Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

# **Supporting Information for**

# Carbon nanotube decorated with nickel phosphide nanoparticles

### as efficient nanohybrid electrocatalyst for enhanced hydrogen

### evolution reaction

Yuan Pan, Wenhui Hu, Dapeng Liu, Yunqi Liu\*, Chenguang Liu\*

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National

Petroleum Corporation (CNPC), China University of Petroleum, 66 West Changjiang Road, Qingdao,

Shandong 266580, P. R. China

<sup>\*</sup> Corresponding author. E-mail address: liuyq@upc.edu.cn; cgliu1962@sina.com

Tel.: +86-532-86981861; +86-532-86981716.

#### **Experimental section**

#### **Materials**

Nickel(II) acetylacetonate (Ni(acac)<sub>2</sub>, 95%), trioctylphosphine (TOP, 90%), oleylamine (OAm, 95%), 1-octadecene (ODE, 95%) and multiwall carbon nanotubes (CNT, 95%, diam: 10-20 nm, length: 5-15  $\mu$ m) were obtained from Aladdin Chemistry Co. Ltd. Hexane ( $\geq$ 99.5%), ethanol ( $\geq$ 99.7%), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Nafion solution (5% in a mixture of lower aliphatic alcohols and water) and Pt/C were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. All reactions were carried out under argon atmosphere using standard air-free techniques.

#### Acid treatment of CNT

The acid treatment of CNT was realized according to a previously reported method [1]. 0.5 g CNT and concentrated nitric acid (100 mL) were placed in a round flask and stirred magnetically. The flask was fitted with a reflux condenser, the mixture was heated to 120 °C with a heating rate of 10 °C ·min<sup>-1</sup> and kept at this temperature for 12 h. After cooling to room temperature, the CNT was filtered off and washed with distilled water until pH = 7. Then the acid-treated CNT was dried in vacuum at 60 °C for 24 h.

#### Synthesis of Ni<sub>2</sub>P/CNT

In a typical synthesis, Ni(acac)<sub>2</sub> (0.256 g, 1 mmol), OAm (7 mL, 21.3 mmol) and CNT (20 mg) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was raised to 120 °C with a heating rate of 10 °C·min<sup>-1</sup> and kept

at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP (3.4 mL, 7.5 mmol) was quickly injected into the solution, the mixture was rapidly heated to 320 °C and maintained for 2 h. After cooling to room temperature, the black precipitate was washed three times with a mixture of hexane and ethanol by centrifugation (4000 rpm, 10 min). Then the Ni<sub>2</sub>P/CNT nanohybrid was obtained by drying in vacuum at 60 °C for 24 h.

#### Synthesis of Ni<sub>12</sub>P<sub>5</sub>/CNT

Ni(acac)<sub>2</sub> (0.256 g, 1 mmol), OAm (6.5 mL, 19.8 mmol), ODE (4.5 mL, 14.1 mmol) and CNT (20 mg) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was raised to 120 °C with a heating rate of 10 °C·min<sup>-1</sup> and kept at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP (0.3 mL, 0.7 mmol) was quickly injected into the solution, the mixture was rapidly heated to 320 °C and maintained for 2 h. After cooling to room temperature, the black precipitate was washed three times with a mixture of hexane and ethanol by centrifugation (4000 rpm, 10 min). Then the Ni<sub>12</sub>P<sub>5</sub>/CNT nanohybrid was obtained by drying in vacuum at 60 °C for 24 h.

#### Synthesis of Ni/CNT

Ni(acac)<sub>2</sub> (0.256 g, 1 mmol), OAm (7 mL, 21.3 mmol) and CNT (20 mg) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was raised to 120 °C with a heating rate of 10 °C·min<sup>-1</sup> and kept at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP (1 mL, 2.2 mmol) was quickly injected into the solution, the mixture was rapidly heated to 200 °C and maintained for 30 min. After cooling to room temperature, the black precipitate was washed three times with a mixture of hexane and ethanol by centrifugation (4000 rpm, 10 min). Then the Ni/CNT nanohybrid was obtained by drying in vacuum at 60 °C for 24 h.

