Recent Progress in the Application of Ionic Liquids in Electrochemical Oxidation and Reduction

Nan Yao and Yu Lin Hu*
College of Materials and Chemical Engineering, Key laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, P. R. China.
huyulin1982@163.com*

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Summary: Electrochemical oxidation and reduction, with clean power, are key to energy conversion and storage. For example, electrochemical oxidation is a determining step for fuel cells, combination of electrochemical oxidation and reduction can form a metal-air battery. Electrochemical oxidation and reduction make significant contributions to prepare valuable chemicals directly and improve yield efficiency and reduce the three wastes, which have become one of the green methodologies. Ionic liquids have attracted increasing attentions in the area of electrochemistry due to their significant properties including good chemical and thermal stability, wide liquid temperature range, considerable ionic conductivity, nonflammability, broad electrochemical potential window and tunable solvent properties. Up to now, abundant studies of ionic liquids have reported for their practical applications for electrochemical reactions. This review covers recent studies on the applications of ILs as green and universal replacements for the traditional reagents in electrochemical oxidation and reduction. The adaptabilities of ILs in these reactions are predicted as a solution to the problems of conventional electrochemical processes and to become a powerful method in electrochemical oxidation and reduction.

Keywords: Ionic liquids; Electrochemistry; Oxidation; Reduction; Application.

Introduction

The use of the electron as reagent in chemical reactions leads to advantages such as atom economy, energy conservation, high reaction selectivity, no auxiliaries, etc. The reaction conditions in electrochemistry are generally simple, the use of reagents is common and sufficient, molecular oxygen and water are mostly tolerated, and the reaction conditions are in accord with many rules of green chemistry [1]. Due to the low solubility of substrates in the traditional electrolyte, organic solvents should be added, which diminishes the ‘‘greenness’’ of the resulting procedures since the solvents need to be removed after the completion of reaction. In this regard, the replacement of the traditional electrolytes is necessary.

Since the commercial significance of methodology processes, the recovery and recycling of novel electrolytes assumes great importance from the point of environmental hazards and economic viability. Ionic Liquids (ILs), completely composed of ions, could be designed to possess a definite set of properties, and can be used both as the reaction media and the electrolyte [2-23]. Characteristic interesting properties of these liquid salts include good ionic conductivity, nonflammability, broad electrochemical window, low/negligible volatility and vapor pressure, and wide solubility, etc. Further, due to their wide liquid ranges, stability at high temperatures, easy recoverability and reusability, ionic liquids were assigned as a class of economic and environmental-friendly materials. As a result, ILs have been widely used in electrochemical science [23]. In recent years, the introduction of ILs to electrochemical systems has aroused great research concern [24], they could be used as modifying materials of electrodes for the fabrication of sensors [25-27] due to their performance of achieving electron transfer (DET) directly. Besides, ILs are also used as reagents such as binders [28-30], co-catalysts [30], stabilizer [31, 32], and nonaqueous electrolytes [33-36]. In light of the above-mentioned advantages of ILs, it is envisaged that ILs would exhibit more highly efficient electrocatalytic activity in the electrochemical process. In this review, we will focus on applications of ILs in electrochemical oxidation and reduction. The purpose of this article is to review the electrochemical catalytic applications of the ILs for some chemical reactions with a strong connection to the chemical industry.

*To whom all correspondence should be addressed.

Electrochemical oxidation

Electrochemical oxidation is the process by which incident electron enables a electrode material to promote a catalytic oxidation reaction. This green technology is simple to operate and can degrade many hazardous pollutants completely, which is proposed as an alternative for treating polluted wastes. Electrochemical oxidation has been successfully used for the treatment of wastewater, hydrogen production, and other applications. Shi *et al.* [37] prepared the Pt/IL1-IL2/GN nanocomposite electrocatalyst for methanol oxidation (Fig. 1). The prepared electrocatalyst exhibited highly catalytic activity and stability toward the oxidation of methanol. They found that Pt/IL1-IL2/GN electrolyte allowed the methanol oxidation occur at a less positive anodic potential with high activity compared to traditional Pt electrolyte. Hirano *et al.* [38] prepared the homogeneously alloyed bimetallic AuPd particles immobilized on an HOPG surface in IL (Fig. 2). The electrocatalytic activity of AuPd nanoalloy particles varied upon changing the fraction of Au and Pd in the particles. They found that alloy particles exhibited an Au fraction of *ca.* 0.61 in the oxidation, being higher than the activity of the pure Pt surface. Kwak *et al.* [39] demonstrated that combining anionic, redox-active Au_{25} clusters with imidazolium cations led to a stable ionic liquid possessing both ionic and electronic conductivity (Fig. 3). They found that Au_{25} ionic liquid acted as a versatile matrix for amperometric enzyme biosensors toward the detection of glucose. Lu *et al.* [40] investigated the direct electrochemistry and bioelectrocatalysis of the horseradish peroxidase (HRP) in three $[BF_4]$-type ILs (Fig. 4). It was certified that a small amount of water in ILs is indispensable for maintaining the electrochemical activity of HRP in Nafion films. Compared with the previous aqueous medium, the ionic liquid media could facilitate the direct electron transfer of HRP. Sugioka *et al.* [41] developed a strategy to prepare a bimetallic Au-Pt particle film through sequential sputter deposition of Au and Pt in IL (Fig. 5). The obtained Au-Pt particle films exhibited good catalytic activity for methanol electro-oxidation reaction superior to the activities of pure Au or Pt particles. Sahraie *et al.* [42] synthesized functionalized carbon hybrids obtained from nitrile-functionalized IL precursors and a ferric chloride mediator (Fig. 6). In particular, both the heteroatom type and iron were found to play crucial roles in improving the catalytic activity of functionalized carbon. The researchers noticed that sulfur–nitrogen codoped functionalized materials synthesized in the presence of ferric chloride showed high activity and stability.

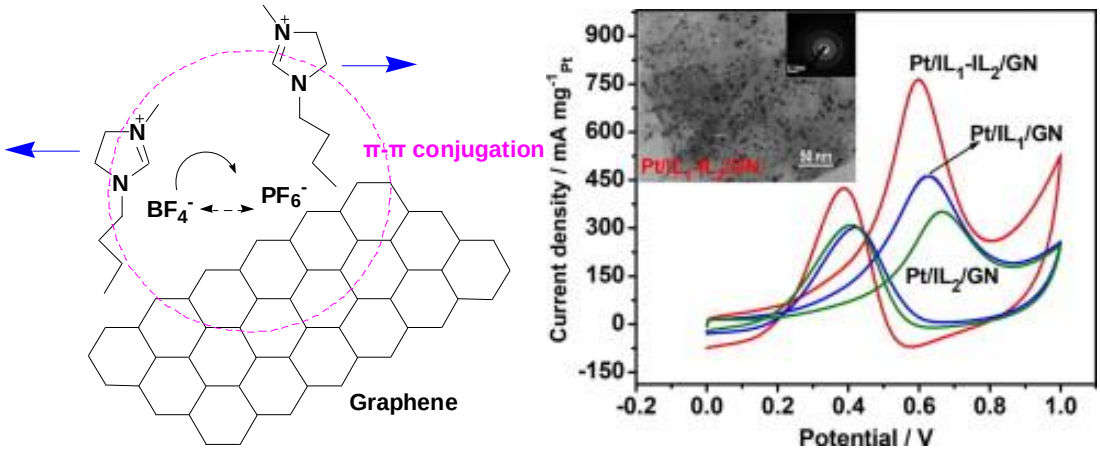


Fig. 1: Methanol oxidation catalyzed by Pt/IL1-IL2/GN.

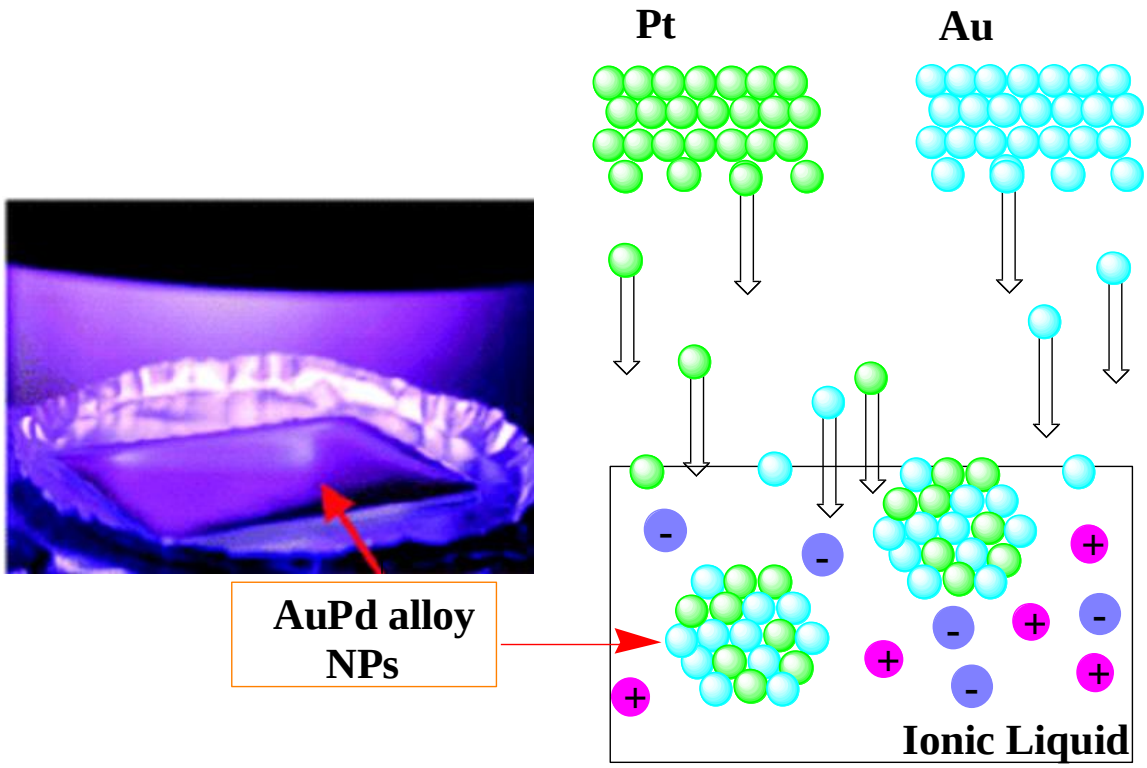


Fig. 2: AuPd NPs preparation and its catalytic activity for ethanol oxidation.

