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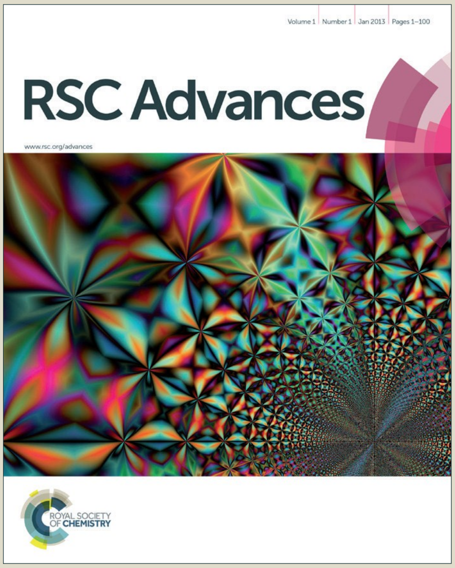

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Ionic Liquid Functionalized Carbon Nanotubes: Metal-free Electrocatalyst for Hydrogen Evolution Reaction

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For the first time, five kinds of ionic liquid functionalized multi-walled carbon nanotubes (IL-MWCNTs) were applied as metal-free electrocatalysts for hydrogen evolution reaction (HER). 1-aminopropyl-3-methylimidazolium bromide functionalized MWCNTs demonstrates the best HER performance due to its strongest proton adsorption ability and conductive MWCNTs for the fastest reduction kinetics.

Nowadays, widely used fossil fuel has led to many environmental impacts, such as global warming and air pollution.[1] Moreover, its price and extraction difficulty are keeping increasing due to the non-sustainable property. Therefore, hydrogen, considered as a clean and high-density energy source and carrier, has gained an increasing attention in the past decades.[2,3] Several hydrogen generation techniques were applied, such as reforming, photo conversion and electrolysis. Among these techniques, water electrolysis is the simplest and cleanest way to produce high purity hydrogen without carbon emissions.[4,5]

In order to improve the electrolysis efficiency and lower the electrolysis cost, an inexpensive and efficient hydrogen evolution reaction (HER) electrocatalyst is usually desired. Many HER catalysts have been prepared and investigated.[6-10] Nobel metal-based catalysts, such as Pt-group metals, obtain high efficiency and are easy implementation into devices, but the critical abundance and high price limit their large scale application.[11,12] Less expensive substitutes (such as Ni and Co) were introduced while these catalysts usually suffered from corrosion, passivation and relative low catalytic activities.[13,14] Recently, metal-free catalysts, including $C_{60}(OH)_8$ and C_3N_4, were prepared and applied in HER,[15-17] which obtained high catalytic activities. However, this type of catalyst is challenged due to complicate synthetic process or relatively high synthesis cost. Moreover, all these above mentioned catalysts still need expensive Nafion as binder to attach the electrode. Therefore, it is significant to develop inexpensive, stable, and highly active metal-free catalysts for HER.

Ionic liquid (ILs), a class of non-molecular ionic solvents with low melting points (<100°C), have been widely used in electrochemistry due to their many unique physicochemical properties such as nearly no measurable vapor pressure at room temperature, high conductivity, and high chemical stabilities.[18] IL containing some specific groups (amine or sulfonic acid group) could attract protons in the aqueous solution.[19,20] On the other side, carbon nanotubes (CNTs) has triggered much interest in electrochemistry since its unique electrical and mechanical properties, especially the good electron mobility.[21,22] Therefore, ionic liquid functionalized CNTs (IL-CNTs) has a great potential for HER as electrocatalyst since this kind of composite combines the proton adsorption and electron transfer properties together from both components. Also, IL in IL-CNTs can be used as binder[23], which could further decrease the cost of HER.