#### **Characterizations**

X-ray diffraction (XRD) was performed on a panalytical X'pert PROX-ray diffractometer with Cu K $\alpha$  monochromatized radiation ( $\lambda$ = 1.54 Å) and operated at 45 kV and 40 mA. The scan rate was 8° min<sup>-1</sup> and the 2  $\theta$  scan range was from 20° to 90°. Transmission electron microscopy (TEM) was performed on a JEM-2100 UHR microscope (JEOL, Japan) at an accelerating voltage of 200 kV. An energy dispersive X-ray (EDX) instrument was attached to the TEM system. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALABMK II spectrometer using an Al K<sub> $\alpha$ </sub> (1486.6 eV) photon source. N<sub>2</sub> adsorption-desorption experiments were carried out on a ChemBET 3000 (Quantachrome, USA) instrument. The element contents of Ni and P were determined by an inductively coupled plasma-mass spectrometry (ICP-MS) 7500 CE (Agilent Technologies, Santa Clara, CA, USA).

#### Electrochemical measurements

All electrochemical measurements were carried out using a Reference 600 instrument (Gamry Instruments, USA) in a standard three-electrode setup. A saturated calomel electrode (SCE) was used as reference electrode (Ag/AgCl) and a Pt electrode as counter electrode. The electrocatalytic activity of the sample towards HER was examined by obtaining polarization curves using linear sweep voltammetry

(LSV) with a scan rate of 5 mV·s<sup>-1</sup> at room temperature in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. A durability test was carried out by cyclic voltammetry (CV) scanning 500 cycles with a scan rate of 100 mV·s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various overpotentials from 50 mV to 200 mV (vs. reversible hydrogen electrode (RHE)) in the frequency range of 100 kHz ~ 0.1 Hz with a single modulated AC potential of 5 mV. Experimental EIS data were analysed and fi tted with the software of Zsimpwin. The electrochemical data are presented with iR compensation. All the potentials reported in our work are versus the RHE. In 0.5 M H<sub>2</sub>SO<sub>4</sub>, E(RHE) = E(SCE) + (0.222 + 0.059 pH).

#### Preparation of working electrodes

5 mg of catalyst and 80  $\mu$ L Nafion solution (5 wt.%) were dispersed in 1 mL ethanol and sonicated for 30 min to form a slurry. Then 5  $\mu$ L of the slurry was loaded onto the surface of a glassy carbon electrode (GCE, 4 mm in diameter), and the electrode was dried at room temperature.

#### Calculation of active sites

The number of active sites (n) was determined using cycle voltammograms (CVs) data (Fig. S6) collected from -0.2 V to +0.6 V vs. RHE in 1.0 M phosphate buffer solution (PBS, pH = 7) with a scan rate of 20 mV·s<sup>-1</sup>. While it is difficult to assign the observed peaks to a given redox couple, n should be proportional to the integrated charge over the whole potential range. Assuming a one-electron process for both reduction and oxidation, the upper limit of n could be calculated with the following

equation:

$$n = \frac{Q}{2F}$$

In addition, turnover frequency (TOF) can be calculated with the following equation:

$$TOF = \frac{I}{2Fn}$$

Where Q is the voltammetric charge, F is Faraday constant (96485  $C \cdot mol^{-1}$ ), I is current (in A) during the linear sweep measurement and n is active sites number (in mol). The factor 1/2 in the equation represents that two electrons are required to form one hydrogen molecule from two protons.

For the Ni<sub>2</sub>P/CNT, Q is  $4.673 \times 10^{-2}$  C, n (mol) =  $4.673 \times 10^{-2}/(2 \times 96485)$  mol =  $2.42 \times 10^{-7}$  mol. For the Ni<sub>12</sub>P<sub>5</sub>/CNT, Q is  $1.683 \times 10^{-2}$  C, n (mol) =  $1.683 \times 10^{-2}/(2 \times 96485)$  mol =  $8.72 \times 10^{-8}$  mol. For the Ni/CNT, Q is  $1.066 \times 10^{-2}$  C, n (mol) =  $1.066 \times 10^{-2}/(2 \times 96485)$  mol =  $5.52 \times 10^{-8}$  mol. The calculated active site number of Ni<sub>2</sub>P/CNT is 2.8 times for Ni<sub>12</sub>P<sub>5</sub>/CNT, and 4.4 times for Ni/CNT, respectively.