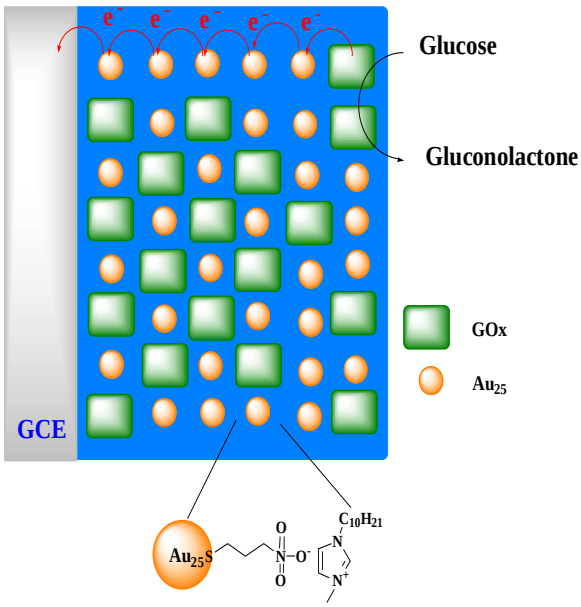


Fig. 3: Illustrative Au_{25} ionic liquid acted as a versatile matrix.

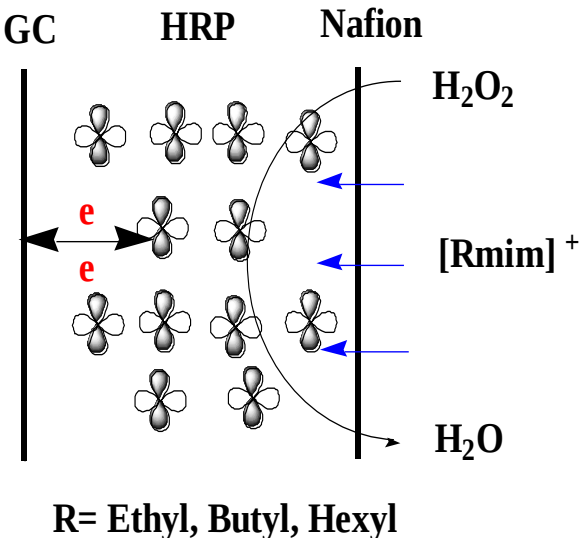


Fig 4: Illustrative of HRP for the detection of H_2O_2.

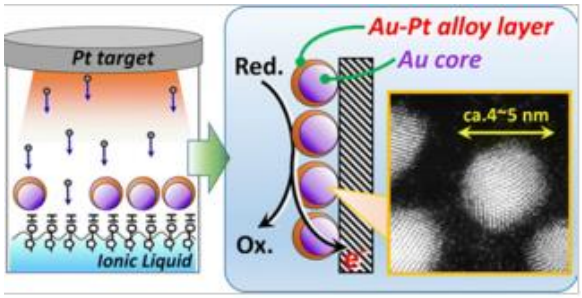


Fig. 5: Illustrative obtained Au-Pt particle for MOR.

Li *et al*. [43] fabricated the palladium-ILs-nitrogen-doped graphene nanocomposites as enhanced catalyst for ethanol electro-oxidation with graphene oxide as raw material and ILs as functional molecules (Fig. 7). They found that the catalyst exhibited good kinetics and catalytic performance, high tolerance and electrochemical stability toward ethanol oxidation. Compared with the previous systems, the present electro-catalytic system have several attractive features such as good kinetics, high tolerance and electrochemical stability, uperior electrocatalytic performance. Faisal *et al*. [44] studied the methanol electro-oxidation in [C_1C_2Im][OTf]-water on Pt(111) electrode and in IL [C_1C_2Im][OTf], respectively (Fig. 8). The results showed that it can modify the adsorption properties and the catalytic activity of the reaction after the addition of ILs. They found that the [C_1C_2Im][OTf] could show specific interactions in the catalyst surface and exhibited high activity in the oxidation. Seguraa *et al*. [45] studied the degradation of two representative ILs, [4mbp]Cl and [emim]Cl by electrochemical oxidation using AO-H_2O_2, electro-Fenton (EF) and photoelectro-Fenton (PEF) (Fig. 9). The results showed that the compounds underwent an almost total mineralization with 97% and 94% of dissolved organic abatement by the most powerful PEF at high current density.

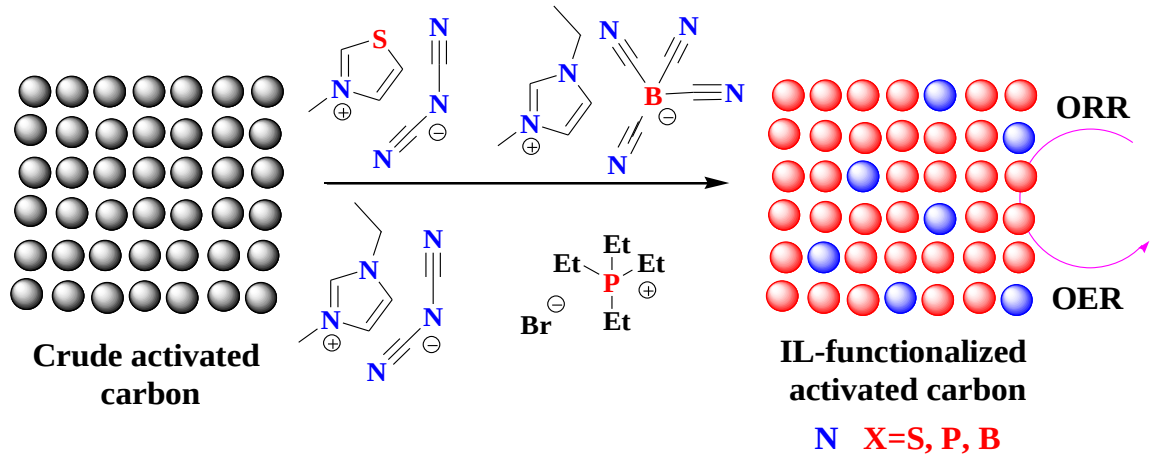
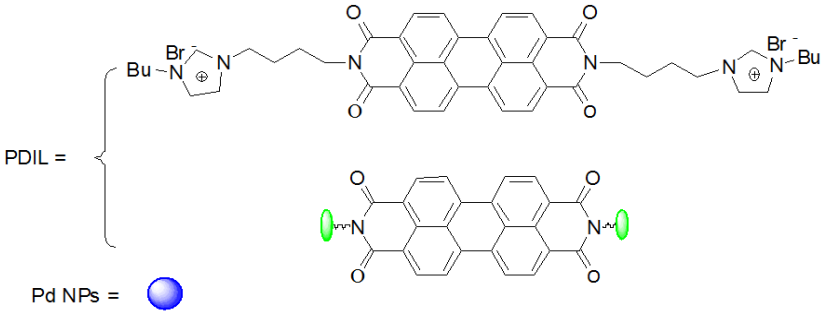


Fig. 6: Illustrative functionalized carbon hybrids toward the ORR.



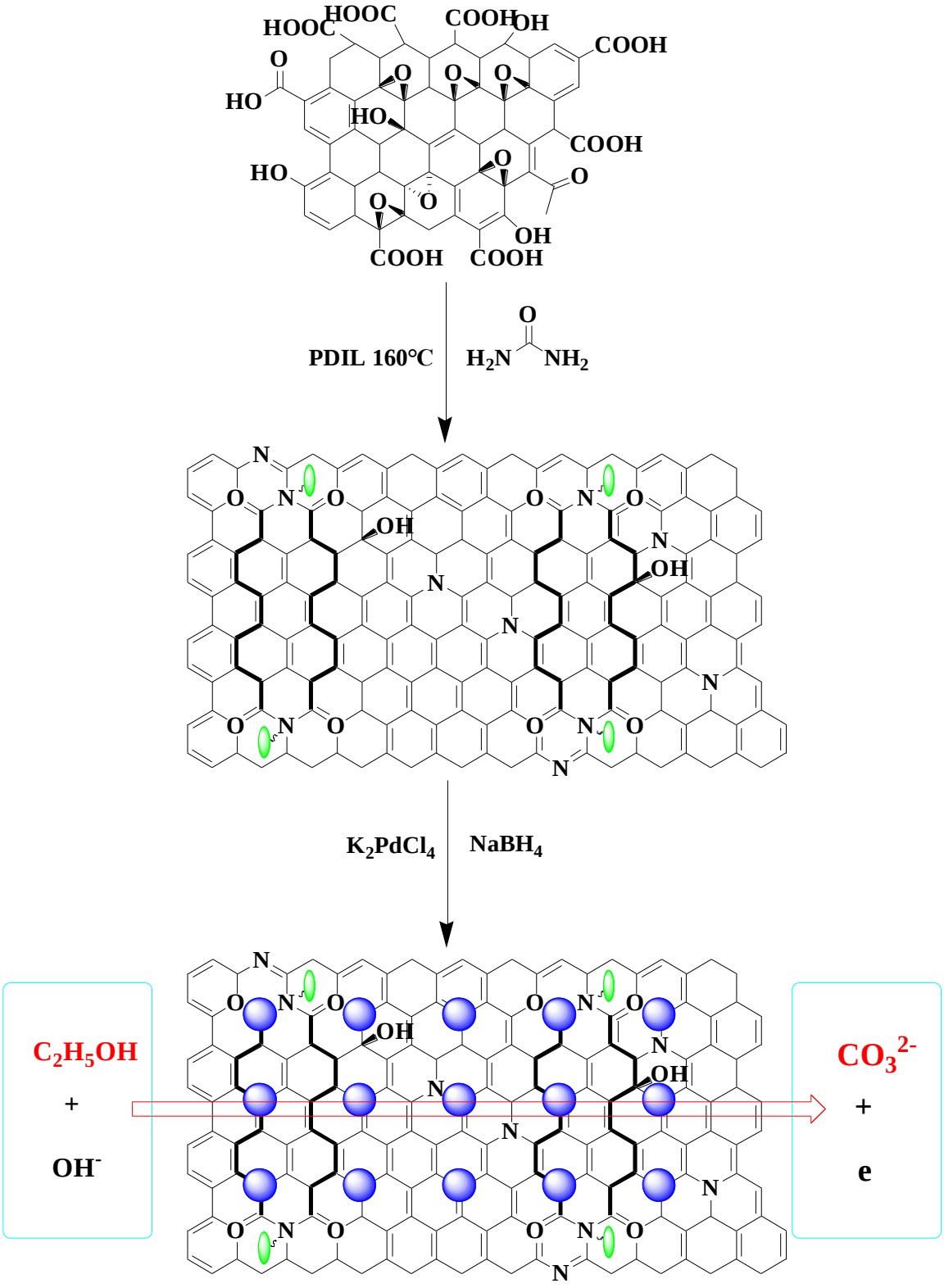


Fig. 7: Pd/PDIL-NGS catalyst for ethanol electro-oxidation.