In this work, five ionic liquid functionalized multi-walled carbon nanotubes (IL-MWCNTs) composites were prepared and applied as metal-free electrocatalysts in HER for the first time (Scheme 1). The effects of IL-MWCNTs preparation methods and IL anion on catalytic activities were studied. Moreover, the catalytic conditions, including IL to MWCNTs ratio and catalyst loading amount, were optimized. 1-aminopropyl-3-methylimidazolium bromide functionalized MWCNTs (AMIM-Br-MWCNTs) possessed the best HER performance. Also, the possible catalytic mechanism of IL-MWCNTs for HER was investigated via fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). All the observations from experiments reveal the electrocatalytic properties of AMIM-Br-MWCNTs originate from a synergistic effect of covalent bond structure, in which AMIM-Br obtains the strongest proton adsorption ability, while the MWCNTs facilitates the electron-transfer process for the proton reduction.[24-26] Moreover, AMIM-Br in

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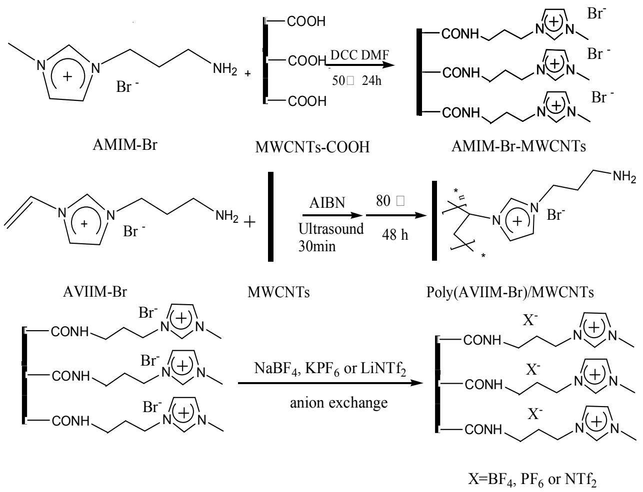
the IL-MWCNTs improved the electrical conductivity and was used as binder to replace the expensive Nafion for attachment of electrode.



Scheme 1. Preparation of five kinds of IL-MWCNTs

Generally, IL-MWCNTs can be prepared in two methods: ILs can be physically mixed with CNTs through mechanical grinding or sonication to form “Bucky Gel”;[27-29] Covalent grafting of ILs with CNTs is another method to obtain IL-MWCNTs.[30-32] In this research, 1-aminopropyl-3-methylimidazolium bromide (AMIM-Br) and 1-aminopropyl-3-vinylimidazolium bromide (AVIIM-Br) were synthesized and further interacted with MWCNTs with different methods to obtain AMIM-Br-MWCNTs and poly[AVIIM-Br]/MWCNTs, respectively (Scheme 1). These two composites, containing the similar group, were studied as electrocatalysts in HER for the first time, and their HER activities were evaluated using linear sweep voltammetry (LSVs). As shown in Fig 1A, pristine MWCNTs and carboxylic acid-functionalized MWCNTs (MWCNTs-COOH) without IL modification were used as control groups displaying negligible HER activity due to their low proton adsorption nature, but anther two IL-MWCNTs catalysts show much better HER performance, which was possibly due to the fact that proton adsorption was promoted after introducing ILs.[20,33] Moreover, AMIM-Br-MWCNTs exhibits the best HER activity possessing an onset potential (E_{onset}) at -0.35 V and highest current densities. These observations reveal that different preparation methods of IL-MWCNTs significantly influenced the HER performance, where poly[AVIIM-Br]/MWCNTs was prepared via the molecular interactions and AMIM-Br-MWCNTs was formed through chemical bonding (Scheme 1). In that case, poly[AVIIM-Br] was not tightly coated on the MWCNTs so that the electron transfer between IL and CNTs was retarded. Moreover, poly[AVIIM-Br] could be desorbed from the MWCNTs surface into electrolyte solution resulting in the decrease of catalytic activity. Accordingly, the HER performance using poly[AVIIM-Br]/MWCNTs was deteriorated. Contrarily, the chemical bonding in AMIM-Br-MWCNTs provides a high and strong interconnectivity between IL and MWCNTs for a rapid electron transfer to boost electrolytic activity. Tafel-plots for HER using pristine MWCNTs, MWCNTs-COOH, AMIM-Br-MWCNTs and poly[AVIIM-Br]/MWCNTs are also displayed in Fig. 1B, yielding the Tafel solpes (b) were determined. Comparison of these slopes reveals that IL-MWCNTs has improved the hydrogen evolution kinetics and AMIM-Br-MWCNTs obtained the lowest Tafel slope. Moreover, Tafel Slope values of catalysts (b ⩾ 120 mV/dec) indicate the Volmer step is rate-limiting step in HER processes and strong proton adsorption ability could promote the HER activity.[34] The possible mechanism for this catalyst might be Volmer-Heyrovsky reaction:[34,35]

