonds is high and the energy storing-releasing process is completely carbon-free.<sup>2</sup> To integrate the water splitting cells, the accomplishment of high performance (*i.e.* low overpotential and high exchange current) hydrogen and oxygen evolution catalysts is the most important scientific issue.<sup>3</sup>

Platinum and its composites have been commonly used in hydrogen evolution reactions (HER) due to the superior electrocatalytic performance of Pt.<sup>4</sup> However, the high price, low availability and carbon monoxide sensitivity of Pt preclude the Pt-based water-splitting from being a true sustainable energy storage technic.<sup>1a,3b</sup> Therefore, non-precious-metal alternatives, such as MoS(Se)<sub>x</sub>,<sup>5</sup> Mo<sub>2</sub>C,<sup>2b,6a,6b</sup> WS<sub>2</sub>,<sup>6c</sup> WC,<sup>2b,6d</sup> and Ni<sub>2</sub>P<sup>6e,6f</sup> with the overpotential range from 0.110 to 0.150 V, have been intensively investigated as HER catalysts in acidic solution. These metallic catalysts usually suffer from corrosion and passivation in acidic electrolyte, which arouses the very recent development of the non-transition metal catalyst (C<sub>60</sub>(OH)<sub>8</sub> anion) and the metal-free ones (C<sub>3</sub>N<sub>4</sub>@nitrogen-doped-graphene and nitrogen-phosphorus dual-doped graphene) with onset overpotential of ca. 0.110, 0.150 and

0.350 V, respectively.<sup>7</sup> More metal-free catalysts need to be developed to provide possible candidates for the alternatives of precious metal catalysts. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a kind of polythiophene derivative with electron-donating groups. PEDOT has been demonstrated HER activity by successfully combining the ability of PEDOT for electrocatalysis and that of polyethylene glycol (PEG) for coordinating protons.<sup>8</sup> Strong electron-withdrawing groups in poly-thiophene derivatives are expected to further decrease the overpotential for HER.

In this work, we report the synthesis and characterization of a novel metal-free HER catalyst Poly(3,4-dinitrothiophene) (PDNT). The catalyst was loaded on single-walled carbon nanotubes (SWCNT) for the purpose of increasing effective surface area and overall conductivity. The hydrogen gas evolution rate was measured by gas chromatograph (GC). The electron-withdrawing nitro groups on thiophene rings improve the electron obtaining capability and eventually lead to the low HER overpotential of ca. 0.040 V. The PDNT/SWCNT composites were prepared via a one-step *in-situ* Yamamoto polymerization<sup>9</sup> of 2,5-dibromo-3,4-dinitrothiophene with SWCNT in DMF, as displayed in Scheme 1.

By adding different amount of SWCNT, the contents of PDNT in composites were able to be adjusted, as measured by thermo gravimetric analysis (see Fig. S1 in Supporting Information). The



Scheme 1. Synthesis strategy of PDNT/SWCNT.

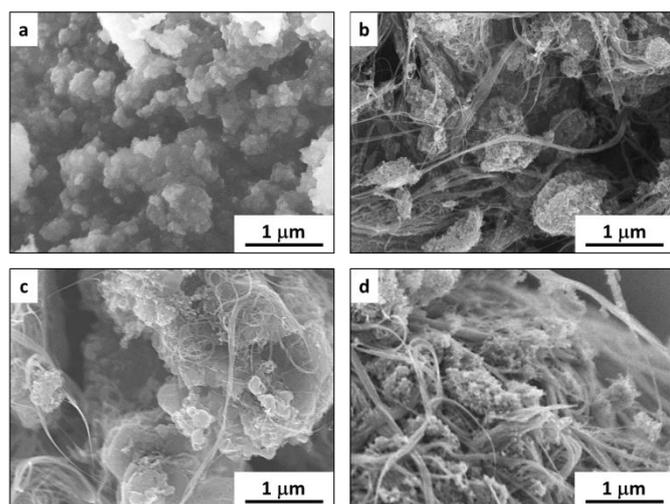


Fig. 1 SEM images showing the morphologies of pure PDNT (a, PDNT0), and PDNT/SWCNT with the PDNT content of 13.3% (b, PDNT1), 41.9% (c, PDNT2) and 62.6% (d, PDNT3).