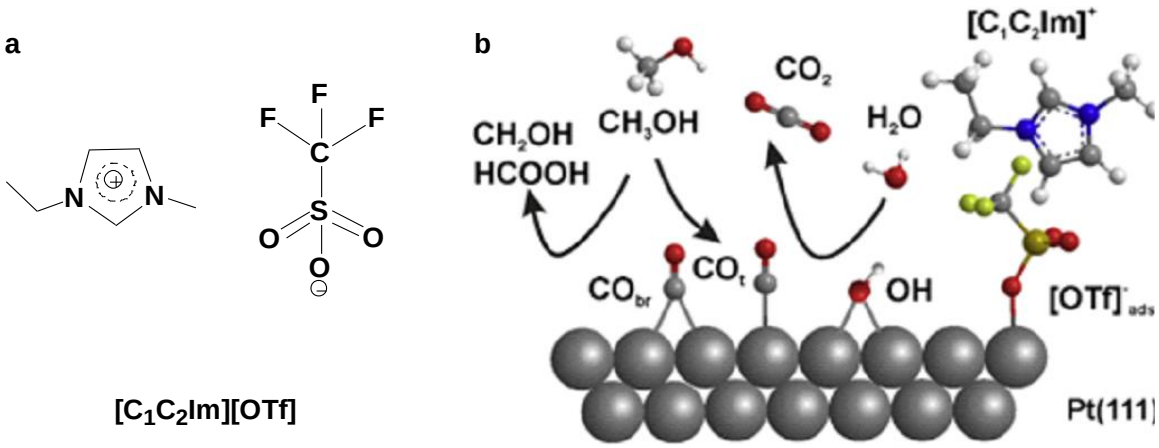


Fig. 8: Electro-oxidation of methanol in $[C_1C_2Im][OTf]$.

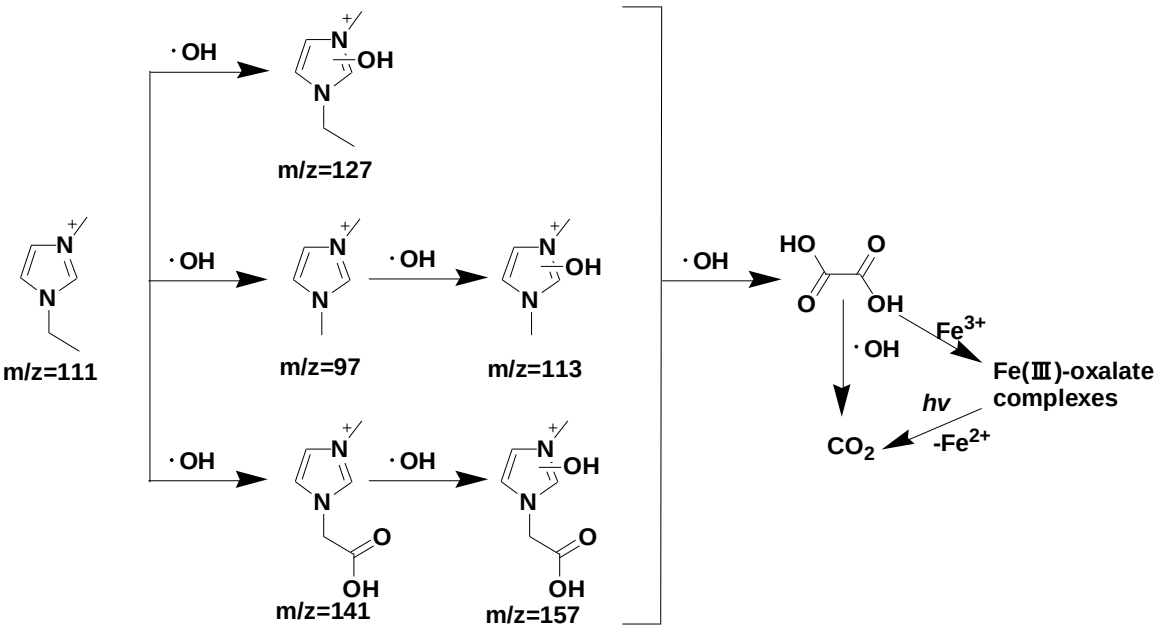


Fig. 9: Reaction process with AO-H_2O_2, EF and PEF.

Chen *et al.* [46] developed a novel sensor based on carbon nanotubes (MWCNTs)/ ILs and applied it for the recognition of propranolol (PRO) (Fig. 10). Compared with the previous system, the MWCNTs/IL sensor could facilitate the efficient electro-oxidation of PRO. The prepared sensor could be successfully applied in the determination of the enantiomeric purity of reagent, and the evaluation of waste water treatment efficiency. Afsharmanesh *et al.* [47] reported the synthesis of ZnO/CNT nanocomposite for the determination of morphine on an IL modified carbon paste electrode (Fig. 11). They found that the ZnO/CNTs/ILCPE could play a good voltammetric sensor and show high sensitivity and reproducibility. Daneshvar *et al.* [48] prepared a carbon IL electrode (CILPE) based on [bmim]NTf_2 modified with GR/MWCNT hybrid composite. The modified electrode GR/MWCNT/CILPE could be used for measurement of carbamazepine (CBZ) in the presence of paracetamol (PA) with an excellent electrochemical catalytic behavior (Fig. 12).

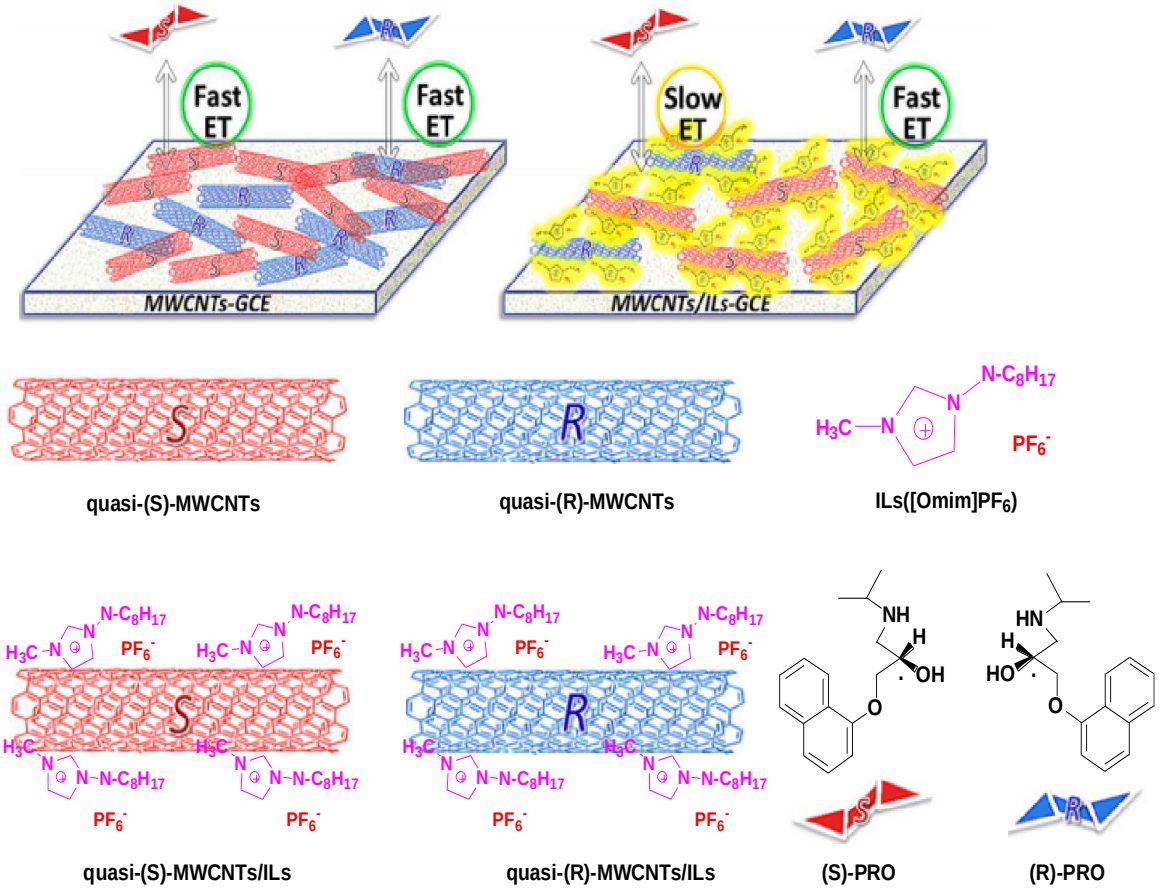


Fig. 10: MWCNTs/ILs nanocomposite based sensor for the recognition of PRO.

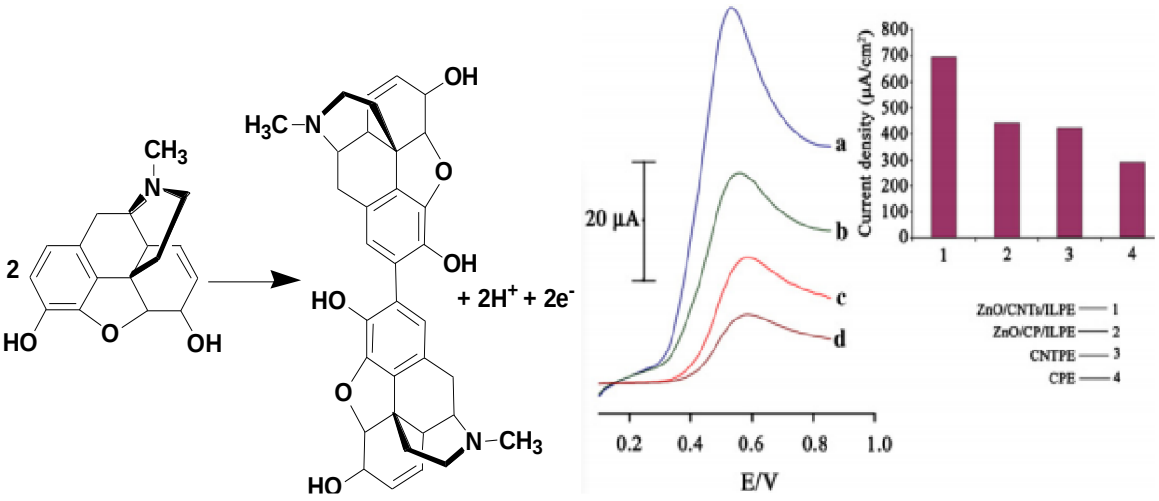


Fig. 11: The mechanism for electrooxidation of morphine.

