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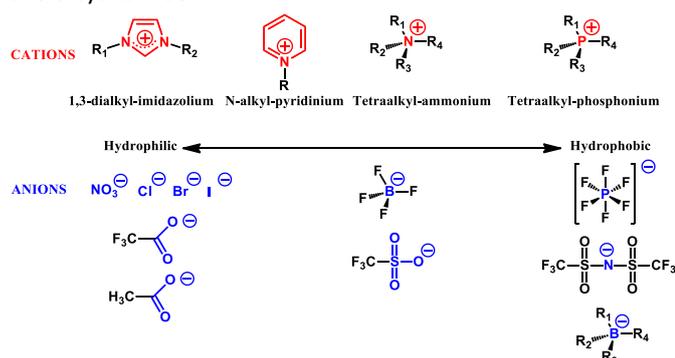
Immobilization of molecules based ionic liquids. A promising approach to improve electrocatalysts performance towards hydrogen evolution reaction

Hao-Zheng Yu,^a Selma Bencherif,^a Thuan-Nguyen Pham-Truong,^b Jalal Ghilane*^a

Abstract. Ionic liquids (ILs) have received continuous attention owing to their unique chemical and physical properties and to their successful integration in several applications. More recently, the ILs moved from their limited use as solvent to their immobilization onto surfaces providing new properties to the interface. The flexible design of these new families allows to transfer some of their properties to the substrate. The aim of this review is therefore to summarize the recent achievement in the immobilization of ionic liquid based molecules and to illustrate their potential use to improve the electrocatalytic activity towards the hydrogen evolution reaction (HER).

Introduction

The first synthesized ionic liquid was reported at the beginning of the last century.¹ Since then, ionic liquids and their derivatives have attracted a lot of interest from the scientific world and have become a real multidisciplinary field.^{2,3} They have several characteristics including a low vapor pressure, and high thermal stability. These properties make them appropriate solvents for green chemistry and for sustainable science.⁴ Ionic liquid is a salt, combination of cation and anion, with the melting point below 100°C. The ILs cations are usually organic ions such as imidazolium, quaternary ammonium, pyrrolidinium, phosphonium and piperidinium. The most frequently used anions include hexafluorophosphate, trifluoromethanesulfonate, bis(trifluoromethylsulfonyl) imide, and dicyanamide.



The physicochemical properties of ionic liquids depend on the nature of cations and/or anions.^{2,4} From an electrochemical point of view, room temperature ionic liquids, RTILs, simultaneously play the role of a solvent and a supporting electrolyte. Besides, depending on the composition of the ionic liquids (imidazolium, pyrrolidinium, ammonium, etc.) they provide a broad electrochemical window (ranging from 3.5 to 6 V).⁵ Thus, different studies have been performed to investigate

the electrochemical behaviors not only of ionic liquids themselves, but also of other materials in ionic liquids.⁶ In addition, the vapor pressure of RTILs is much lower than that of other organic solvents providing strong stability over time, which is extremely beneficial for long-term, non-volatile electrochemical devices.⁷ By possessing advantageous electrochemical properties, ionic liquids are being used in numerous applications in electrochemistry.^{8,9} Besides that, the attachment of organic layers onto solid supports provides new properties to the interface.^{10,11} Depending on the electronic configuration, there are a defined number of neighboring atoms which are closely packed to the central one to satisfy its electronic shells. Indeed, the atoms at the surface of a material behave completely different compared to the bulk atoms due to lower coordination numbers.¹² As a consequence, they have a different free energy, density of states, structure and reactivity. The immobilization of organic molecules has been successfully integrated in several applications including, smart surfaces, molecular electronics, photovoltaics, catalysis and surface wettability. Several reviews have been devoted to this topic and related applications.¹³⁻¹⁸

Recently, the research in ionic liquids has been extended from their exclusive use as solvent to their immobilization onto the electrode materials. Different approaches have been proposed in order to immobilize ionic liquid onto various substrates which can reduce the quantity of IL and generate new interesting interfaces from thin layer ionic liquid to polymeric ionic liquid. In this context, self-assembled monolayer and electrochemical tools are among the most powerful techniques to graft IL onto material surfaces from nanoscale to large area. Several available reviews highlight the unusual properties of IL-modified materials such as wettability, lubricating property, functional materials for catalysts, surface modifying agents, stationary phases in separation technologies, and electrodes in electrochemistry.¹⁹⁻²² Within this review, different approaches to

produce either thin ionic liquid layers or polymeric film containing ionic liquid framework will be reported. Finally, the recent achievements on using ionic liquid modified solid support as an electrocatalyst and/or as a host-guest electrocatalytic for driving the hydrogen evolution reaction will be presented.

Ionic liquid supported surface.

Within the context of this review, ionic liquid supported surface (ILSS) is defined as the ionic liquids moieties immobilized onto solid surfaces. Therefore, ILSS could be classified in two main categories; thin layers supported surface and polymeric ionic liquids supported layer.

Approaches to form Thin Layers of Ionic Liquids

Self-assembled monolayers (SAMs) of organic molecules consist of organic assemblies formed by the well-arranged adsorption of organic molecules that have a specific functionalized head group from the solution or the gas phase onto the surface of a solid or onto the surface of a liquid (in the case of liquid metals and its alloys). The most widely studied branch of SAMs is the adsorption of alkanethiols on gold, silver and copper.²¹ The strong affinity of thiols ($-SH$) for the surface of noble metals is the key factor leading to the generation of well-defined organic layers that have other functionalities at the exposed interface.¹⁰

Thiol-terminated imidazolium-based ionic liquids have been immobilized onto Au substrates by dipping the Au substrate into a millimolar ethanolic solution of the thiol-terminated IL for a few hours.²² This procedure is widely used for the formation of alkanethiols derivatives on gold substrates (Fig. 1). Actually, a well-defined structure of the SAM can be achieved by immersing the substrate for a few hours in order to overcome the slow rearrangement rate of the adsorbates. Different parameters such as temperature, purity of the adsorbate, concentration of oxygen in the solution, solvent, immersion time, etc., should be considered to achieve a well-organized SAM.

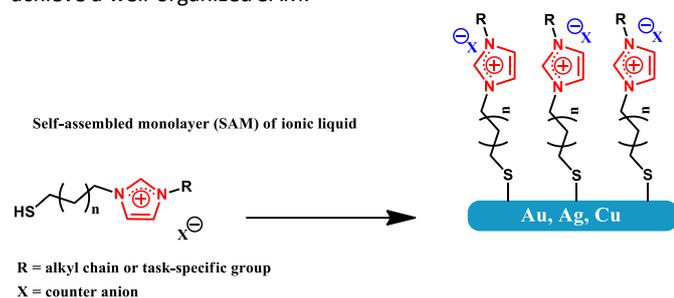


Fig. 1. Self-assembled monolayer of thiol-functionalized imidazolium based ionic liquid on noble metal.