products are referred as PDNT0, PDNT1, PDNT2 or PDNT3, corresponding to the PDNT content in the products of 100%, 13.3%, 41.9% or 62.6%, respectively. Typical scanning electron microscope (SEM) images of these composites are shown in Fig. 1a-d. The pure PDNT was obtained as the aggregated particle clusters with the sizes of ca. 0.2~0.5  $\mu\text{m}$ , as seen in Fig. 1a. Observed in Fig. 1b (PDNT1), 1c and S2a (PDNT2), and 1d (PDNT3), the sizes of the PDNT cluster attached on SWCNT range from ca. 0.2  $\mu\text{m}$  to ca. 0.4  $\mu\text{m}$ , in consistent with that of PDNT in Fig. 1a.

The HER performances of PDNT0 to PDNT3 and SWCNT deposited on glassy carbon electrodes were firstly investigated by cyclic voltammetry (CV) in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> using a three-electrode setup. The HER performances of Pt plate were also measured as the reference of overpotential, since Pt possesses high HER activity with nearly zero overpotential.<sup>5a,5e,8</sup> Corresponding curves are illustrated in Fig. 2a and 2b, which reflect the 10th cycle of the samples for stable results. As seen in Fig. 2a, the CV curve of the SWCNT shows typical electrochemical double layer feature with neglectable HER activity, while all the other samples exhibit close HER onset potential at ca. -0.032 V vs. reversible hydrogen electrode (RHE), ca. 0.040 V lower than that of Pt (ca. +0.008 V vs. RHE) measured in the same condition as shown in Fig. 2b. Accordingly, the HER overpotential of PDNT is ca. 0.040 V, lower than those of non-precious-metal catalysts in acidic electrolyte.<sup>5a,5c,5e,6c,6e</sup>

As seen from the inset of Fig. 2b, PDNT0 presents HER activity despite the polarization current density is as low as 0.05 mA cm<sup>-2</sup>, implying the insulation of the pure PDNT particles. In addition, as the PDNT content rises, the polarization current densities of the samples at -0.177 V vs. RHE firstly increase from 3.3 mA cm<sup>-2</sup> (PDNT1) to 8.3 mA cm<sup>-2</sup> (PDNT2), and then decrease to 3.1 mA cm<sup>-2</sup> (PDNT3). Similar pattern is observed in the background current densities of those materials, which are contributed by both the electrochemical double layer capacitance from SWCNT and the pseudo-capacitance from poly-thiophene derivative.<sup>11</sup> The increasing polarization and background current from PDNT1 to PDNT2 is ascribed to the content increment of the PDNT, which possesses HER activity and capacitance higher than those of SWCNT. Further increment of the PDNT content leads to the drop of both polarization

