

Electronic Supplementary Information

## **Ionic Liquid Functionalized Carbon Nanotubes: Metal-free**

### **Electrocatalyst for Hydrogen Evolution Reaction**

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## Experimental Section

### Chemicals

*N*-methylimidazole, *N*-vinylimidazole and 3-bromopropylamine hydrobromide were supplied from Aladdin Chemistry Co. MWCNTs were purchased from Shenzhen Nanotech Port Ltd., Co. China. All other reagents were purchased from Beijing Chemicals, China. Aqueous solutions were prepared with deionized water (18 M $\Omega$  cm) obtained from a Milli-Q Plus system (Millipore).

### Instruments

The HER experiments were performed on an electrochemical workstation (CHI-660E) in a three-electrode configuration comprised of a glassy carbon electrode (GCE) loaded with catalyst as the working electrode, a platinum plate and a saturated calomel electrode (SCE) as the counter electrode and the reference electrode, respectively. For preparation of the working electrode, 20  $\mu$ L of 5 mg ml<sup>-1</sup> catalyst solutions was dropped on the clean GC electrode and then dried. It is noted that no Nafion was added for IL-MWCNTs and IL played a role of binder in preparation. As control group, carboxylic acid-functionalized MWCNTs was applied as catalyst in the same conditions with Nafion added (mass ratio of Nafion to catalyst is 1 to 20). The electrolysis runs were repeated at least three times for each experiment. The linear sweep voltammograms (LSV) were recorded at a scan rate of 2 mV s<sup>-1</sup>. Tafel plots for electrolytes (*iR*-corrected) were obtained by following equation  $\eta = b \log j + a$ . Then, the corresponding Tafel slopes (*b*) were used to determine the reaction kinetics.<sup>1,2</sup> Five kinds of IL-MWCNTs composites were applied as electrocatalyst for HER. The electrochemical impedance spectroscopy (EIS) measurements of catalysts were recorded with a scan rate of 2 mV s<sup>-1</sup> and EIS was conducted at 0.8 V in a range of frequency (0.1 Hz-1000 kHz) with 5 mA amplitude of current perturbation. pH values were measured using a pH meter (Sartorius PB-10).

Fourier transform infrared spectroscopy (FT-IR) spectra were collected using a Thermo-Fisher Nicolet 6700 Spectrometer and samples in KBr pellet form. X-ray photoelectron spectroscopy (XPS) of the catalyst and catalyst/PIL was performed using ESCALAB 250Xi spectrometer under vacuum ( $\sim 2 \times 10^{-9}$  mbar). Excitation source was monochromatic Al K $\alpha$  (150 W, 1486.6 eV) radiation, and the C1s peak at 284.8 eV was used as the reference for calibration.