Lee et al. reported the formation of SAM layer of Imidazolium Ion on Au substrate.²¹ It has been demonstrated that the presence of the IL monolayer changes the physicochemical properties of the Au surface. On the basis of measured contact angles ranging from $65 \pm 1^\circ$ to $23 \pm 1^\circ$, the mobile anions exhibit

a strong influence on the hydrophobicity of the surface in the following order $NTf_2^- > PF_6^- > CF_3SO_3^- > ClO_4^- > NO_3^- > BF_4^- > Br^-$. Besides, self-assembled ionic liquid monolayer was reported to selectively switch the electron transfer of some redox probe.²³ Indeed, the electron transfer occurs through the monolayer with Ru^{3+}/Ru^{2+} in presence of ferrocyanide ion while the transfer was cut off by replacing $[Fe(CN)_6]^{3-}$ by SCN^- or OCN^- . A self-assembled monolayer of ionic liquid was also applied to gold nanoparticles in order to selectively detect counter-anions²⁴ or to make a new class of enzymatic biosensors by studying the displacement of the plasmonic band of the IL-functionalized Au nanoparticles.²⁵

Besides the formation of a self-assembled monolayer using thiol-terminated ILs on noble metal surfaces, IL-SAMs can also be formed on hydroxyl modified surfaces by using alkoxysilanes bearing imidazolium moieties.²⁶ This process leads to extend the immobilization of ionic liquid moieties to various substrates and nanomaterials (Fig. 2).

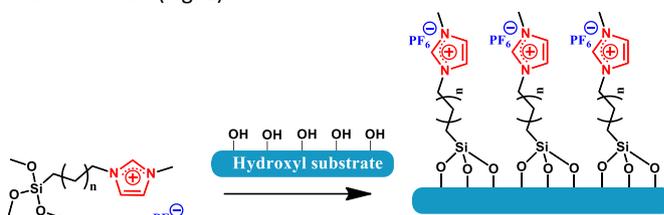


Fig. 2. Self-assembled monolayer of alkoxysilanes bearing imidazolium moieties on hydroxyl modified surfaces.

As reported by B. Gadenne et al.,²⁷ well-ordered silica particles were synthesized via template-directed polycondensation of triethoxysilylated imidazolium. The materials prepared via this technique depend strongly on the length of the alkyl side chain. Whereas a short alkyl chain (methyl, allyl) gave a lamellar structure, longer chains lead to the formation of nanostructured silica with hexagonal symmetry, which can be attributed to the micellar arrangement of the surfactant molecules. In the case of short chains, the ionic liquid molecules interact only with the polar head of the surfactant, while in the case of longer chains, in addition to the interaction described for the previous case, the alkyl chain of the surfactant can also interact with the hydrophobic tail of the surfactant by being incorporated into a micellar arrangement. More recently, the surface of modified silica gels functionalized with a monolayer of covalently attached 1-(1-trimethoxysilane) propyl-2,3-dimethyl-imidazolium chloride, tetrafluoroborate or hexafluorophosphate ionic moieties were used to catalyze the aldol reaction.²⁸ In another approach, Huang et al.²⁹ reported the functionalization of graphene oxide with IL molecule by means of nucleophilic ring-opening reaction between epoxy group at the surface of GO and primary amine group of 1-(3-aminopropyl)-3-methylimidazolium bromide. The presence of this IL layer prevents the stacking of graphene layers, leading to the formation of porous 3D reduced graphene oxide structure. Moreover, the presence of immobilized positive charges allows anion exchange with metallic anion from the solution (i.e.

PdCl_4^{2-}), resulting to homogeneous distribution of nucleation sites during formation of palladium nanoparticles ($d_{\text{PdNPs}} = 1.76$ nm when the mass ratio of GO/NH₂-IL = 1/1.6). It should be noted that an excess of amine terminated IL at the surface of GO results to aggregation of Pd NPs. This phenomenon is mainly due to the stacking of ionic liquid on the top of the GO-NH-IL layer, leading to the formation of larger NPs through aggregation of non-stabilized clusters of Pd. Besides the alkoxy silane group, other functional groups can be used for the formation of a self-assembled monolayer via a condensation process, such as alkyl phosphonium-bearing ionic liquids.³⁰

In parallel to the self-assembled monolayers with highly oriented molecules, the electrochemical assisted grafting offers additional method to immobilize ionic liquid moieties onto different conductive surfaces. This method involves the generation of radicals from

formation of a thin ionic liquid layer (Fig. 3a). The immobilization of the ionic liquid on the surface was evidenced by XPS. The cyclic voltammogram shows the electrochemical characterization of the modified electrode recorded in acidic solution and exhibited the presence of irreversible reduction of the nitro group and a redox reversible signal of the generated NHOH/NO group at 0.3 V. These results give rise to a promising material functionalization technique, which combines the attachment of ionic liquids to the surface, the presence of a redox active interface, and the ability to perform anion exchange.

In parallel with oxidative grafting, electrochemical reductive grafting of ionic liquids has also been a subject of scientific investigation. Among the different functional groups, diazonium derivatives are the most investigated molecules for electrochemical grafting.¹¹ S. Bouden et al.³² immobilized a bi-redox ionic liquid, 1-nitrophenylethyl-3-methylferrocenylimidazolium TFSI, onto an