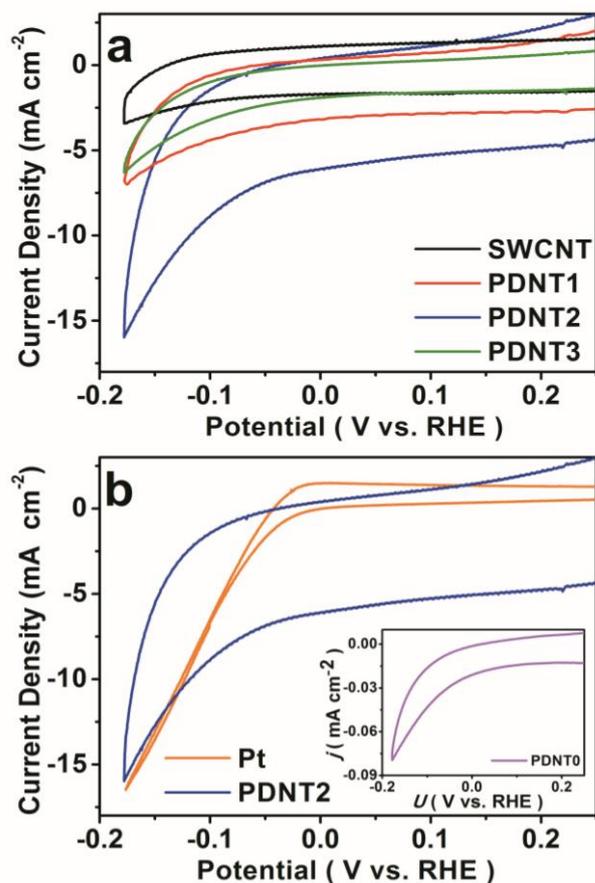


Fig. 2 Cyclic voltammetry (CV) measurements on the HER performance with IR correction in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at the scan rate of 20 mV s<sup>-1</sup>. (a) CV curves of SWCNT, PDNT1, PDNT2 and PDNT3. (b) CV curve of PDNT2, in comparison with the platinum plate; the inset in the corner shows the CV curve of the pure PDNT (PDNT0). All the CV curves presented here are recorded after 9 cycles.

and background current from PDNT2 to PDNT3 because the insulation of the PDNT lower the overall conductivity of the composite. The onset overpotential of ca. 0.040 V for PDNT2 is lower than that of the reported metal-free and transition metal based catalysts (e.g. the sulfide and carbide of Mo and W) whose typical onset overpotentials range from 0.110 to 0.200 V (refer to Supporting Information Table S1). And the polarization current density of 8.3 mA cm<sup>-2</sup> at the potential of -0.177 V vs. RHE (0.145 V lower than the onset potential of PDNT2) is also comparable to the recent results of the HER catalysts without transition metal.<sup>7,8</sup>

The electrochemical kinetics of PDNT0 and PDNT2 on glassy carbon electrodes were studied by electrochemical impedance spectroscopy (EIS) in the range of 0.01~5×10<sup>5</sup> Hz. The corresponding Nyquist plots at typical potentials are displayed in Fig. 3a and 3b. The Nyquist plots of both samples show little difference at the potentials that are higher than the HER onset potential of PDNT (0.223, 0.123 and 0.023 V vs. RHE), indicating similar electrode kinetics at those potentials. Further decrease of the potential from 0.023 to -0.077 V vs. RHE resulted in a dramatic reduction of charge transfer resistance ( $R_{ct}$ ) for both PDNT0 and PDNT2 due to the evocation of HER, in agreement to the onset potential of ca. -0.032 V vs. RHE obtained from CV. Moreover, the

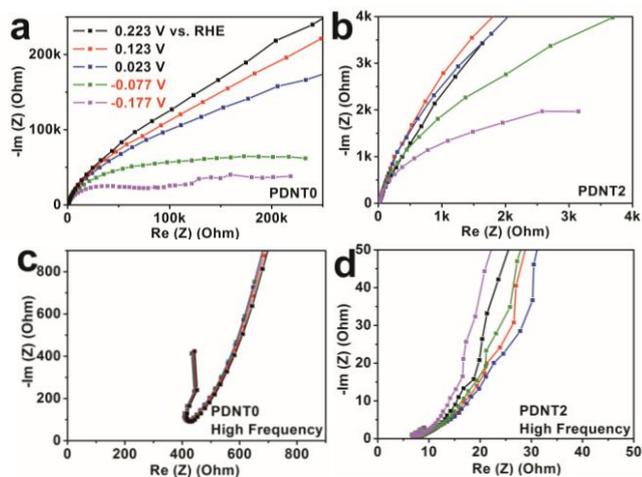


Fig. 3. Nyquist plots from electrochemical impedance spectroscopy (EIS) of PDNT0 (a, c) and PDNT2 (b, d) at different potentials.