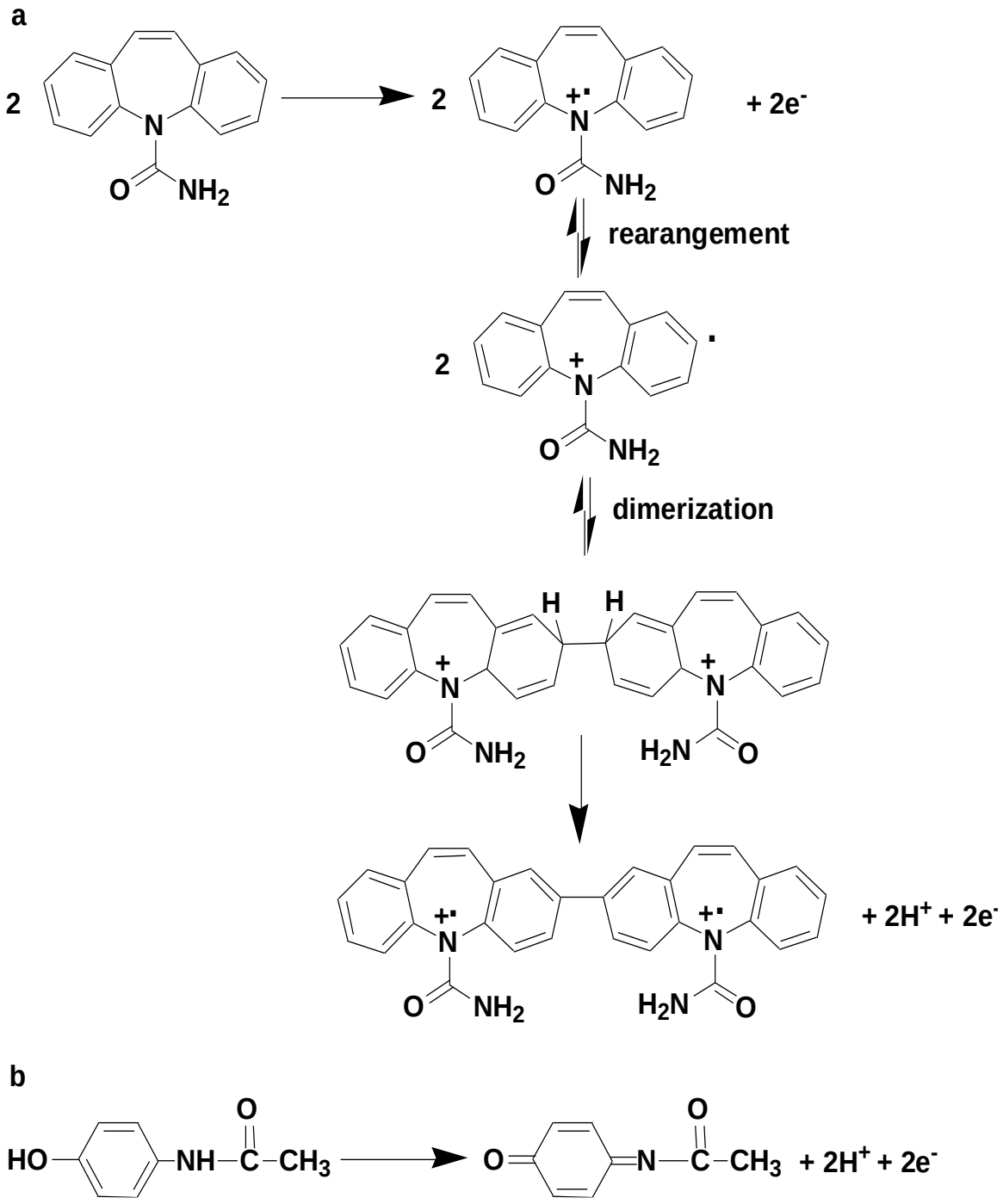


Fig. 12: Electrooxidation of CBZ and PA with GR/MWCNT/CILPE.

Soltani *et al*. [49] used modified electrode employing NiO nanoparticle (NiO/NPs) and IL BMITFB in the analysis of hydroquinone (Fig. 13). The results showed that, the electro-oxidation signal was increased to about 2.5 times on NiO/NPs/BMITFB/MCPE compared to CPE, which is an effective electrode. It was found that NiO/NPs/BMITFB/MCPE showed more effective in the oxidation and could be applied for the determination of HQ and water sample.

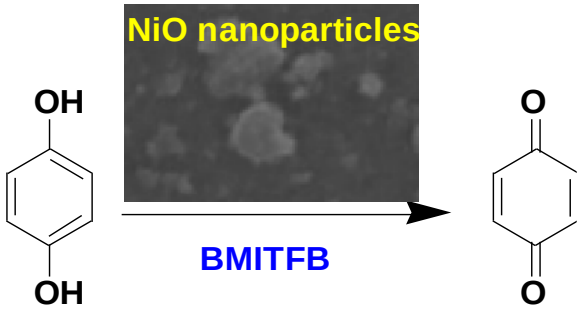


Fig. 13: Illustrative electrooxidation of HQ.

Majidi *et al*. [50] used room temperature ionic liquid [Amim][BF_4] to modify surface of carbon-ceramic electrode for simultaneous electrochemical determination of dopamine (DA) and acetaminophen (AP) (Fig. 14). The results showed that the prepared electrode could be successfully applied in the determination of DA and AP with satisfactory results. Similarly, Raoof *et al*. [51] also conducted the direct electro-oxidation of acetaminophen by using carbon paste electrode modified with ZnO nanoparticle (ZnO/NPs) and [Bmim]Cl with satisfactory results. Serr *et al*. [52] reported the preparation of magnetic CoPt nanorods depending on IL-in-water, bicontinuous (β) or water-in-IL (Fig. 15). The prepared nanorods showed a much enhanced electrocatalytic activity for methanol oxidation in comparison with compact Pt nanorods (up to 12 times) or Pt/C. Liu *et al*. [53] prepare the AuPd nanoparticles on graphene and then use as a catalyst in electro-oxidation of ethanol, which showed much higher catalytic activity compared with a Pd/C catalyst (Fig. 16).

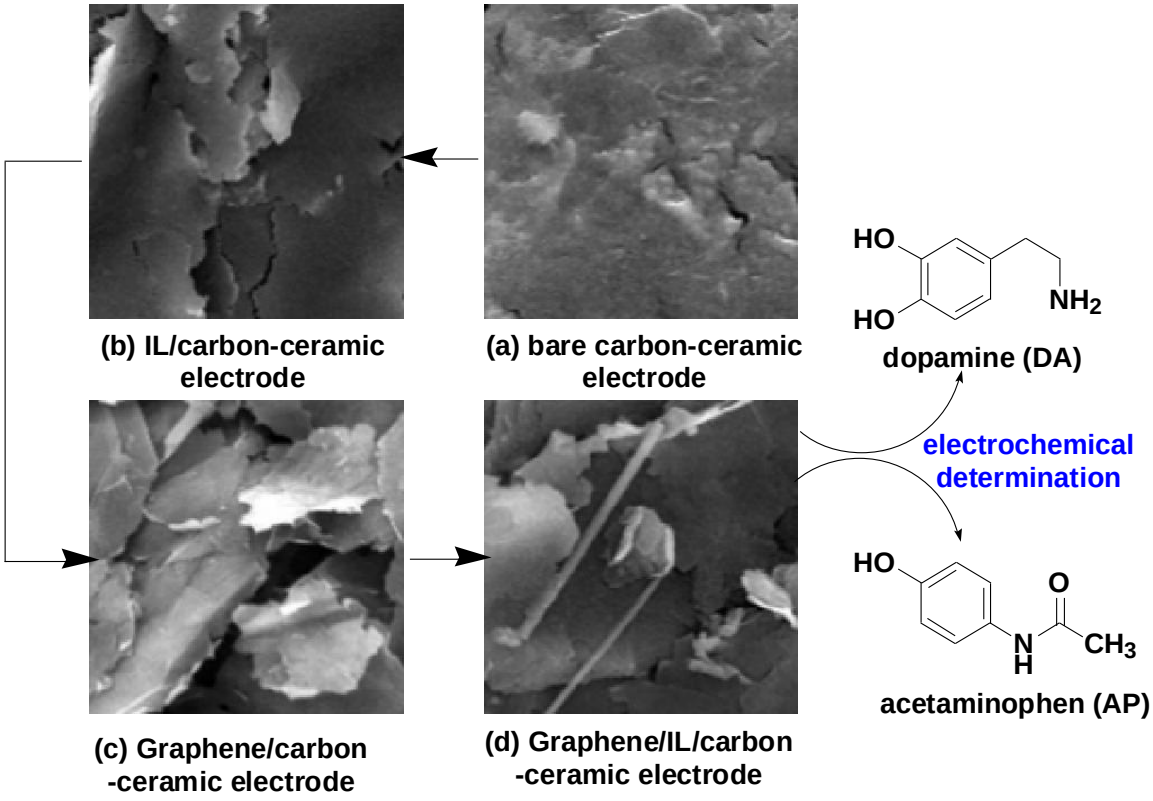


Fig. 14: Electrochemical determination of DA and AP in ILs.

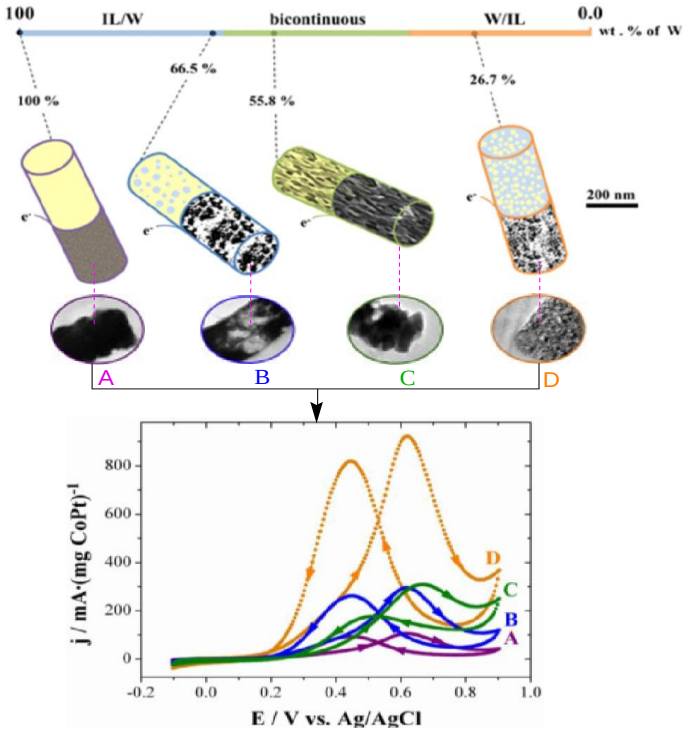


Fig. 15: Catalytic electro-oxidation of methanol.