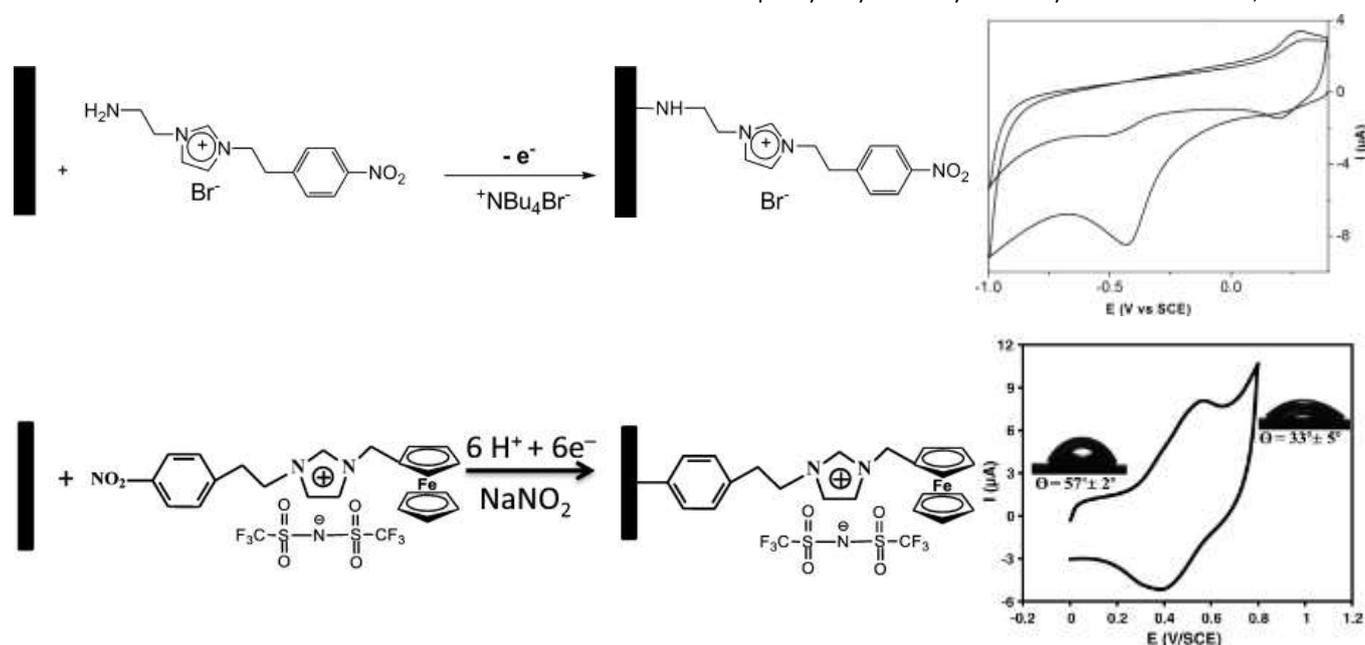


Fig. 3. Schematic illustrating the grafting of redox based ionic liquid through the electrochemical oxidation of primary amine onto a carbon electrode and the cyclic voltammetry of carbon modified electrode in 0.1 M H₂SO₄. Data originally presented in ref 31 (b) Scheme for the electrochemical grafting of ferrocene based ionic liquid molecule. Cyclic voltammetry of grafted electrode in acetonitrile solution containing 0.1 M LiTFSI as. Inset: contact angles obtained before and after electrochemical oxidation. Reproduced from ref. 32 with permission from [Elsevier], copyright [2015].

oxidizable or reducible group by applying a suitable potential to the substrate. Although this technique is one of the most powerful, there are very few reports on electrochemically assisted surface functionalization with molecules based on ionic liquids. Electrochemically assisted oxidative grafting of ionic liquid moieties can be carried out in one or multiple steps. The oxidative grafting of a redox-molecule-based ionic liquid onto an electrode surface was first reported by M. Gomez-Mingot et al.³¹ In this report, N-(2-aminoethyl)-N-(4-nitrophenylethylimidazolium) bromide was grafted onto a glassy carbon electrode via electrochemical oxidation of the amine group at around 1.2 V vs. SCE. During the grafting process, aminyl radicals that were electrochemically generated near the electrode surface reacted rapidly with the surface leading to the

electrode surface by the electrochemical reduction of in situ-generated diazonium functional groups. In this work, the diazonium derivative was generated in-situ within the diffusion layer.³³ Thus, the nitro group was electrochemically reduced to its corresponding amine and after diazotation reaction the corresponding diazonium is generated. Next and under the reductive potential the diazonium compound is reduced into the corresponding radical who is rapidly attached to the electrode surface. This approach leads to generate the diazonium within the diffusion layer avoiding or minimizing the spontaneous grafting observed when the diazonium is generated in the electrochemical cell. The immobilized ionic liquid layer was evidenced by XPS and electrochemistry by observing the signature of the ferrocene moieties (Fig. 3b). This new approach leads to the

generation of a multifunctional material bearing redox-active molecules and ionic liquid components. This new interface showed versatile applications toward electrochemically switchable wettability.

In addition, the attachment of desired molecules could be achieved using a stepwise method. The latter is based on the immobilization of primary organic layer followed by one and/or several surface chemical reactions such as peptide coupling, Gomberg–Bachmann reaction or click chemistry. The general procedure is based on the electrochemical grafting of a first layer bearing terminal groups that can be engaged in a surface chemical reaction. Fig. 4 presents examples of stepwise grafting leading to the immobilization of imidazolium based ionic liquid moieties.

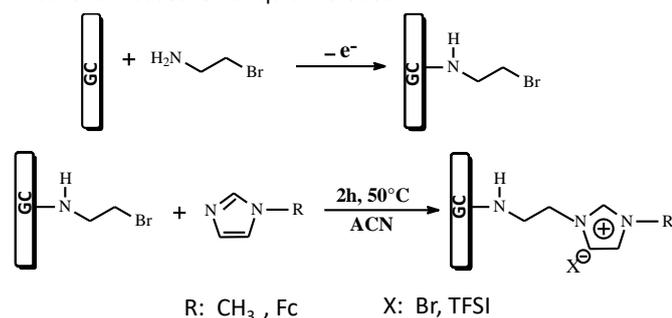


Fig. 4. Strategy for the stepwise process for the surface-initiated attachment of molecules based ionic liquid. Reproduced from ref. 34 with permission from [American Chemical society], copyright [2016].

Recently, a simple and general route for the immobilization of molecules containing an ionic liquid framework was proposed as shown in Fig. 4. Inspired by the classical synthesis of ionic liquids, surface-initiated synthesis was reported. This process is based on building the ionic liquid structure on the surface. Thus, a bromide-terminated layer was immobilized on the electrode surface, and the modified surface was then immersed in a solution containing imidazole derivatives. The generated structures provide multifunctional systems containing ions, immobilized cations and mobile anions, and redox species.³⁴

In another study, the oxidative grafting of 2-(4-aminophenyl) acetic acid was performed onto a glassy carbon electrode. Next, in the presence of sodium nitrite and perchloric acid, a diazotization reaction occurs at the surface leading to the conversion of the attached NH₂ head group into a diazonium group. The latter is accessible for further transformation through the Gomberg–Bachmann reaction leading to the attachment of an aryl radical to one of the cyclopentadienyl moieties of the ferrocene-based ionic liquid.³⁵ In this work, the immobilization of the ferrocene-based ionic liquid was evidenced by electrochemical characterizations and surfaces analyses.