Fig. S1 The average particle size distribution of (a) Ni/CNT, (b)  $Ni_{12}P_5$ /CNT and (c)  $Ni_2P$ /CNT.





Fig. S2 EDX spectra of  $Ni_{12}P_5/CNT$  (a) and  $Ni_2P/CNT$  (b).



**Fig. S3** STEM image and EDX elemental mapping of C, P and Ni for the Ni<sub>2</sub>P/CNT nanohybrid.





Fig. S4 Nitrogen adsorption-desorption isotherm (a and c) and the BJH pore-size distribution curve (b and d) of  $Ni_2P/CNT$  and  $Ni_{12}P_5/CNT$ , respectively.





Fig. S5 XPS spectra of (a) survey spectrum, (b) C 1s, (c) Ni 2p and (d) P 2p regions for  $Ni_{12}P_5/CNT$ .



Fig. S6 Calculation of exchange current density of the Pt/C,  $Ni_2P/CNT$ ,  $Ni_{12}P_5/CNT$  and Ni/CNT.



**Fig. S7** CVs of the Ni<sub>2</sub>P/CNT, Ni<sub>12</sub>P<sub>5</sub>/CNT, Ni/CNT and bare GCE at a scan rate of 20 mV·s<sup>-1</sup> over a range of -0.2~0.6 V vs. RHE in 1.0 M PBS (pH = 7).



Fig. S8 Polarization curves of the  $Ni_{12}P_5/CNT$  and Ni/CNT nanohybrids in 0.5 M  $H_2SO_4$  initially and after 500 CV sweeps.



Fig. S9 Equivalent electrical circuit used to model the HER kinetics process.  $R_s$  is the solution resistance,  $Q_1$  and  $R_1$  are the element and resistance describing electron transport at GCE/Ni<sub>2</sub>P/CNT interface, respectively.  $Q_2$  is the element of the Ni<sub>2</sub>P/CNT/electrolyte interface, and  $R_{ct}$  is the charge transfer resistance at Ni<sub>2</sub>P/CNT/electrolyte interface.

Catalyst	Current density	Potential	Electrolyte	Tafel slope	Reference
	(mA·cm <sup>-2</sup> )	(mV)		$(mV \cdot dec^{-1})$	
MoS <sub>2</sub> /RGO	10	150	0.5 M H <sub>2</sub> SO <sub>4</sub>	41	22
Ni <sub>2</sub> P/Ti	20	138	1 M H <sub>2</sub> SO <sub>4</sub>	60	31
Mo <sub>2</sub> C/CNT	10	152	0.1 M HClO <sub>4</sub>	55	23
NiP <sub>2</sub> NS/CC	20	99	0.5 M H <sub>2</sub> SO <sub>4</sub>	51	32
CoSe <sub>2</sub> NP/CP	10	139	0.5 M H <sub>2</sub> SO <sub>4</sub>	42.1	27
CoP/CNT	10	122	0.5 M H <sub>2</sub> SO <sub>4</sub>	54	12
MoS <sub>2</sub> /FTO	2	190	0.5 M H <sub>2</sub> SO <sub>4</sub>	50	25
MoP-CA2	10	125	0.5 M H <sub>2</sub> SO <sub>4</sub>	54	24
CoP/Ti	10	90	0.5 M H <sub>2</sub> SO <sub>4</sub>	43	30
MoS <sub>3</sub> /FTO	2	170	0.5 M H <sub>2</sub> SO <sub>4</sub>	40	26
MoP/CF	100	200	$0.5 \text{ M H}_2 \text{SO}_4$	67.4	34
MoN/C	2	290	0.1 M HClO <sub>4</sub>	54.5	28
NiMoNx/C	10	152	0.1 M HClO <sub>4</sub>	35.9	28
Cu <sub>3</sub> P NW/CF	10	143	0.5 M H <sub>2</sub> SO <sub>4</sub>	67	35
WS <sub>2</sub> /rGO	23	300	0.5 M H <sub>2</sub> SO <sub>4</sub>	58	29
	20	100	0.5 M H <sub>2</sub> SO <sub>4</sub>	51	11
CoP/CC	2	65	1M PBS	93	11
	10	209	1М КОН	129	11
Mo <sub>2</sub> C/XC	3.2	150	0.1 M HClO <sub>4</sub>	59.4	23