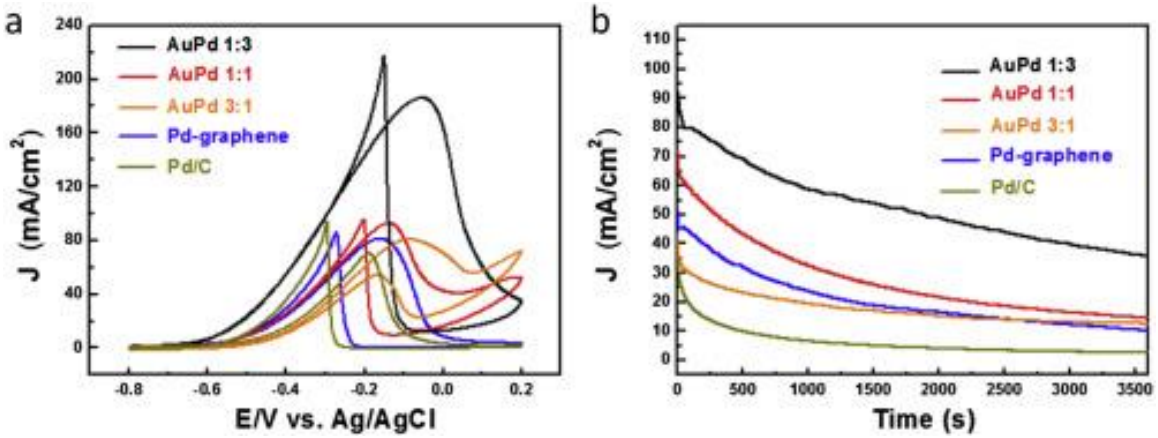


Fig. 16: Catalytic electro-oxidation of ethanol with AuPd NPs.

Maleha *et al.* [54] reported the fabrication of NiO/nanoparticles modified carbon IL paste electrode (IL/NiO/NPs/CPE) and investigated the electrochemical behavior of NADH (Fig. 17). They found that the electro-oxidation signal was increased to about four times on IL/NiO/NPs/CPE electrode compared to CPE. This method was highly selective, sensitive with a fast response for NADH analysis. Ensafi *et al.* [55] conducted the determination of morphine and codeine with Pt nanoparticles supported on silicon modified IL carbon paste electrode (Fig. 18), and they fuond that Pt/PSi nanocomposite in carbon IL electrode (CILE) had synergetic effect on the oxidation of morphine and codeine. The features of the modified IL carbon electrode include: high sensitivity, good reproducibility, low detection limit, and high synergetic activity.

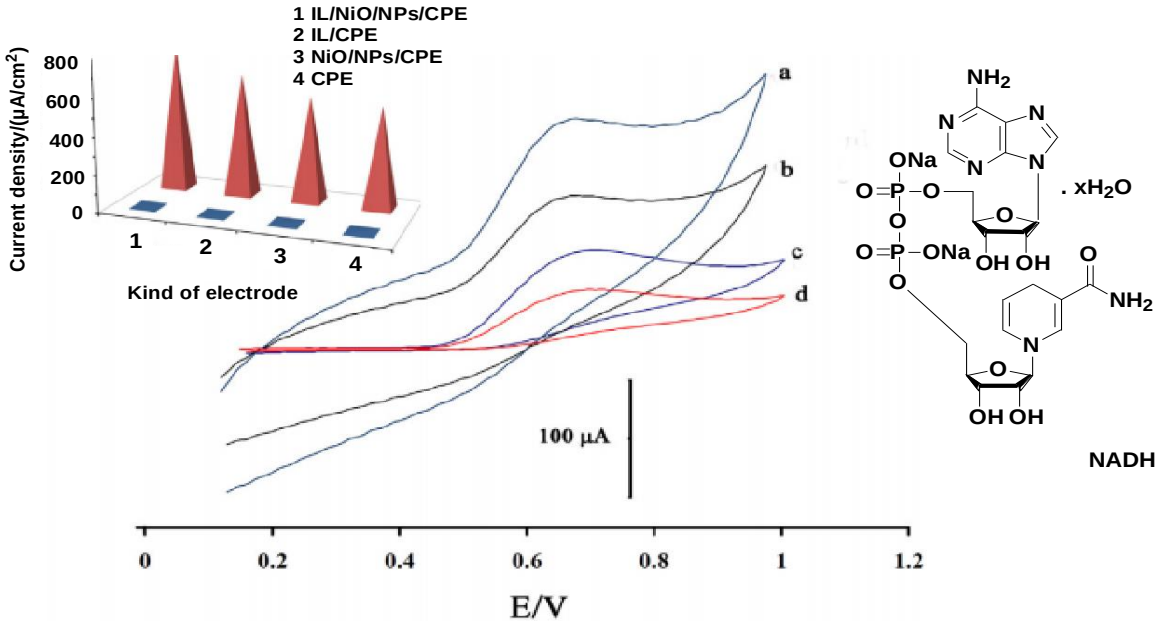


Fig. 17: Electrochemical behavior of NADH in IL.

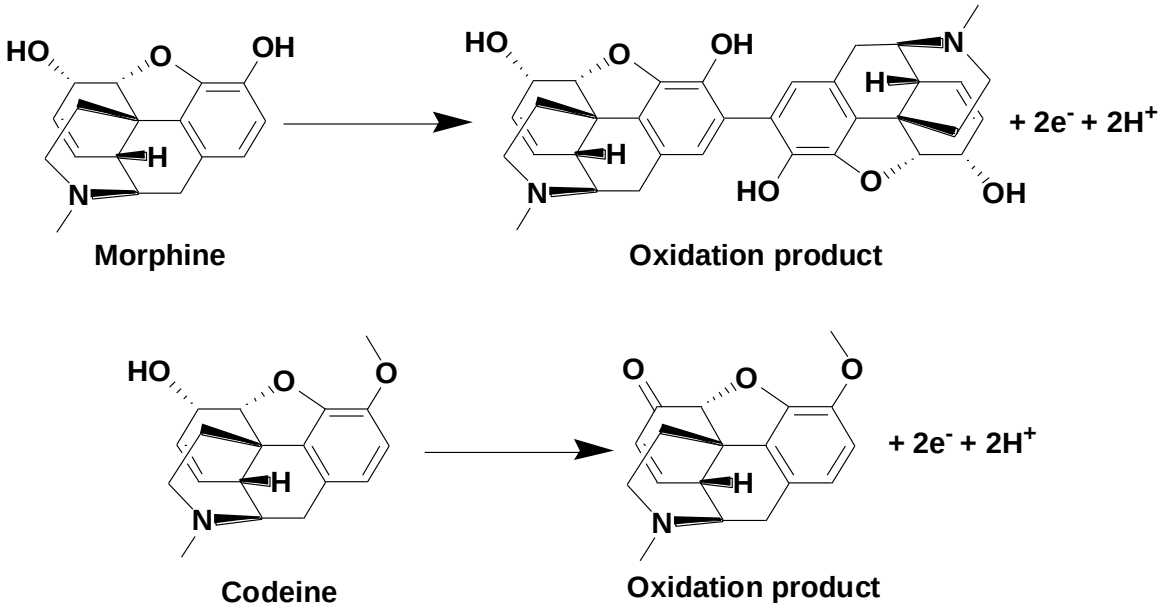


Fig. 18: Electroxoidation mechanism of morphine and codeine.

Shojaei *et al*. [56] developed the carbon paste electrode modified in situ with $ZnFe_2O_4$ magnetic nanoparticles ($ZnFe_2O_4$/MNPs) and IL [1,3-Pr_2im]Br for the determination of 5-fluorouracile (5-FU) (Fig. 19). They found that the electrode $ZnFe_2O_4$/MNPs/IL/CPE had some advantages such as high sensitivity, good detection limits and excellent reproducibility. Kaur *et al*. [57] synthesized the ILs including [Hmim][Cl], [Bmim][Cl], $[C_{16}H_{33}N(CH_3)_3][Br]$, $[C_{18}H_{37}N(CH_3)_3][Cl]$ coated Fe_3O_4 based inorganic-organic hybrid materials for the simultaneous determination of DNA bases (Fig. 20). The results demonstrated that Fe_3O_4/MIM modified electrode had higher catalytic activity toward the electro-oxidation of all DNA bases with good stability, sensitivity, selectivity and antifouling ability.

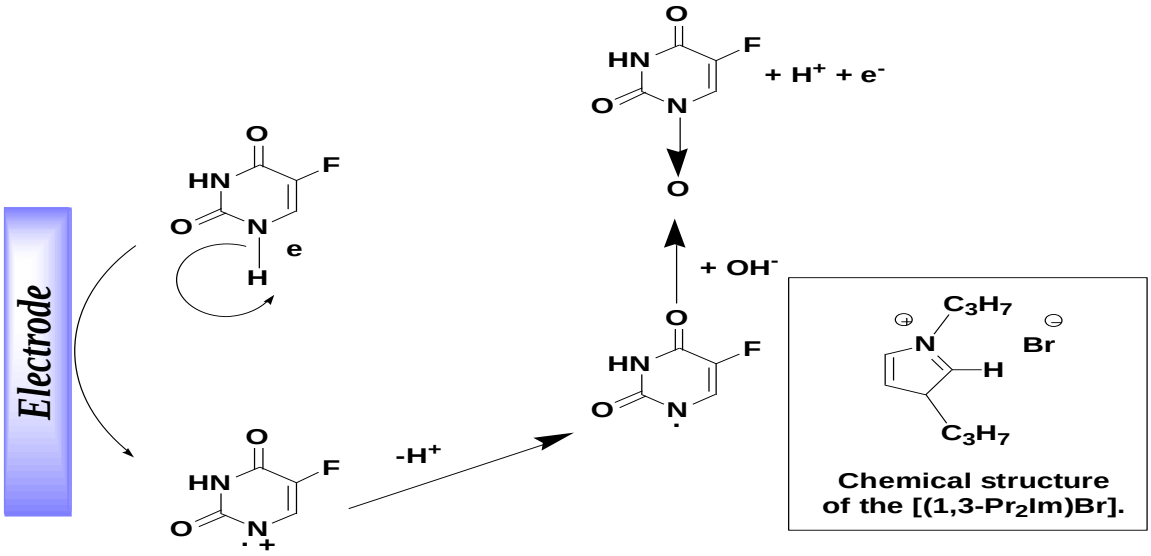


Fig. 19: Electro-oxidation of 5-FU with $ZnFe_2O_4$/MNPs/IL/CPE.