Li et al. have successfully immobilized various imidazolium derivatives onto multi-walled carbon nanotubes (MWCNT) through the surface peptide coupling reaction between aminopropyl-3-methyl imidazolium and COOH head group attached onto MWCNT.³⁶

The effects of IL-MWCNTs preparation method and IL anion exchange were investigated. Overall, the attachment of ionic liquids based molecules provides new properties to the surface enlarging their potential applications.³⁷⁻⁴⁰

Approaches to form polymer Ionic Liquids

Recent developments in polymer science have allowed the synthesis of various polyelectrolytes that are continuously being introduced with controlled morphology, such as linear polymers, nano/micro particles, and dendritic and star structures. The term poly(ionic liquids) (PILs) refers to a subclass of polyelectrolytes that feature an ionic liquid (IL) species in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular structure.⁴¹ In the last decade, poly(ionic liquid)s have been widely investigated as new polyelectrolytes, leading to rapid growth in terms of publications and applications in diverse fields.⁴²⁻⁴⁵

Ohno et al. were the pioneers on reporting PILs as solid electrolytes in electrochemical applications.⁴⁶⁻⁴⁸ These studies inspired researchers to use PILs with different structures and properties in several applications. There are several excellent reviews by Texter, Mecerreyes, Antonietti and Azzaroni that summarize the synthesis, characterization, and applications of PILs.^{41,49-53} Monomer-based ionic liquids have been studied leading to the emergence of novel solid materials bearing ionic liquid frameworks. Depending on the nature of the polymeric backbone, two types of PIL are classified, called polymerized cationic ionic liquids and polymerized anionic ionic liquids. For each series of PILs, different approaches can be used, such as direct polymerization of ionic liquid monomers or modification of polymeric polymers by forming repeating units containing ionic liquids.

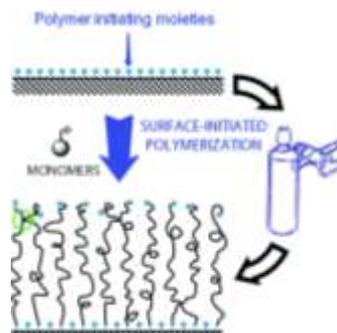


Fig. 5. Scheme illustrating the principle of SI-ATRP polymerization. Reproduced from ref. 53 with permission from [The Royal Society of Chemistry], copyright [2019].

In general, PILs can be synthesized by conventional radical polymerization. In addition, other polymerization approaches can also be applied, such as atom transfer radical polymerization (ATRP)^{54,55} and reversible addition–fragmentation transfer polymerization (RAFT).^{56,57} The only part that determines the structure and properties of the PIL is the chemical structure of the ionic liquid monomer. The PILs were successfully synthesized in bulk

solution, in micro-emulsions or in dispersed media. Besides that, it has been shown to be feasible to polymerize ionic liquids monomer onto material surfaces by surface-initiated atom transfer radical polymerization (SI-ATRP).^{54,58,59}

Chen et al. report the thermal initiator free radical polymerization of the imidazolium based ionic liquid monomer.⁶⁰ As a result, the poly(IL) is formed onto the carbon nanotube (CNT) surface. In addition the generated CNT/Poly(IL) was further used to anchor and grow metal nanoparticles (Fig. 6).

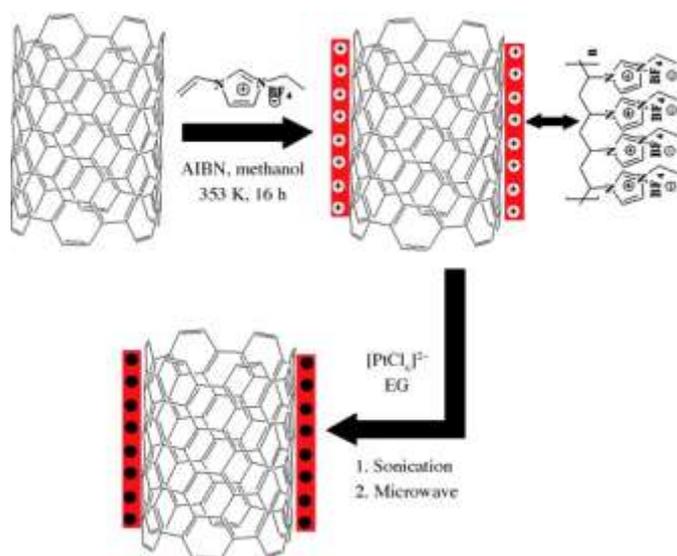


Fig. 6. Scheme illustrating the modification of CNTs with Poly(IL) followed by the formation of Pt/CNTs-Poly(IL). Reproduced from ref. 60 with permission from [Wiley-VCH], copyright [2009].

They demonstrate that the immobilization of poly(IL) on the CNT induces stable nanotube suspensions in water due to the ionic species within the polymeric film. Interestingly, the CNT/Poly(IL) was used as functional groups for the immobilization of Pt and Ru precursors followed by the metal nanoparticles growth. In this configuration the generated particles had an average diameter about 1.3 nm and no nanoparticles aggregation was observed on the CNTs surfaces. The grown PtRu nanoparticles within the poly(IL) supported CNT have a smaller particles size, better dispersion and higher electrochemical surface area when compared to those generated in the absence of the poly(IL) film.

In another study, the polymer ionic liquid attached onto a glassy carbon electrode was prepared using surface-initiated atom transfer radical polymerization (SI-ATRP) (Fig. 7A).^{59,61} The surface morphology investigations of the poly(VImM) showed homogeneous polymer film as well as the organization in a brush-like structure with an average thickness about 18 nm (Fig. 7B).

Furthermore, The electrochemical investigations demonstrate that the poly(VImM) brush structure enhances the electrochemical response of ferricyanide inner-sphere redox probe. This effect was attributed to the presence of ferricyanide moieties within the Poly(IL), occurring after anion exchange, which promotes the 2D-electron transfer.

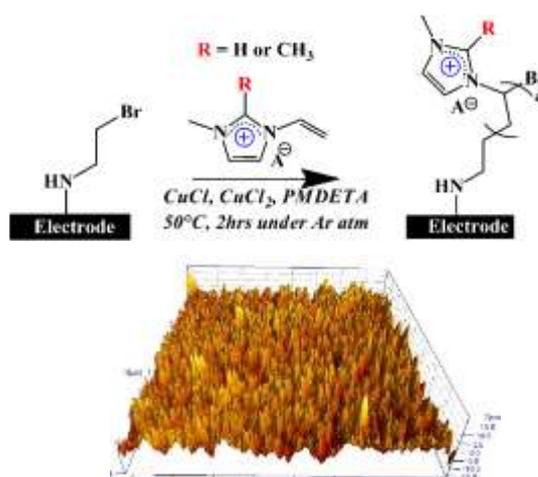


Fig. 7. Scheme illustrating the SI-ATRP polymerization of vinyl-imidazolium monomer. (B) 3D-AFM of Poly(VImM) deposited onto surface. Reproduced from ref. 61 with permission from [American Chemical society], copyright [2018].