### Preparation of IL

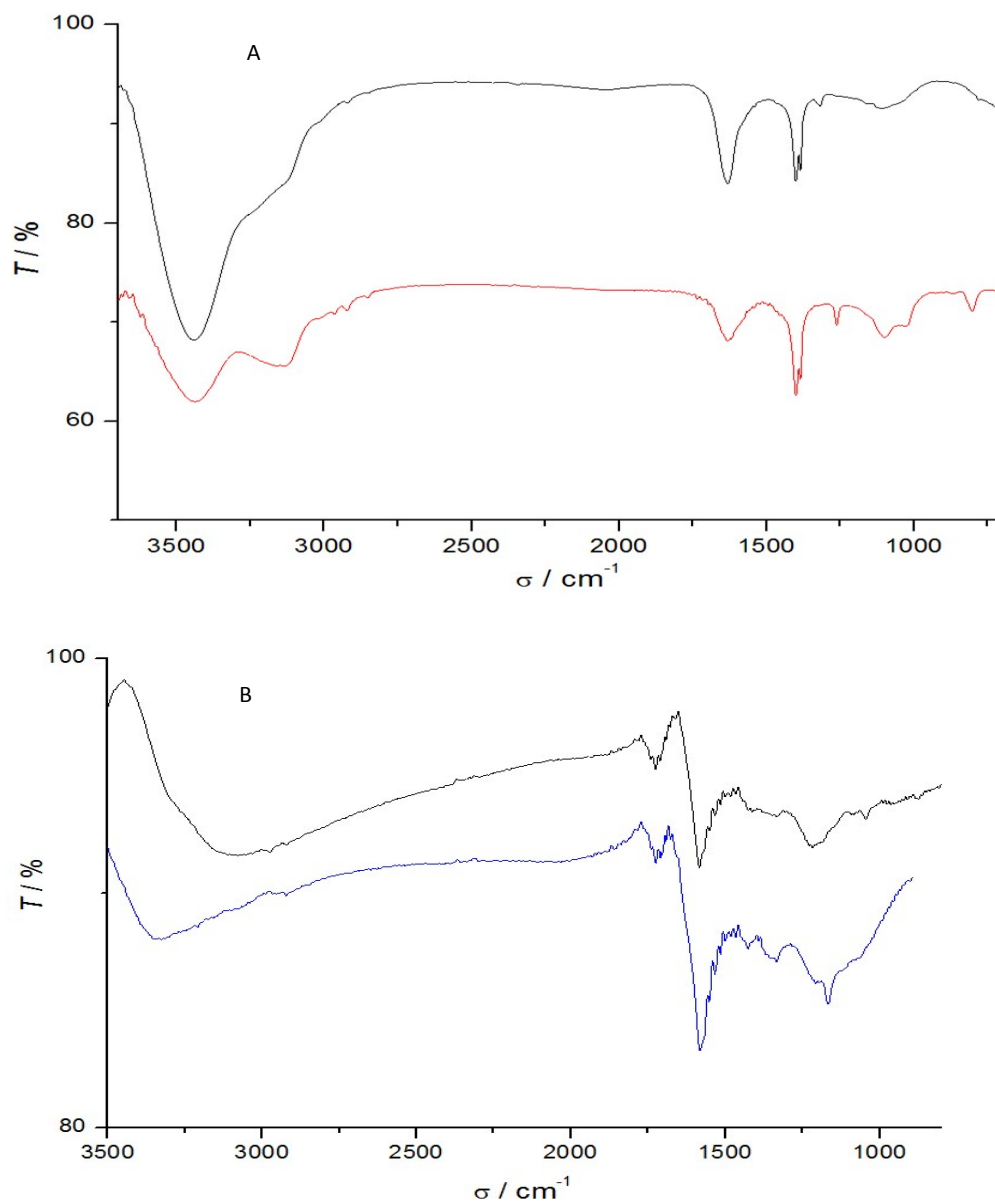
Six different IL-MWCNTs composites were examined as electrocatalyst in the study for HER. 1-aminopropyl-3-methylimidazolium bromide (AMIM-Br) and 1-aminopropyl-3-vinylimidazolium bromide (AVIIM-Br) were synthesized according to previous reports.<sup>3</sup> Generally, *N*-methylimidazole or *N*-vinylimidazole mixed with 3-bromopropylamine hydrobromide in ethanol under stirring for 48 h at 70  $^{\circ}$ C. After removal of solvent, the residue was dissolved in distilled water. Then, the pH of this solution was adjusted to 7 by additional of potassium hydroxide, and the subsequent solution was washed with ethyl acetate. After washing, water was removed under reduced pressure for 24 h at 65  $^{\circ}$ C and the product subsequently dried in vacuum to afford AMIM-Br or AVIIM-Br in high purity.

### Preparation of MWCNTs-COOH

In order to prepare carboxylic acid-functionalized MWCNTs (MWCNTs-COOH), the pristine MWCNTs (500 mg) was added to the a mixture of concentrated sulfuric acid and nitric acid (3:1 v/v, 10 mL) for 8 h at 75 °C. Then, the black mixture was washed with distilled water and vacuum-filtered until the pH of the filtrate was 7. The filtered solid was dried under vacuum for 24 h at 60 °C.

### Preparation of IL-MWCNTs

For the preparation of IL-MWCNTs composites, two methods were applied. (a) Covalent grafting: A mixture of MWCNTs-COOH (50 mg) and AMIM-Br (100 mg) was stirred in *N,N*-dimethylformamide (DMF) (15 mL) at 55 °C for 24 h. The solid was filter and washed successively with DMF, water and methanol. After drying 12 h in a vacuum at 55 °C, the AMIM-Br functionalized MWCNTs (AMIM-Br-MWCNTs) was obtained. 1-aminopropyl-3-methylimidazolium tetrafluoroborate functionalized MWCNTs (AMIM-BF<sub>4</sub>-MWCNTs) were prepared by anion exchange. AMIM-Br-MWCNTs (50 mg) was stirred with NaBF<sub>4</sub> (100 mg) in 10 mL of water at room temperature for 24 h. The mixture was filtered and washed to remove the NaBF<sub>4</sub> residue and NaBr. Then, the resulting solid was dried for 12 h in vacuum at 55 °C to give AMIM-BF<sub>4</sub> functionalized MWCNTs. 1-aminopropyl-3-methylimidazolium hexafluorophosphate functionalized MWCNTs (AMIM-PF<sub>6</sub>-MWCNTs) and 1-aminopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (AMIM-NTf<sub>2</sub>-MWCNTs) were prepared in the similar procedure using KPF<sub>6</sub> and LiNTf<sub>2</sub> as anion exchange reagents. (b) Physical adsorption: AVIIM-Br (100 mg), AIBN (7 mg) and pristine MWCNTs were sonicated in 30 mL of ethanol for 20 min. Then, this mixture was stirred under nitrogen atmosphere for 12 h at 75 °C. AVIIM-Br was polymerized to poly[AVIIM-Br] and absorbed on the surface of MWCNTs. The solid was filtered and washed with ethanol. After washing, the product subsequently dried in vacuum to afford poly[AVIIM-Br]/MWCNTs composite. AMIM-Br-MWCNTs and poly[AVIIM-Br]/MWCNTs were characterized by FT-IR and XPS.