$M + H^+ + e^- = M\cdots H_{ad}$ (Volmer)

$M\cdots H_{ad} + H^+ + e^- = M + H_2$ (Heyrovsky)

Therefore, it is suggested that this high electrocatalytic activity of AMIM-Br-MWCNTs results from a synergistic effect of the covalent bond structure, in which AMIM-Br promotes the protons adsorption, while the MWCNTs facilitates the electron-transfer process for the proton reduction.

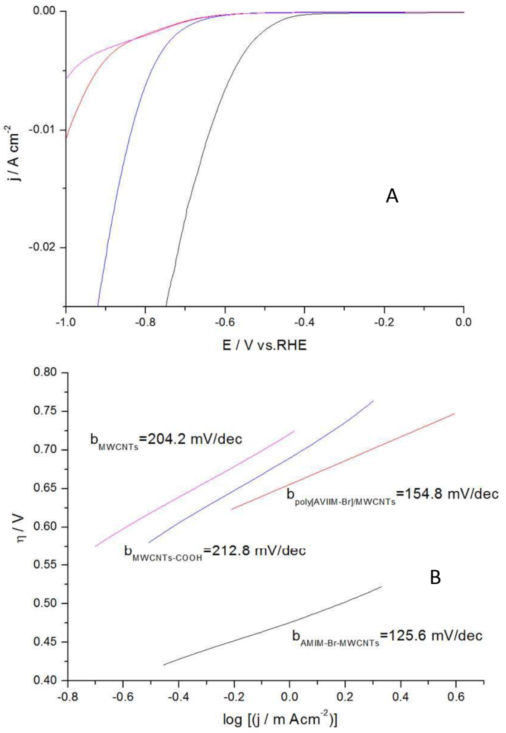


Figure 1. **A:** Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs (Black), poly[AVIIM-Br]/MWCNTs (Blue), MWCNTs-COOH (Red) and pristine MWCNTs (Pink); B: Tafel plots for HER using AMIM-Br-MWCNTs (Black), poly[AVIIM-Br]/MWCNTs (Blue), MWCNTs-COOH (Red) and pristine MWCNTs (Pink); Catalyst loading amount: 100 μg. IL to MWCNTs amount ratio: 2:1. Electrolyte: 0.5 M H_2SO_4.

Then, electrochemical impedance spectroscopy (EIS) measurements of AMIM-Br-MWCNTs, MWCNTs-COOH and MWCNTs-COOH with Nafion (5 %， w/w) were carried out to further investigate the role of IL in HER. EIS spectra from Fig. 2 show apparent the lowest Faradaic resistance of AMIM-Br-MWCNTs, which is related to a charge transfer process in HER,[36] indicating the IL in AMIM-Br-MWCNTs not only was involved in proton adsorption, but also improved the electrical conductivity.