Application of ionic liquids modified support for hydrogen evolution reaction (HER)

Hydrogen evolution reaction (HER), as a cathodic half-reaction of water splitting via electrocatalysts driving, has attracted intense scientific interest.^{62,63} Hydrogen production is environmentally clean sources of energy and provides high-purity, high-energy-density, renewable, hydrogen energy.⁶⁴⁻⁶⁷ During the last decade, extensive researches were devoted to the synthesis of nanomaterials in ionic liquids and their use as electrocatalytic materials.⁶⁸ The majority of the reported works have focused on the use of ionic liquids as environment for the synthesis of the nanomaterials and/or covering the as-prepared nanomaterials with a thin layer of ionic liquid through a direct deposition of undiluted IL droplets or through a deposition of diluted IL in volatile solvent.^{69,70} During the synthesis of nanoparticles, the ionic liquid can act not only as stabilizer to protect the nanoparticles from aggregation, a template to control the morphology of the synthesized materials but also as an enhancer to improve the performance of the catalyst. Several reviews are available highlighting the tremendous effort performed in the generation of nanomaterials in ionic liquids and the enhanced electrocatalytic performances towards the hydrogen evolution reaction equalling and/or out performing that of the state-of-the-art of platinum based catalysts.⁶⁰ Up-to-date, the most known theory to describe the interaction between the charges at the surface of nanoparticles and isolated charges of the stabilizing agent is proposed by DLVO (Derjaguin – Landau – Verwey and Overbeek) model.⁷¹⁻⁷³ This theory combines Van der Waal forces and electrostatic double layer to describe the stability of charged particles in suspension. However, this theory could not be applied to the interaction between the nanoparticles and the complex charged system as ionic liquid, resulting from the formation of steric ionic clusters by aggregation of ion pairs. Furthermore, the role of ionic liquid in enhancing the catalytic properties of prepared NPs is still unclear. It is worth noting that Antonietti et al.⁷⁴ has proposed

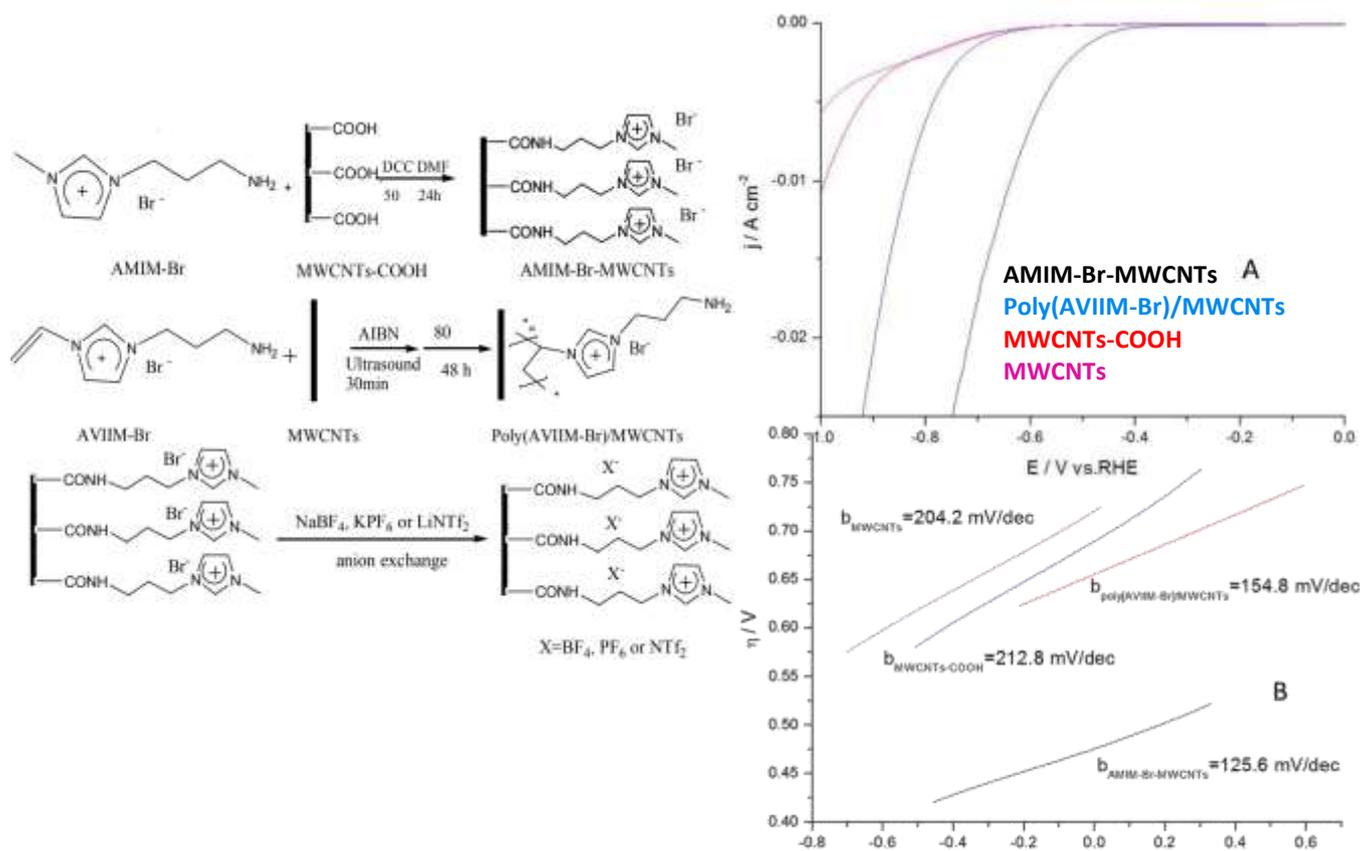


Fig. 8. Presentation of synthetic procedure for different IL-MWCNTs. A) Linear sweep voltammograms at working electrode using AMIM-Br-MWCNTs (black), poly[AVIIM-Br]/MWCNTs (blue), MWCNTs-COOH (red) and pristine MWCNTs (pink); (B) Tafel plots for HER using AMIM-Br-MWCNTs (black), poly[AVIIM-Br]/MWCNTs (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 . Reproduced from ref. 36 with permission from [The Royal Society of Chemistry], copyright [2016].

a possible explanation by considering that IL acts as a pure universal ligand which lowers the interfacial tension of the solvent.⁷⁵⁻⁷⁷ Although in the literature the combination of ionic liquids and nanomaterials for electrocatalytic applications is widely reported, the use of as-prepared immobilized ionic liquids layers is still rare. In the following, we will discuss the most recent works describing the use of covalently grafted ionic liquid moieties, onto carbon support, and their use in the electrochemical activation of hydrogen evolution reaction.