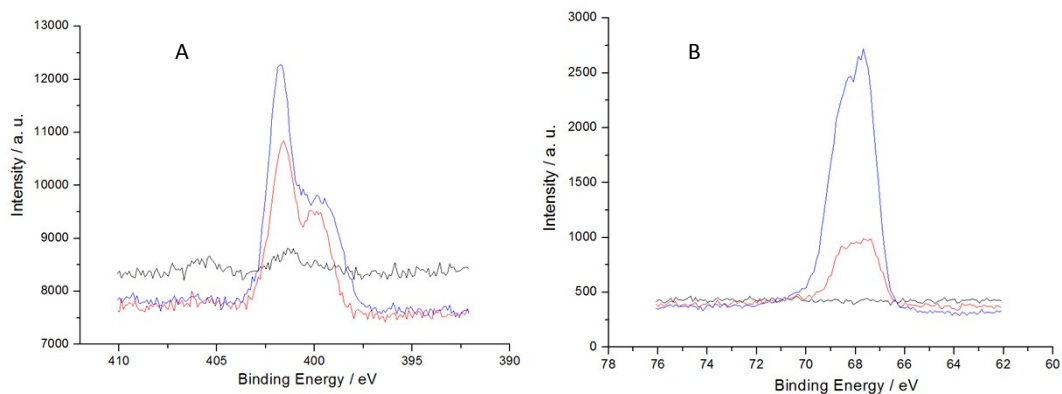


**Fig. S1** A: FT-IR spectra of pristine MWCNTs (Black) and poly[AVIIM-Br]/MWCNTs (Red). B: FT-IR spectra of pristine MWCNTs-COOH (Black) and AMIIM-Br-MWCNTs (Blue).

Figure S1(A) shows the FT-IR spectra of MWCNTs and poly[AVIIM-Br]/MWCNTs. Compared to spectrum of MWCNTs, peaks located at 3130 and 800  $\text{cm}^{-1}$  in spectrum of poly[AVIIM-Br]/MWCNTs can be assigned to the N-H stretching vibration and bending vibration from amine group ( $\text{NH}_2$ ) in the poly(AVIIM-Br), respectively. Moreover, stretching vibration of C-N bond was found at 1250  $\text{cm}^{-1}$ .<sup>4</sup> Thus, all these observations provide strong evidence that poly[AVIIM-Br] was successfully loaded on MWCNTs.

Also, Figure S1(B) shows the FT-IR spectra of MWCNTs-COOH and AMIIM-Br-MWCNTs. In the spectrum of MWCNTs-COOH, peaks at 1725 and 1600  $\text{cm}^{-1}$  belonged to the carboxylic C=O and C=C stretching vibration in MWCNTs, respectively. In the AMIIM-Br-MWCNTs spectrum, these two peaks shifted to 1725 and 1580  $\text{cm}^{-1}$  since the carboxylic acid changed to amide.<sup>5,6</sup> Furthermore, there are two characteristic absorption bands in the AMIM-Br-MWCNTs spectrum

including stretching vibrations of N-H and C-N bonds at around 3400 and 1200  $\text{cm}^{-1}$ , respectively.<sup>4,5</sup> Thus, all these observations provide strong evidence that poly[AVIIM-Br]/MWCNTs and AMIIM-Br-MWCNTs were successfully prepared.



**Fig. S2** A: XPS spectra of N 1s in MWCNTs-COOH (Black), poly[AVIIM-Br]/MWCNTs (Blue) and AMIIM-Br-MWCNTs (Red). B: XPS spectra of Br 3d<sub>5/2</sub> MWCNTs-COOH (Black), poly[AVIIM-Br]/MWCNTs (Blue) and AMIIM-Br-MWCNTs (Red).

Figure S2 shows the XPS spectra of N 1s and Br 3d<sub>5/2</sub> in MWCNTs-COOH, poly[AVIIM-Br]/MWCNTs and AMIIM-Br-MWCNTs. The presence of peaks for N 1s and Br 3d<sub>5/2</sub> in IL-MWCNTs indicated the existence of IL cation and anion, respectively. Therefore, it is further confirmed that ILs were absorbed or covalent bonded to the MWCNTs.