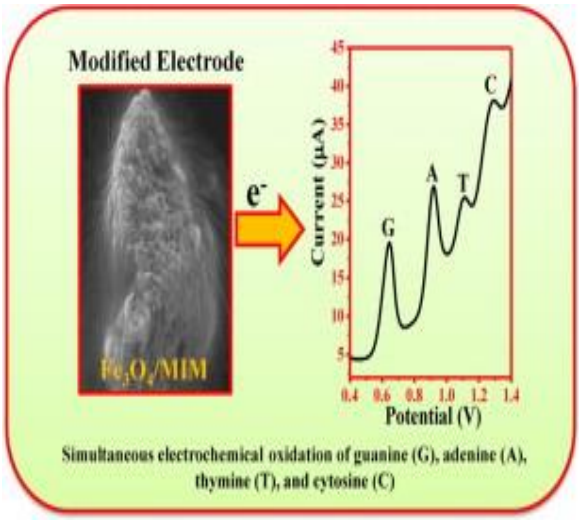


Fig. 20: Determination of DNA bases using ILs coated electrode.

Sun *et al*. [58] proposed a electrochemical method for the determination of adenosine-5-triphosphate (ATP) based on a chitosan (CTS) and graphene (GR) composite film modified carbon IL electrode (CTS–GR/CILE) (Fig. 21). They found that the prepared electrode had excellent reproducibility, stability, anti-interference ability.

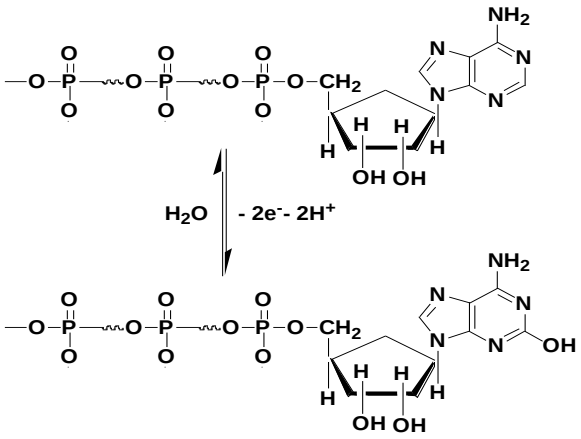


Fig. 21: The electrochemical oxidation mechanism of ATP.

Zhan *et al*. [59] used the synthesized electrochemical sensor based on ILs-LDH modified glass carbon electrode (GCE) for bisphenol A (BPA) determination (Fig. 22). The results showed that ILs-LDH/GCE had excellent electro-oxidation ability toward BPA with an acceptable reproducibility, good stability and high sensitivity. Shan *et al*. [60] carried on the electrochemical determination of NADH and ethanol based on IL-functionalized graphene. The resulting biosensor showed rapid, stable, and highly sensitive amperometric response to NADH and ethanol with a low detection limit (Fig. 23).

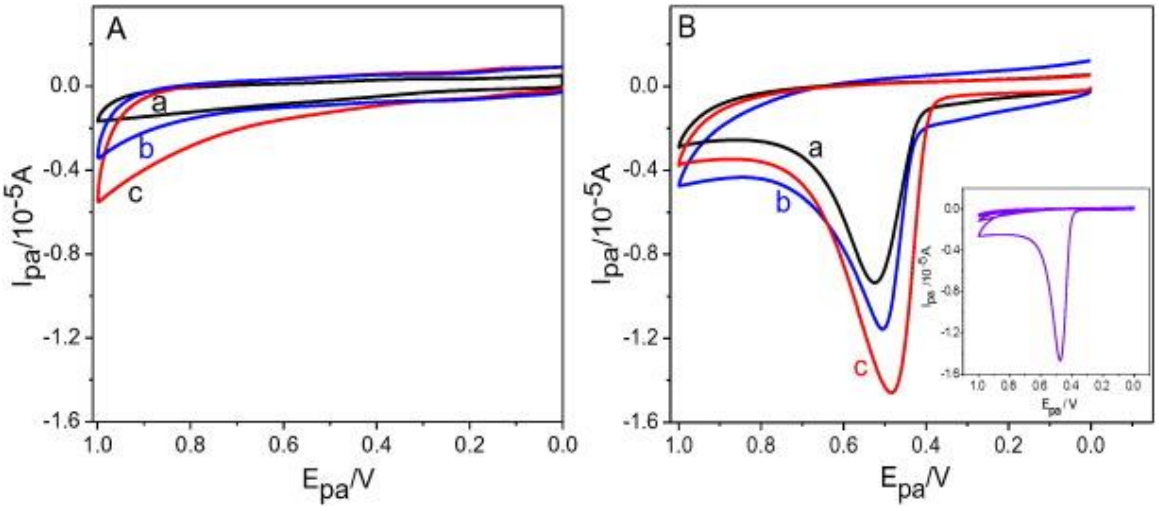


Fig. 22: Electrochemical behaviors of BPA.

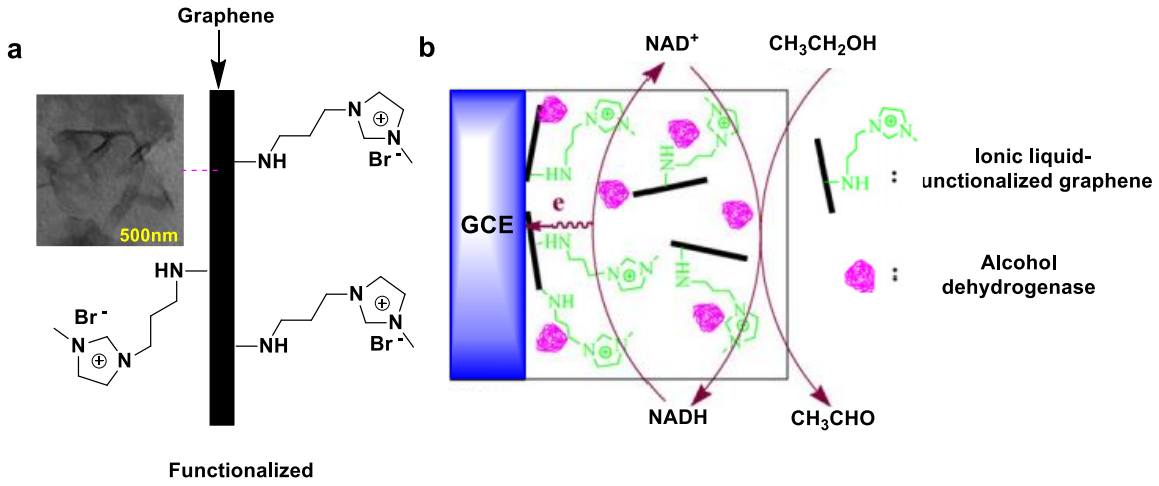


Fig. 23: Schematic representation for the bioelectro-catalytic sensing of ethanol.

Berton *et al*. [61] investigated the potential of silicon nanowires (SiNWs) as electrode material for large-voltage window micro-supercapacitors (Fig. 24). An ionic liquid electrolyte (EMI-TFSI) was used in order to prevent the etching of silicon electrodes. Electrochemical oxidation of silicon surface at high anodic potentials led to an extended operating voltage range (up to 4 V) and slightly enhanced specific capacitance of silicon electrodes. The research demonstrated the ability of SiNW electrodes to operate at high frequency and obtained a specific power of 472 μWcm^{-2}.

Valentini *et al*. [62] synthesized the new nano-gels based on graphene and ILs, and used for the assembly of chemically modified carbon paste electrodes (Fig. 25). They found that the alkaloid molecule could be successfully detected with high sensitivity, excellent reproducibility and a fast response time. Ardakani *et al*. [63] used carbon-paste electrode modified with DBC, IL and carbon nanotube for the determination of hydrazine (Fig. 26). They found that the DBC-IL/CNPE over CP electrode had some advantages such as high conductivity, high sensitivity and selectivity, reproducibility and fast electron transfer.

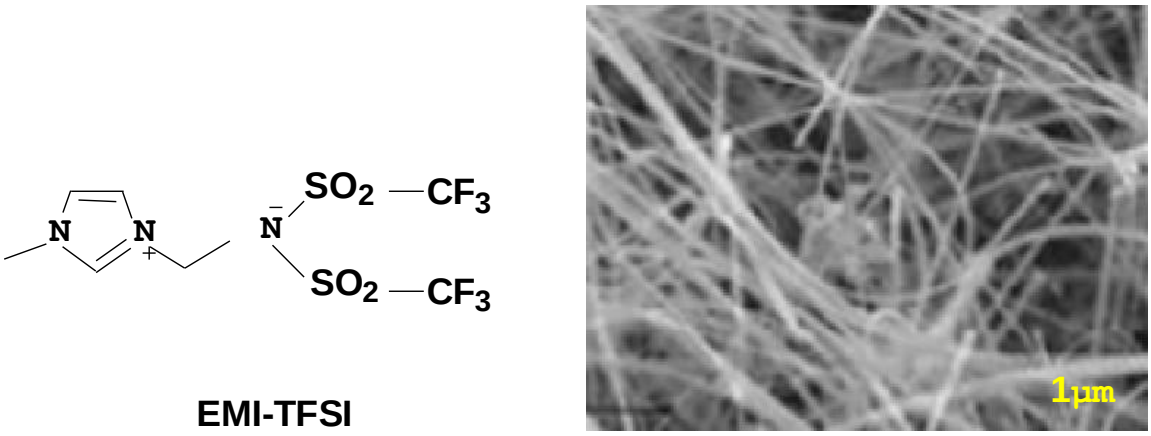


Fig. 24: SEM images of 20 μ-SiNW electrode after repeated CV cycling in EMI-TFSI.