In this regard, Li and co-workers proposed the covalent grafting of imidazolium moieties using the surface chemical reaction, by means of peptide coupling, between the 1-(3-aminopropyl)-3-methylimidazolium bromide with carboxylic acid functionalized multiwall carbon nanotubes (MWCNTs).³⁶ Next, the electrocatalytic activities of the generated IL-CNTs towards hydrogen evolution reaction were investigated (Fig. 8).

Compared to pristine and carboxylic acid-functionalized MWCNTs, the IL modified MWCNTs displays higher HER performance as attested by a higher current density and lower onset potential. The electrocatalytic investigation proved that the preparation methods of IL modified MWCNTs as well as the nature of the interaction between the ILs and the MWCNTs influence the HER performance. It was found that a better HER performances were obtained when the ILs are covalently bonded to MWCNTs. Besides that, the authors also reported that depending on the used counter anion the hydrogen bond basicity could be modulated ($\text{Br}^-/\text{Cl}^- \gg \text{NTf}_2^- \approx \text{BF}_4^- > \text{PF}_6^-$). It

should be noted that an ionic liquid possessing high hydrogen bond basicity would be more preferably attract protons, thus enhance the catalytic properties towards proton reduction.⁷⁸ The best performances were obtained in the case of AMIM-Br-MWCNTs. Tafel slopes investigations suggest that Volmer step is the rate limiting step in HER processes suggesting the presence of strong proton adsorption of catalyst. This behaviour was attributed to several features including the strong chemical bonding that provide a rapid electron transfer to boost electrolyte activity and to the chemical composition of the ionic liquid. In the AMIM-Br-MWCNTs the imidazolium cation and the anion (high hydrogen bond basicity) promote the adsorption of protons. Although the observed HER performances are lower than the state-of-the-art Pt based catalyst, this first example point out the possibility to use IL layer as a metal free electrocatalyst.

Few years later, the same group reported an in-situ approach to functionalized CNTs to generate highly performing metal free electrocatalyst towards HER (Fig. 9).⁷⁹ In this approach, glyoxal and formaldehyde were mixed in methanol followed by addition of ammonium acetate and amine functionalized CNT to generate imidazole functionalized CNTs. The as-prepared CNTs were then mixed with butyl chloride (or butyl bromide) in MeOH to produce imidazolium modified CNTs. The Cl^-/Br^- anions were used as synthesized or replaced by $\text{BF}_4^-/\text{PF}_6^-$ using a conventional anion exchange reaction (Fig. 9). The comparison of the polarization curves recorded on different

grafted IL on CNT exhibits that the best electrocatalytic activity was observed in the case of CNT-IM-Cl. This was supported by a lower onset potential (80 mV) and higher current density as well as a lower over potential value (135 mV) to reach a current density of $-10 \text{ mA}\cdot\text{cm}^{-2}$. In addition, the same catalyst displays a lower Tafel slope value ($38 \text{ mV}\cdot\text{dec}^{-1}$) suggesting faster electrochemical process and kinetic. These results confirm that the electrocatalytic performance of CNT-IM-Cl catalyst is close

205 mV overpotential to reach $-10 \text{ mA}\cdot\text{cm}^{-2}$).⁸⁶ This performance was ascribed to the synergistic effect, i.e. misfit lattices of unique $\text{NiS}_2\text{-MoS}_2$ heterostructures supported on Poly(IL). The latter was reported to play several roles including the hierarchical lamellar nanostructures which acts as a connector and induce the formation of metallic 1T-MoS₂. In addition, the polymeric layer stabilized more electrons and facilitates the Heyrovsky reaction and introduces more exposed