HER  $R_{ct}$  of PDNT2 is lower than that of PDNT0, as concluded from the Nyquist plots at  $-0.077$  and  $-0.177$  V vs. RHE.<sup>6c,6d</sup> SWCNTs in the composite have basically two functions. Firstly the SWCNTs framework serves as the “electric cables framework” which transports electrons from external power source to PDNT for HER catalysis. Furthermore, SWCNTs were used to anchor PDNT particles by  $\pi$ - $\pi$  interaction and in this way disperse them in the framework, suppressing the aggregation of PDNT particles. The aggregation of nano-sized catalysts usually decreases their activity by reducing the accessibility of the catalyst surface. Therefore, in the case of PDNT2, the protons in electrolyte are more likely to coordinate with the active site and hence it is easier for the electrons to move from PDNT to the protons, both of which result in lower  $R_{ct}$ . The intercept of Nyquist plot on  $x$ -axis could be used to evaluate the system's equivalent series resistance (ESR), which is predominated by the conductivity of electrode materials.<sup>12</sup> From Nyquist plots of PDNT0 and PDNT2 in high-frequency region illustrated in Fig. 3c and 3d, it is seen that the ESR of PDNT2 (8 ohm) is much lower than that of PDNT0 (350 ~ 400 ohm), meaning the much higher overall conductivity of PDNT2. This result is again consistent to that in CV measurements. As observed, SWCNT in the composite significantly enhance the HER activity of PDNT by increasing the conductivity of the electrode and the effective surface area of the PDNT particles.

To evaluate the performance of PDNT2 in a real system, the hydrogen gas evolution rates and electrochemical stability of PDNT2 were estimated by GC coupled with static potential I-t test. As shown in Fig. 4, the current density (black line) firstly decayed from  $7.50 \text{ mA cm}^{-2}$  to  $1.08 \text{ mA cm}^{-2}$  within *ca.* 1600 seconds and then remained nearly constant for the next *ca.* 5600 seconds at the operation potential of  $-0.177$  V vs. RHE. The hydrogen gas evolution rate at this potential was  $20.1 \mu\text{mol h}^{-1} \text{ cm}^{-2}$ , according to the fitted slope of the “normalized  $\text{H}_2$  amount-time plot” (red dots) in the stabilized part of this measurement (*i.e.* 1600~7200 s). After that, the potential applied on the electrode was changed to  $-0.277$  V vs. RHE. The current density immediately leaped to  $7.09 \text{ mA cm}^{-2}$  and then progressively decayed to the stable value of  $2.41 \text{ mA cm}^{-2}$  during *ca.* 500 seconds. The hydrogen gas evolution rate at this potential achieved  $44.2 \text{ mol h}^{-1} \text{ cm}^{-2}$ . Typically the HER catalysts hat contain organic groups (e.g. Ni complex and Co complex)

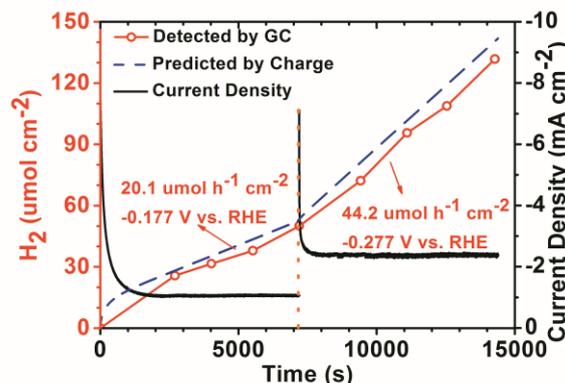


Fig. 4. HER stability of the PDNT2 measured by gas chromatograph and static potential I-t at the potential indicated.

present Faradaic efficiencies in the range of 20~95%,<sup>2a,3b</sup> which is lower than the nearly 100% Faradaic efficiencies of inorganic HER catalysts,<sup>5g,10</sup> probably due to some side electrochemical reactions (e.g. reduction of  $-\text{NO}_2$  groups). In this study, PDNT2 presented high Faradaic efficiencies of 93.5% and 92.4% for  $-0.177$  and  $-0.277$  V vs. RHE respectively, which is comparable with the highest value among catalysts of organic compound.<sup>2a,3b</sup>