Figure S3

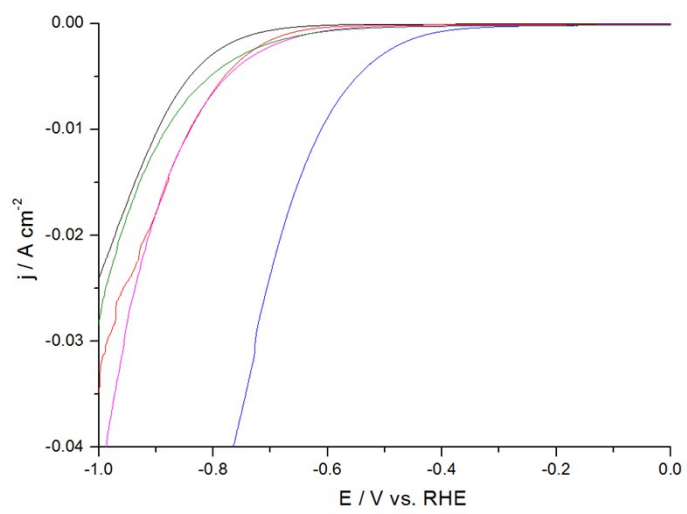


Figure S3: Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs with loading amount. 25  $\mu\text{g}$  (Black), 50  $\mu\text{g}$  (orange), 100  $\mu\text{g}$  (Blue), 150  $\mu\text{g}$  (Purple), 200  $\mu\text{g}$  (Green). IL to MWCNTs amount ratio: 2:1. Electrolyte: 0.5 M  $\text{H}_2\text{SO}_4$ .

Figure S4.

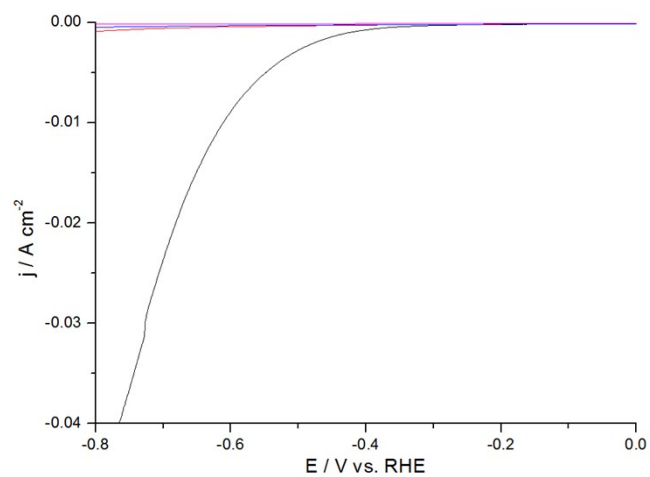


Figure S4: Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs at different pH. pH: 0.3 (Black), pH: 2.4 (orange), pH: 3.5 (Blue), pH: 4.3 (Purple). Catalyst loading amount: 100  $\mu\text{g}$ . IL to MWCNTs amount ratio: 2:1.

Figure S5.

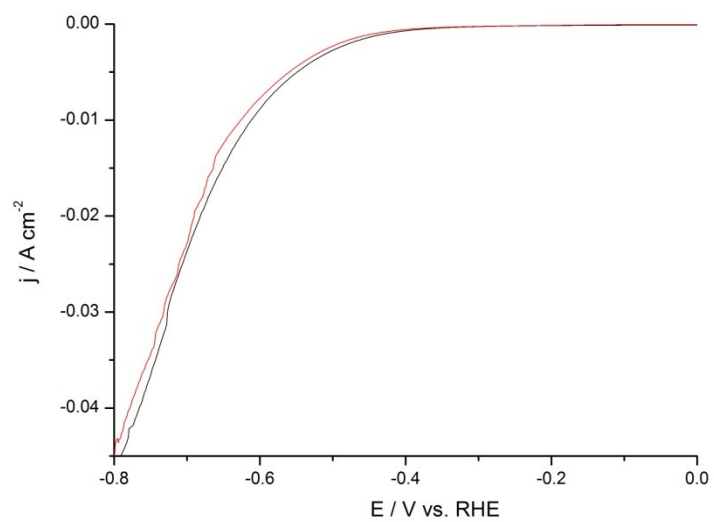


Fig. S5: Linear sweep voltammograms at working electrode using the same AMIM-Br-MWCNTs. Initial trial (Black), trail after 700 scanning cycles (Red). Catalyst loading amount: 100  $\mu\text{g}$ . IL to MWCNTs amount ratio: 2:1. Electrolyte: 0.5 M  $\text{H}_2\text{SO}_4$



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