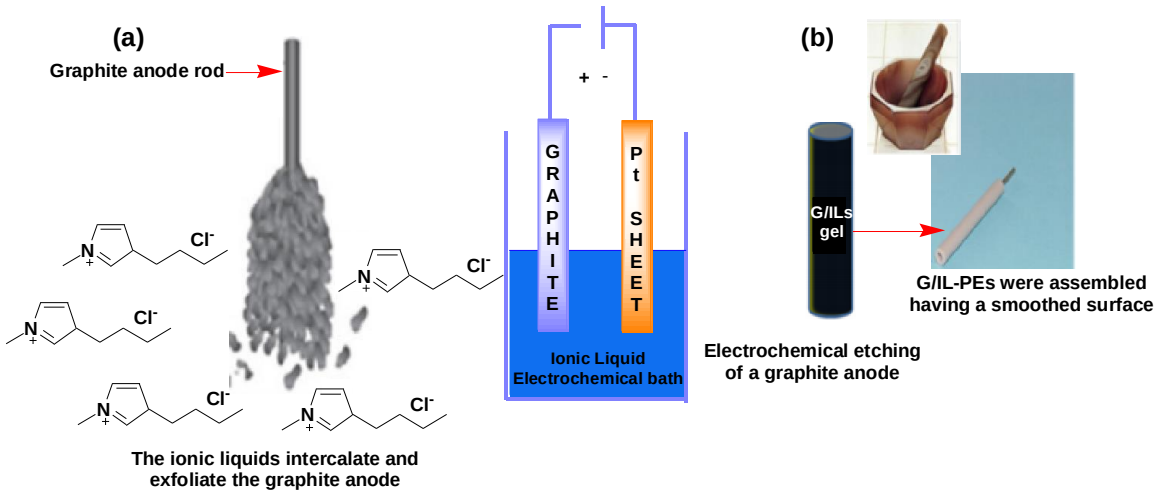


Fig. 25: Electrochemical oxidation of caffeic acid in ILs.

Ardakani *et al*. [64] reported the synthesis and application of DDF-CNT-TiO /IL/GC electrode as high sensitive sensors for simultaneous determination of isoproterenol (IP) and serotonin (5-HT) using glassy carbon electrode (Fig .27). They found that the electrocatalytic activity of the modified electrode could be dramatically enhanced in the oxidation compared to the DDF-CNT-TiO electrode. As a result, dramatically enhanced catalytic activity for the electrooxidation of IP and 5-HT was achieved. Serrà *et al*. [65] synthesized CoNi-Pt Core@Shell stable mesoporous nanorods with very high active surface for methanol electro-oxidation (Fig. 28). The results showed that mesoporous CoNi@Pt nanorods demonstrated much better performance for methanol oxidation, which possessed good stability and significant electrocatalytic stability under the reaction conditions. Kaur *et al*. [66] synthesized ILs coated nanocrystalline zeolite based inorganic-organic hybrid materials modified electrodes for the simultaneous determination of all four DNA bases (Fig. 29). They found that the analytical performance of the proposed method demonstrated in the simultaneous determination of all four DNA bases in calf thymus DNA sample.

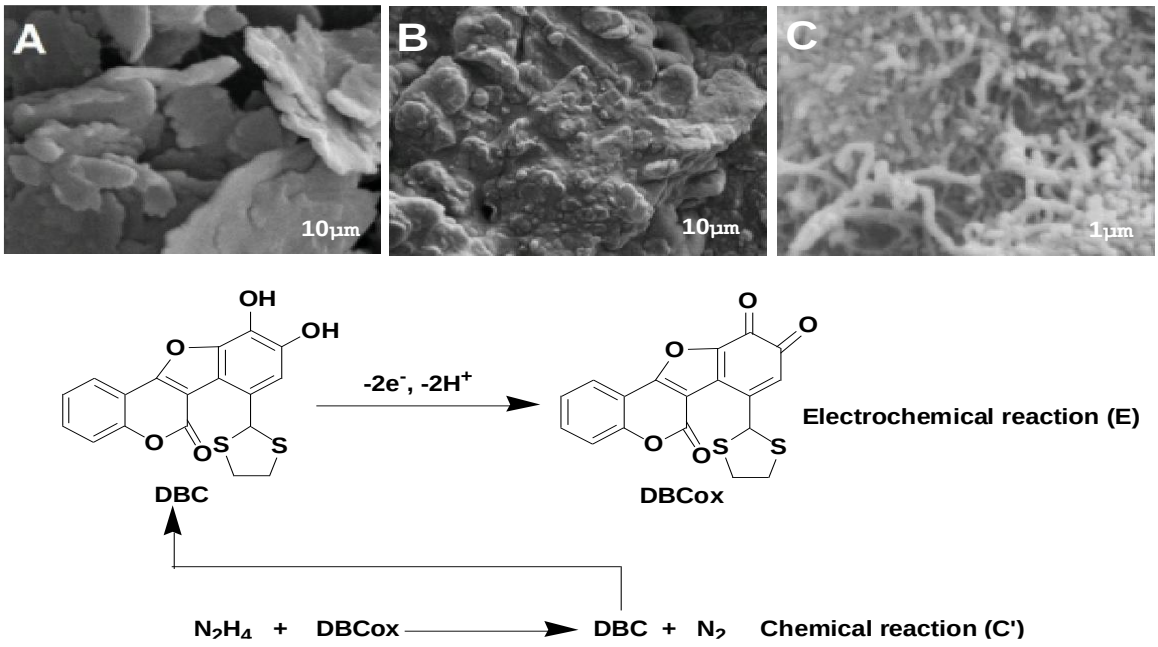


Fig. 26: Electrocatalytic reaction of hydrazine with DBC IL/CNPE.

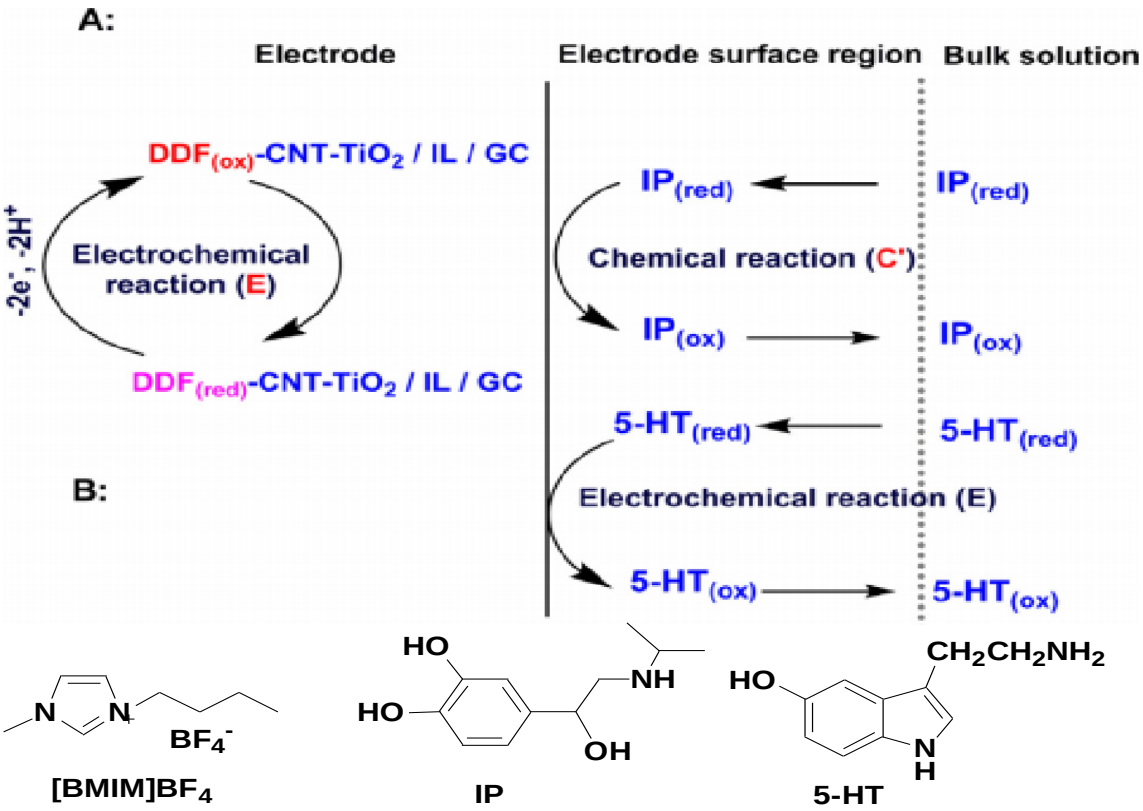


Fig. 27: Electrocatalytic oxidaiton of 5-HT with DDF-CNT-TiO_2/IL/GC electrode.

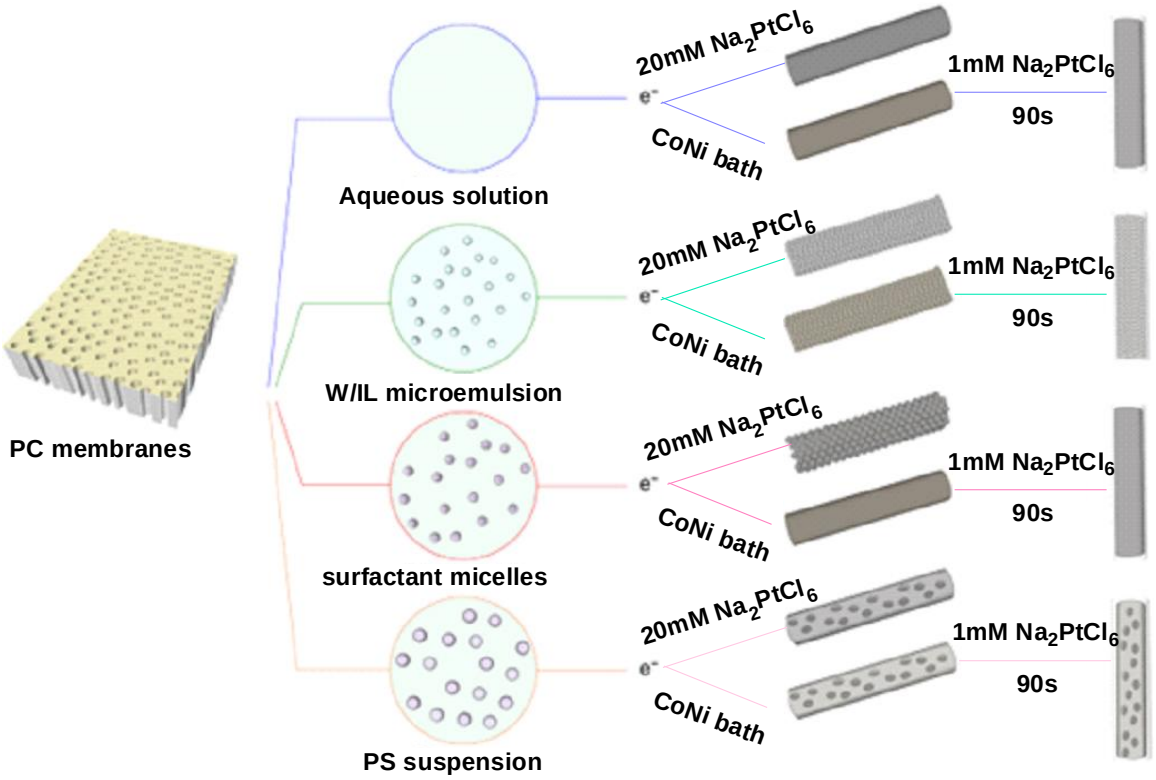


Fig. 28: Methanol electro-oxidation using eight types of nanorods.