The anion of IL can signifiantly influence the properites of IL. Thus, the effect of IL anion on the HER performance was investigated by chosing different anions, including bromide (Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and bis(trifluoromethylsulfonyl)imide (NTf_2^-), for preparation of AMIM-Br-MWCNTs, AMIM-BF_4-MWCNTs, AMIM-PF_6-MWCNTs and AMIM-NTf_2-MWCNTs, respectively (Scheme 1). These composites, containing the same cation with different anions, were applied as electrocatalysts for HER. As shown in Fig. 3A, AMIM-Br-MWCNTs possesses the highest E_{onset} and current densities while the AMIM-PF_6-MWCNTs gave the poorest HER performance. The possible reason for this outcome is related to the hydrogen bond basicity of ILs which was defined as the ability of a compound being the hydrogen-bond acceptor to form hydrogen bond. This value is influenced by their anions as follow: X^- (Br^- or Cl^-) >> $NTf_2^- \approx BF_4^- > PF_6^-$.[37, 38] Generally, IL possessing higher hydrogen bond basicity could be more likely to attract protons. Tafel-plots for HER using these IL-MWCNTs catalysts are displayed in Fig. 3B, and AMIM-Br-MWCNTs has the lowest slop value. Therefore, all these observations indicate that AMIM-Br-MWCNTs obtained the superior HER activity to other IL-MWCNTs catalysts due to its highest hydrogen bond basicity value for the enhancing of the proton adsorption ability, and this catalyst would be used in following experiments.

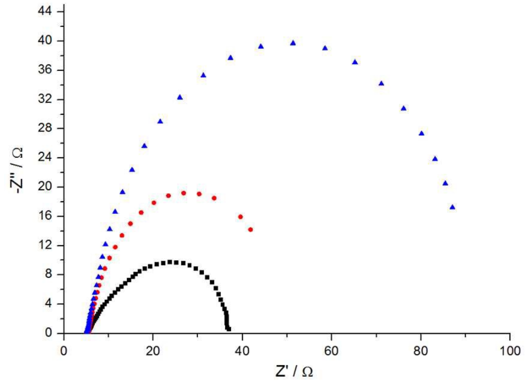


Figure 2. Electrochemical impedance spectroscopy data for AMIM-Br-MWCNTs (Black dots), MWCNTs-COOH with Nafion (mass ratio of Nafion to CNTs is 1 to 4) (Red dots) and pristine MWCNTs-COOH (Blue dots). Data were collected for the electrode under HER overpotential: -700 mV.

The IL to MWCNTs ratio was optimized by varying the amount of AMIM-Br from 25 mg to 200 mg while keepting the MWCNTs at 50 mg during preparing the IL-MWCNTs composties. Fig. 4 reveals that the HER activity was improved when the IL amount increased to 100 mg, and a smallest E_{onset} of -0.3 V was observed. It is possibly attributed to the fact that the increase of IL that covalent bonded with MWCNTs improved the proton adsorption. Then, the E_{onset} and current densities were start to decrease as more IL was added in preparation step. Thus, 100 mg of AMIM-Br was used for preparation of catalyst. The total amount of catalyst loaded on the electrode is another important factor to influence the HER activities. In this study, the loading amout of AMIM-Br-MWCNTs was increased from 25 to 200 μg for each experiment. The highest HER activty was obtained as 100 μg of catalyst applied (see Fig S3 in ESI†). It is noteworthy that increasing the load amout of catalyst improves the HER activities while the excessive loading amount leads to reducing the HER activies. This decrease of HER activity is possible related to fact that the thick catalyst layer on the eletrode might change the morphologh of catalyst and hinder the charge trasfer. Moreover, catalyst started to drop from the electrode with the increasing of the catalyst amount.