The electron-withdrawing groups on thiophene rings usually result in a decrease of the LUMO level of the poly-thiophene, leading to an increase of the n-doping (reduction) potential, as widely reported.<sup>11b,13</sup> In our case, there are two nitro groups, which is one of the strongest inductive groups, on the thiophene ring. Eventually, the LUMO level is dramatically decreased, which improves the capability for grasping electrons from external power source of the PDNT at a relatively high potential, resulting in a negatively charged PDNT. The n-doping potential of PDNT2 was obtained from its CV measurement in organic electrolyte as illustrated in Fig. S4 of the supporting information. As seen, the onset n-doping potential is  $-0.51$  V vs.  $\text{Ag}^+/\text{Ag}$ , which is higher than any other poly-thiophene derivatives at the similar condition as we know.<sup>13</sup> In other words, the electrons are much easier to be transferred from external power source to PDNT and then used to reduce the proton in the case of PDNT than that of other poly-thiophene derivatives. Moreover, negative charges on PDNT also improve the absorption of protons due to the electrostatic force, which is a critical step in HER process.<sup>5,7a</sup> These are supported by the fact that the onset overpotential of pure PEDOT ( $\sim 0.5\text{V}$ ) is much higher than that of pure PDNT ( $\sim 0.04\text{V}$ ).<sup>8</sup> This n-doping reaction, on the other hand, is a potential initiation of PDNT chain-chain radical crosslinking, which leads to its deactivation for HER. Anchored on SWCNT, these radicals are stabilized due to the delocalization effect of  $\text{Sp}^2$  hybridized carbon atoms. So the SWCNT can also enhance the stability of the catalyst. The pH of the electrolyte is another important factor for HER. In general the inorganic HER catalysts are used in acidic solutions because of their passivation in neutral-alkaline solutions which results from the surface oxidation of these materials.<sup>2b</sup> According to our study, the PDNT based catalysts are also incompatible to conventional neutral (KCl, NaCl) or alkaline (KOH, NaOH) electrolytes since their HER performance decay quickly during the electrochemical measurements in those electrolytes. This should be ascribed to the irreversible doping of alkali ions into the poly-thiophene matrix at low potential.<sup>11b</sup>

Although the aggregation of PDNT particles was successfully suppressed in some degree (according to the improved performance from PDNT0 to PDNT1~3), it seems the PDNT particles still have a tendency to aggregate into micron-sized clusters in the framework of SWCNT (from Fig. 1b~1c and Fig. S2). As a consequence, some of the PDNT might not be accessible for HER, and there is still space to optimize the morphology and performance of PDNT based catalysts. In future we can further improve the performance of PDNT based HER catalysts by optimizing the preparation process, and using other carbonaceous supportters such as graphene or surface functionalized CNTs.

In summary, PDNT/SWCNT composites are prepared by one-step *in-situ* Yamamoto polymerization of 2,5-dibromo-3,4-dinitrothiophene with SWCNT and applied as a metal-free HER catalyst in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The polarization current could be tuned by regulating the ratio of SWCNT in the composite, which improves the overall performance by increasing the conductivity of the electrode and the effective surface area of the PDNT. The HER performance of PDNT/SWCNT composites has been optimized to PDNT2 with the overpotential of ca. 0.04 V and polarization current density of 8.3 mA cm<sup>-2</sup> at the scan rate of 0.020 V s<sup>-1</sup>. The function of electron-withdrawing groups demonstrated in this work could be used to develop and optimize other high efficiency metal-free HER catalyst.

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### Notes and references

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†Electronic Supplementary Information (ESI) available: [Experimental details, comparison of HER performance, thermo gravimetric analysis data of catalysts, additional electron microscopy characterizations, FT-IR spectrum of PDNT0 and the CV measurement of PDNT2 in organic electrolyte]. See DOI: 10.1039/c000000x/

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