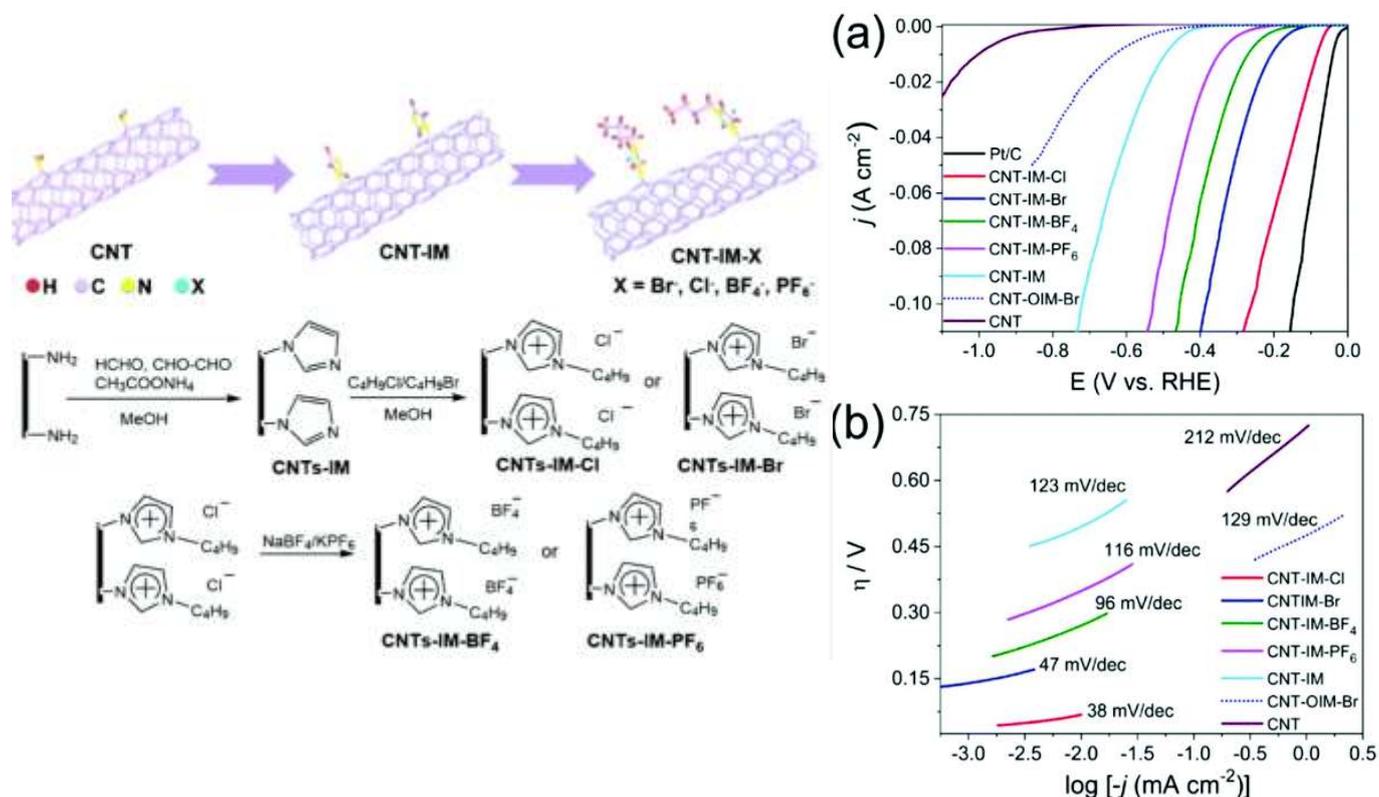


Fig. 9. Scheme illustrating the preparation of IL-MWCNTs. a) Linear sweep voltammograms response of different IL-MWCNTs electrodes in 0.5 M H₂SO₄. b) The corresponding Tafel plots. Reproduced from ref. 79 with permission from [The Royal Society of Chemistry], copyright [2021].

to the commercial Pt/C catalyst and outperform several metal-free electrocatalysts.⁸⁰⁻⁸⁵ This electrocatalytic performance was attributed to the strong bonding between the CNT and the ionic layer through a covalent grafting and to the ionic liquid cation and anion. Thus, the theoretical investigations demonstrated that the free energy of hydrogen adsorption on IL modified CNT decreased below 0 eV and thus enhance the proton adsorption. Contrarily to the previous work, the imidazolium is directly connected to the CNT causing rapid adsorption of protons and rapid transfer of electrons. In addition, the ionic liquid anion affects the HER performances by affecting the electron transfer efficiencies. Overall, a great care on selecting the chemical structure of the IL (cation and anion) should be considered to promote in an efficient way the HER.

Besides thin layer ionic liquid, polymer ionic liquids were also used to generate hybrid Poly(IL)/nanomaterial as electrocatalysts for HER. Thus, a new approach was reported based on the integration of electrocatalysts onto polymer ionic liquids modified electrode. Song and co-workers reported the $\text{NiS}_2\text{-MoS}_2$ generated on the poly(IL) functionalized graphene oxide nanosheets, which exhibited an excellent HER activity (-

active edge sites.

In another study, anionic MoS_4^{2-} was incorporated on polymer brushes structure, poly(dimethylaminoethyl methacrylate) through anion exchange reaction. Next, amorphous MoS_x was generated by electrochemical oxidation. The polymer brushes structure leads to orientate the 3D assembly of the catalyst. The highest electrocatalytic performance was recorded on sample generated by 20 min polymerization with a 10% grafting density of the initiator (Fig. 10.).⁸⁷

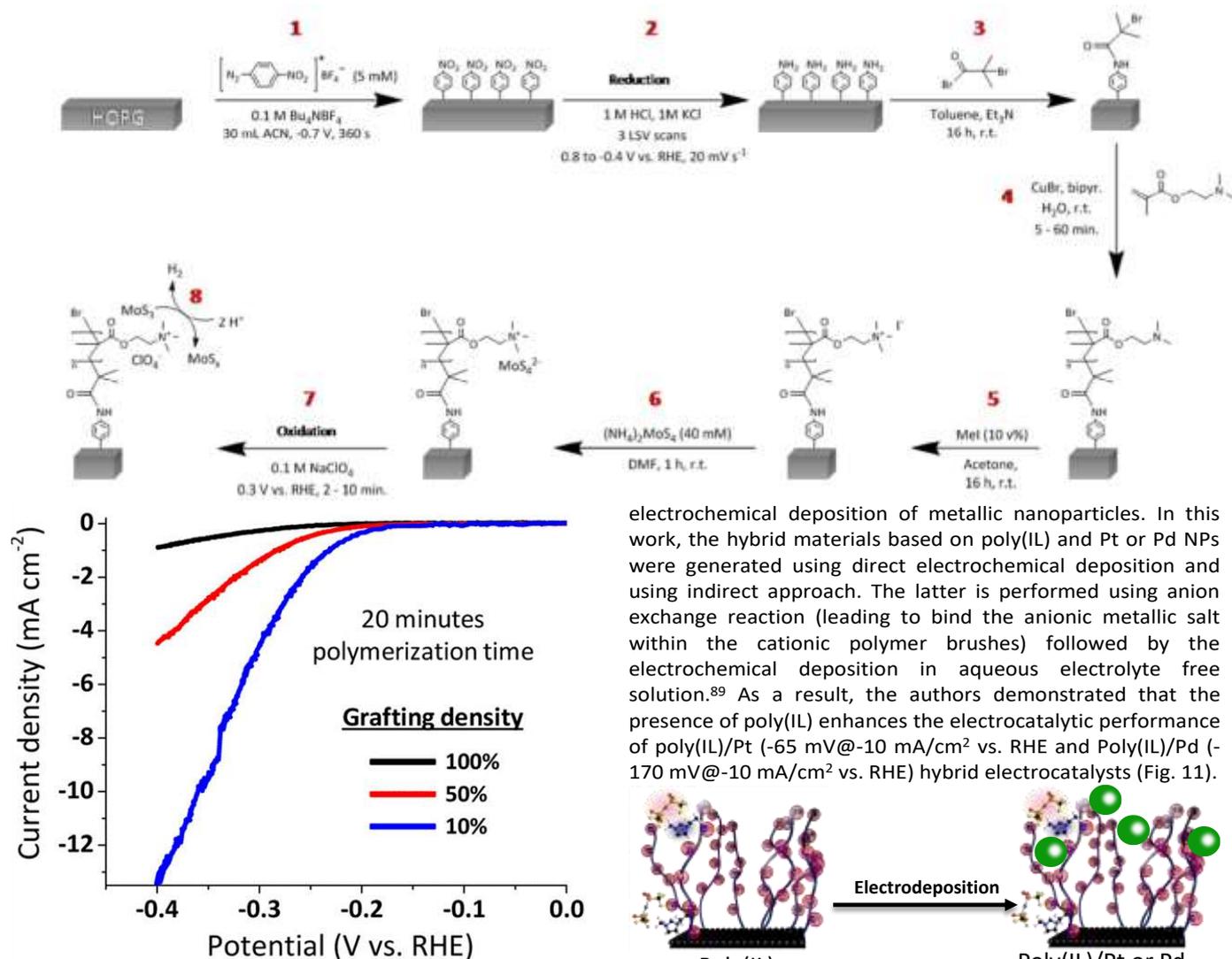


Fig. 10. Synthetic approach for the formation of MoS_x-polymer brush and the corresponding LSV scans in 1 M H₂SO₄. Reproduced from ref. 87 with permission from [American Chemical Society], copyright [2018].