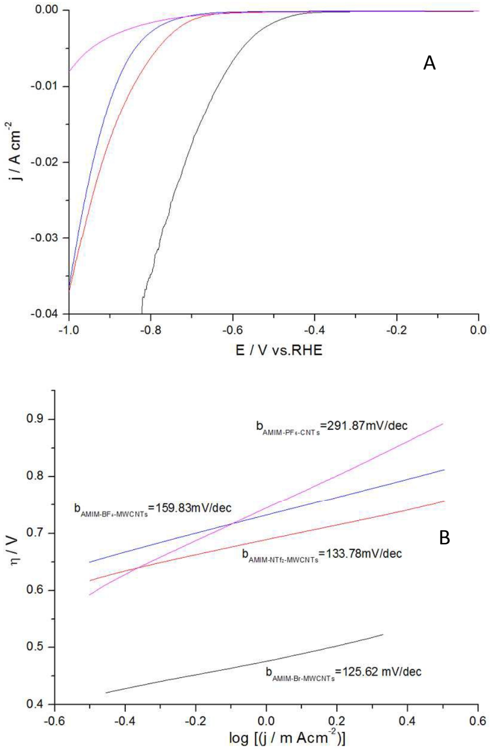


Figure 3. A: Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs (Black), AMIM-BF_4-MWCNTs (Blue), AMIM-PF_6-MWCNTs (Purple) and AMIM-NTf_2-MWCNTs (Orange) ; B: Tafel plots for HER using AMIM-Br-MWCNTs (Black), AMIM-BF_4-MWCNTs (Blue), AMIM-PF_6-MWCNTs (Purple) and AMIM-NTf_2-MWCNTs (Orange); Catalyst loading amount: 100 μg. IL to MWCNTs amount ratio: 2:1. Electrolyte: 0.5 M H_2SO_4.

Therefore, 100 μg of AMIM-Br-MWCNTs was appiled for each experiment. The effect of pH was evaluated by varying the electrolyte (H_2SO_4) concentration. Fig. S4 (ESI†) shows that HER activity was dramatic dropped when the pH of the electrolyte solution increaed from 0.3 to 4.3. It is obvious that this metal-free catalyst can be utilized at acidic condition with a high HER activity.

In addition, the durability of the catalyst for HER was preliminarily examined. After 700 scanning cycles, LSV for HER using AMIM-Br-MWCNTs similar to that before this test was observed, with a negligible decrease in current density (Figure S5, ESI†). It is suggested this catalyst did not be deteriorate in acidic condition and was quite stable during HER process, which was attributed to the high chemical stability of IL and strong chemical adhesion between the IL and MWCNTs.

The mechanism of IL-MWCNTs electrocatalyst on HER was investiageted using FT-IR spectroscopy and XPS, respectively. As mentioned above, it is probabley that IL in catalyst promotes the proton adsportion to boost the HER activities. To investigate this adportion of protons, AMIM-Br-MWCNTs was added to the electrolyte solution (0.5 M H_2SO_4) for 10 minutes. The solid was filtered and washed with water three times. After washing, the solid subsequently dried in vacuum to afford AMIM-Br-WMCNTs (H^+), FT-IR sepectra for MWCNTs-COOH, AMIM-Br-MWCNTs and AMIM-Br-MWCNTs (H^+) are shown in Fig. 5A. Comparing the with MWCNTs-COOH, there are two characteristic absorption bands in the AMIM-Br-MWCNTs spectrum including stretching vibrations of N-H and C-N bonds in amide groups at around 3400 and 1200 cm^{-1}, respectively.[39] This amide group was formed when AMIM-Br covalently bonded with MWCNTs-COOH. After treatment with electrolyte solution, it is obvious as illustrated that the absorption bands of C=O stretching stretching vibration was switched from 1580 cm^{-1} (AMIM-Br-MWCNTs) to 1565 cm^{-1} (AMIM-Br-MWCNTs (H^+)) since the O could be protonated in the electrolyte solution. Moreover, the stretching vibrations of C-N bonds shifted from 1200 to 1130 cm^{-1} since the p-π conjugation of amide groups was destroyed by protonation. These results preliminary indicate that amide group of AMIM-Br-MWCNTs could attract the H^+ for improving the proton adsorption. To further confirm this mechanism, XPS was performed to indentify the protonation behavior. The binding energies (BEs) of O 1s AMIM-Br-MWCNTs and AMIM-Br-MWCNTs (H^+) are 531.9 and 532.5 eV, respectively (Fig. 5B). This increasing in the BEs suggests that the electron density in the vicinity of O was decreased, which should be attributed to the protonation of C=O in amide group from AMIM-Br-MWCNTs. Moreover, N 1s for AMIM-Br-MWCNTs and AMIM-Br-MWCNTs (H^+) are 401.8 and 402.1 eV, respectively (Fig. 5C). Thus, AMIM-Br in the IL-MWCNTs significantly improves HER performance due to its cation (amide group) and anion (high hydrogen bond basicity), as they promote adsorption of protons (Scheme 2).