 Table S1 Comparison of the HER performance of some non-noble-metal catalysts.

FeP NAs/CC	10	58	0.5 M H <sub>2</sub> SO <sub>4</sub>	45	37
FeP NA/Ti	20	72	0.5 M H <sub>2</sub> SO <sub>4</sub>	38	36
MoSe <sub>2</sub> /RGO	10	150	0.5 M H <sub>2</sub> SO <sub>4</sub>	69	33
Ni/CNT	10	345	0.5 M H <sub>2</sub> SO <sub>4</sub>	124	This work
Ni <sub>12</sub> P <sub>5</sub> /CNT	10	240	0.5 M H <sub>2</sub> SO <sub>4</sub>	81	This work
Ni <sub>2</sub> P/CNT	10	124	0.5 M H <sub>2</sub> SO <sub>4</sub>	41	This work

Catalyst	log( j (mA·cm <sup>-2</sup> ) ) at η=0 V	Exchange current densities $j_0 [mA \cdot cm^{-2}]$
Pt/C	-0.3	0.5012
Ni <sub>2</sub> P/CNT	-1.27	0.0537
Ni <sub>12</sub> P <sub>5</sub> /CNT	-1.58	0.0263
Ni/CNT	-1.76	0.0173

**Table S2** Calculations of the exchange current densities of Pt/C, Ni2P/CNT, $Ni_{12}P_5$ /CNT and Ni/CNT by using extrapolation methods.

Potential	R <sub>s</sub>	Q1	$n_1$	$R_1$	Q <sub>2</sub>	$N_2$	R <sub>ct</sub>
(V) vs. RHE	(Ω)	$(F \cdot cm^{-2} \cdot S^{n-1})$		$(\Omega)$	$(F \cdot cm^{-2} \cdot S^{n-1})$		$(\Omega)$
-0.05	8.302	8.98E-04	0.7394	57.15	5.46E-04	0.4732	6277
-0.06	8.243	1.03E-03	0.7489	60.35	5.73E-04	0.4672	3567
-0.07	8.175	1.14E-03	0.7564	61.08	5.58E-04	0.4695	2159
-0.08	8.096	1.22E-03	0.7628	60.76	5.23E-04	0.4761	1363
-0.09	7.949	1.24E-03	0.7673	60.55	4.95E-04	0.4812	888.4
-0.10	8.659	1.19E-03	0.7707	60.88	4.64E-04	0.4862	597.1
-0.11	8.002	1.09E-03	0.7716	61.8	4.61E-04	0.4858	419.3
-0.12	8.016	9.61E-04	0.7595	59.56	3.89E-04	0.5065	308.4
-0.13	8.295	8.27E-04	0.8	59.39	3.65E-04	0.8	230
-0.14	9.073	7.08E-04	0.8	65.85	4.47E-04	0.8	171.5
-0.15	8.565	5.88E-04	0.8	51.18	2.67E-04	0.8	150.1
-0.17	9.18	4.92E-04	0.8	55.19	2.44E-04	0.8	99.03

 Table S3. Values of elements in equivalent circuit resulted from fitting the EIS data.

# Reference

[1] T. W. Lin, C. G. Salzmann, L. D. Shao, C. H. Yu, M. L. H. Green, S. C. Tsang,

Carbon, 2009, 47, 1415-1420.