The observed performances at low grafting density were attributed to several factors including, a higher catalyst loading, more accessibility of active sites leading to higher intrinsic activity (turnover frequencies of 1.3 and 4.9 s⁻¹ at overpotentials of 200 and 250 mV), the flexibility of the polymer chain and the increase of the interchain distance generating collapsed polymer chain conformation. However, the authors reported that at low overpotentials the generated current densities is relatively weak. Within this framework, Moutet and co-workers investigated the formation of structured hybrid cathode material using electrochemical deposition of molybdenum sulfide into a poly(pyrrole-alkylammonium) supported carbon electrode. The generated material displayed efficient electrocatalytic activity toward HER outperforming that of amorphous MoS_x deposited on bare carbon support. This enhancement has been ascribed to the homogeneous distribution of the catalyst.⁸⁸

Recently, Ghilane and co-workers reported an approach using the polymer brush structures, poly(1-allyl-3-methylimidazolium), as a platform for guiding the

electrochemical deposition of metallic nanoparticles. In this work, the hybrid materials based on poly(IL) and Pt or Pd NPs were generated using direct electrochemical deposition and using indirect approach. The latter is performed using anion exchange reaction (leading to bind the anionic metallic salt within the cationic polymer brushes) followed by the electrochemical deposition in aqueous electrolyte free solution.⁸⁹ As a result, the authors demonstrated that the presence of poly(IL) enhances the electrocatalytic performance of poly(IL)/Pt (-65 mV@-10 mA/cm² vs. RHE and Poly(IL)/Pd (-170 mV@-10 mA/cm² vs. RHE) hybrid electrocatalysts (Fig. 11).

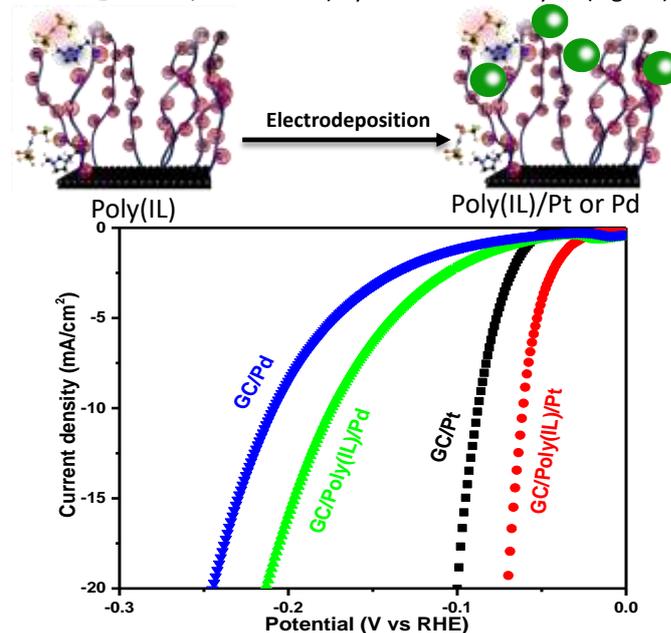


Fig. 11. Scheme illustrating the approaches for the formation of poly(IL)/Pt or Pd using direct and indirect approach and the corresponding LSV response in 0.5 M H₂SO₄. Reproduced from ref. 89 with permission from [American Chemical Society], copyright [2019].

This effect has been ascribed to the 3-D nanostructure, to the presence of nitrogen atoms in the imidazolium ring inducing a high electron density and as consequence favour hydrogen

adsorption and to the presence of a higher electron transfer between the catalyst and the electrode surface. In the same work, the author's report that the indirect approach, based on anion-capturing properties, leads to generate hybrid electrocatalysts with a low catalyst loading in the range of 10^{-2} $\mu\text{g}\cdot\text{cm}^{-2}$ (up to 2 orders of magnitude when compared to classical drop casting method) while maintaining a strong electrocatalytic activity toward HER. Overall, this part illustrates the potential of polymer brushes as a platform to control the 3D assembly of electrocatalysts and/or to boost the electrocatalytic performances.

Conclusions

Surface functionalization is not anymore the exclusive concern of a specific field, but a rich source of inspiration for academics and industrials. The immobilization of molecules containing ionic liquid framework provides new properties to the interface. This process is still in the earlier investigations and several fundamental questions related to the thin film organization, morphology, grafting density and the role of the ionic framework are still in debate. This review summarizes the different approaches related to the immobilization of ionic liquid moieties and their potential use to improve the electrocatalytic activity towards the hydrogen evolution reaction (HER). Interestingly, the use of immobilized ionic liquid as a platform for host-guesting a given electrocatalytic materials improves the catalytic activity of the hybrid materials towards the HER. This improvement has been attributed to the presence of synergistic effect between the ionic layer and the electrocatalyst materials. More precisely, it was found that the 3-D nanostructuring, the covalent immobilization, as well as the chemical composition (heteroatoms doping and electrostatic interactions) of the ionic layer are the key parameters that boost the electrocatalytic activities. The ability to synthesis various tasks specific ionic liquids (estimated around 10^5 ionic liquids) combined with the surface immobilization will open new opportunities for the design of novel interfaces. In the last decade, several works have been reported on ionic liquid modified materials. In the next stage, researches should focus on rational design of ionic liquids with efficient hydrogen evolution performance. As prospective direction, the development of high-performance ionic liquid composite materials and applications will move towards combination with materials-genome, artificial intelligence and machine learning. Small molecules task-specific ionic liquid can be predicted and designed by materials-genome as described in recent works.^{90,91} We anticipate that the grafted ionic layer on carbon-based materials will be the surface of choice in the field of electrochemical activation of small molecules.

Author Contributions

Hao-Zheng Yu: writing – original draft. Selma Bencherif: writing – original draft. Thuan-Nguyen Pham-Truong: writing – review & editing. Jalal Ghilane: conceptualization, writing – review & editing, and project administration.

Conflicts of interest

There are no conflicts to declare.

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