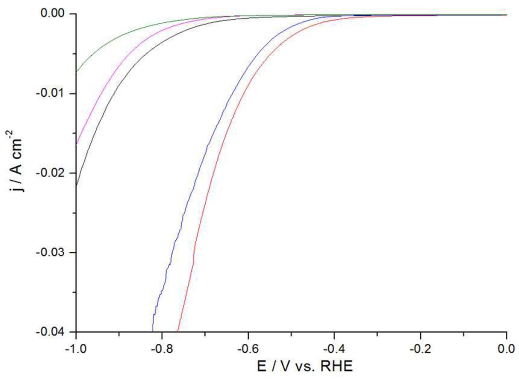
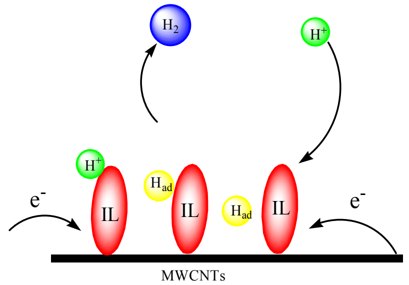


Figure 4: Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs with different IL to prepare catalyst. 25 mg IL (Black), 50 mg IL (Red), 100 mg IL (Blue), 150 mg IL (Purple), 200 mg IL (Green). MWCNTs: 50 mg; Catalyst loading amount: 100 µg. Electrolyte: 0.5 M H_2SO_4.



Scheme 2. Mechanism of IL-MWCNTs catalyst

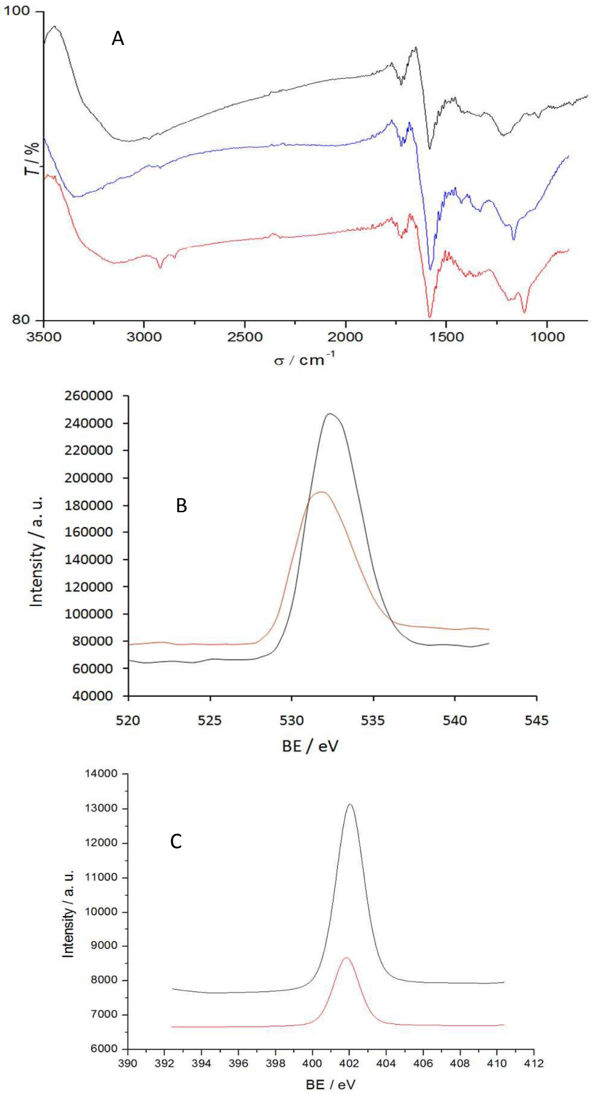


Figure 5 A: FT-IR spectra of pristine MWCNTs-COOH (Black), AMIIM-Br-MWCNTs (Blue) and AMIIM-Br-MWCNTs (H+) (Red). B: XPS spectra of O 1s in AMIIM-Br-MWCNTs (Red) and AMIIM-Br-MWCNTs (H+) (Black). C: XPS spectra of N 1s in AMIIM-Br-MWCNTs (Red) and AMIIM-Br-MWCNTs (H+) (Black).

Conclusion

In this study, several IL-MWCNTs were prepared and applied as metal-free electrocatalysts for HER for the first time. The effects of IL-MWCNTs preparation method and IL anion were studied in an effort to find the best catalyst. In the optimized conditions, AMIM-Br-MWCNTs catalyst demonstrates the highest current density and the most positive onset potential (-0.3 V). Compared with metal-based and other metal-free catalysts, IL-MWCNTs can be prepared in moderate conditions with low cost. This catalyst possesses comparable HER activities. IL in catalyst not only improved the electrical conductivity, but also was directly used as binder without adding Nafion to further reduce the cost of HER. Tafel slopes indicate that Volmer step is the rate-limiting step in HER processes, which reveals that strong proton adsorption of catalyst can promote the HER activity. Therefore, the significantly enhanced HER performance using AMIM-Br-MWCNTs originates from a synergistic effect, in which AMIM-Br has the strongest proton adsorption ability and the MWCNTs facilitates the electron-transfer process for the proton reduction.

Accordingly, all the findings obtained in this study indicate that the AMIM-Br-MWCNTs is undoubtedly one kind of brand new and comparable metal-free electrocatalyst for HER. Compared with other reported electrocatalysts, the HER activity of IL-MWCNTs catalyst is not good. One main reason could be related to the fact that its proton adsorption ability was lower than the metal-based catalysts. Therefore, investigations about catalytic mechanism related to the proton adsorption and desorption behavior are being carried out. IL-MWCNTs with stronger proton adsorption ability and functionalization of MWCNTs using basic groups will be prepared and investigated for HER in future study.

Acknowledgements

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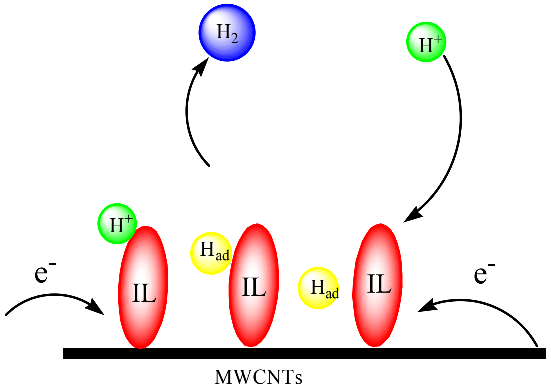

Scheme . Mechanism of IL-MWCNTs catalyst for HER

Electrocatalytic properties of AMIM-Br-MWCNTs originate from a synergistic effect of covalent bond structure, in which AMIM-Br obtains the strongest proton adsorption ability, while the MWCNTs facilitates the electron-transfer process for the proton reduction.