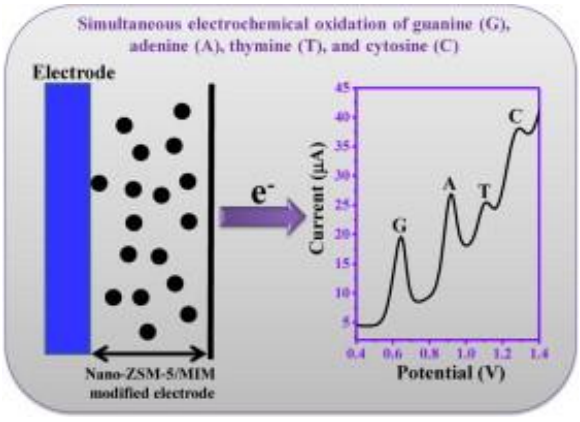


Fig. 29: Determination of DNA bases using ILs coated Nano-ZSM-5.

Tran *et al*. [67] synthesized PtNPs whose size and shape were controlled by plasma reduction time in IL under atmospheric pressure plasma (Fig. 30). They found that the PtNPs could be use as excellent electrochemical catalysts for the methanol oxidation, the PtNPs with a 10 min plasma reduction time showed better catalytic performance in the forward sweep and lower catalytic performance in the backward sweep than the long reduction time. Ni *et al*. [68] prepared N-doped mesoporous carbon-supported CoO@Co nanoparticles in situ using IL $[Bmim]_2[CoCl_4]$ as the precursor with silica as the hard template (Fig. 31). They found the catalyst showed superior activity for oxygen evolution reaction (OER) manifested in its lower charge potential. The features of the modified CoO@Co nanoparticles include: coulombic efficiency, rate capability, cycling stability (55 cycles), and high catalytic activity.

Our group developed the synthesis of lactones and esters involving the application of an molecular oxygen-based electro-catalytic oxidation system and ionic liquid [bmim][OTf] as electrolyte [69]. The reaction between various ketones with molecular oxygen proceeds in a three-electrode cell under constant current conditions in [bmim][OTf] to give the corresponding esters and lactones in good to high isolated yield (Fig. 32). Compared with the previous catalytic systems, the present catalytic system have several attractive features such as good to excellent yields, high catalytic activity and selectivity, environmentally benign and safe. Zahran

et al. [70] reported the simple synthesis of crystalline α-Mn2O3 and calcium-incorporated manganese oxide (CaMn-oxide) thin film composite catalyst electrodes on a fluorine-doped tin oxide (FTO) electrode (FTO/EMI α-Mn2O3 and FTO/EMI CaMn-oxide) in ionic liquid [Emim]OTf (Fig. 33). They found that the electrocatalysts could be use as excellent electrochemical catalysts for the water oxidation at a very low energy cost

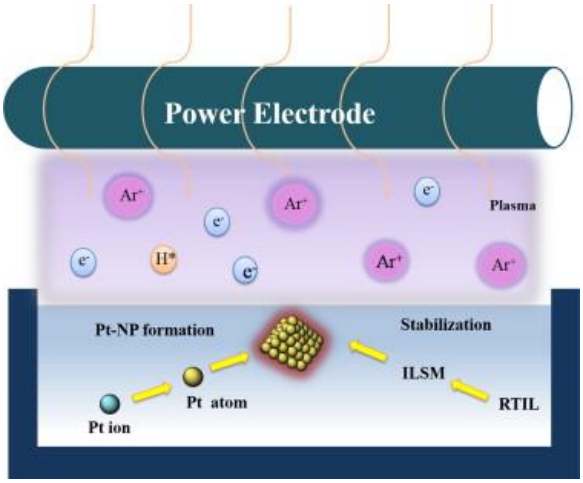


Fig. 30: Electrochemical oxidation of methanol using PtNPs.

Electrochemical reduction

Electrochemical reduction technology has also received major attention in recent years due to its many advantages over other reaction processes. Li *et al*. [71] reported a method for electrochemical determination of iron based on the ionic liquid-reduced graphene oxide (IL-rGO) supported gold nanodendrites (AuNDs) (Fig. 34). The IL-rGO/AuNDs/Nafion modified electrode showed good responses for iron ions. They found that the modified electrode had a good anti-interference ability and showed a remarkable increase of the catalytic activity in the determination of iron in coastal waters.

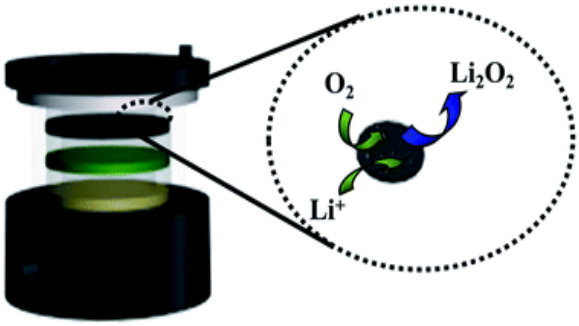


Fig. 31: Illustrative prepared CoO@Co nanoparticles for oxygen evolution reaction.

Zhou *et al*. [72] examined the electrochemical reduction of CO_2 using a Ag-modified Cu catalyst cathode in a series of mixed ILs in the presence or absence of $CoCl_2$ (Fig. 35). The results showed that the Ag-modified Cu electrode in $[Emim]BF_4$+$[Bmim]NO_3$ with $CoCl_2$ exhibited excellent synergy for the electrochemical reduction of CO_2 to CO with a stable area specific activity, and the selectivity of CO was 98%.

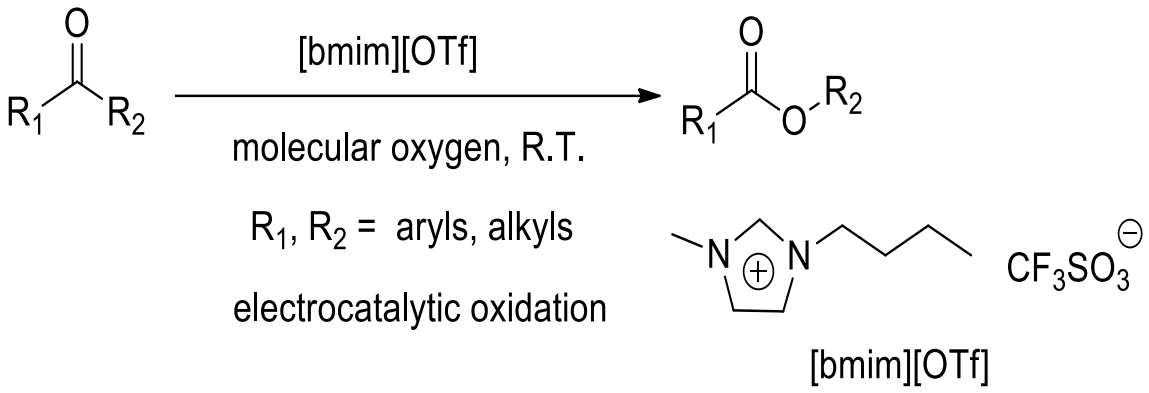


Fig. 32: Baeyer–Villiger electro-oxidation of ketones.

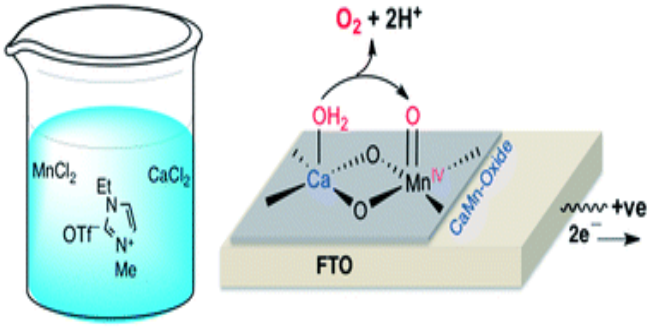


Fig. 33: Low-cost and energy-efficient electrocatalytic water oxidation.

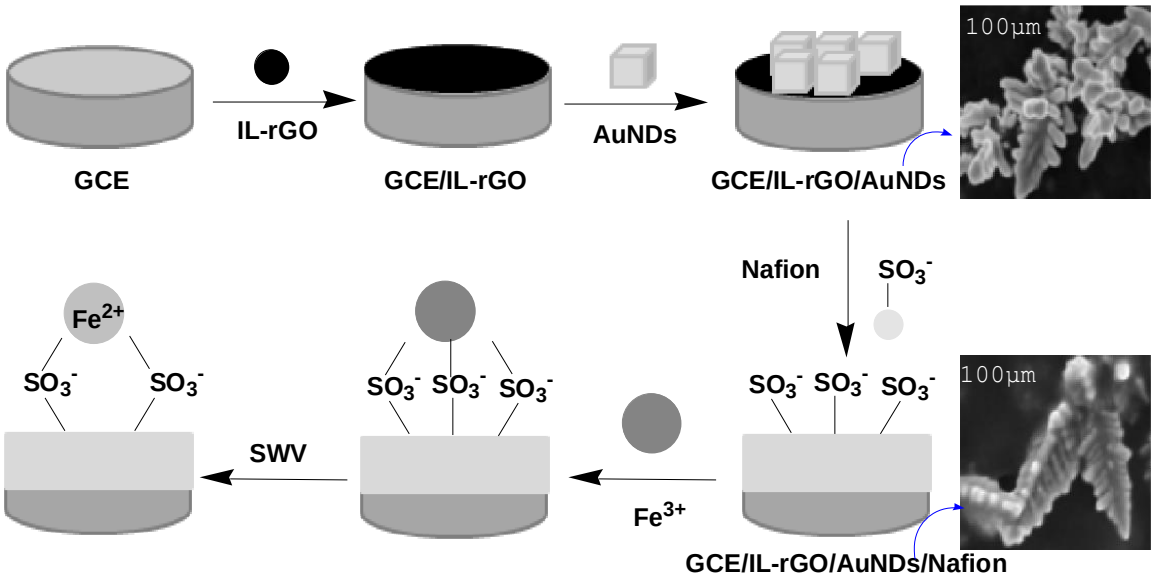


Fig. 34: Schematic illustration of the stepwise self-assembly procedure.

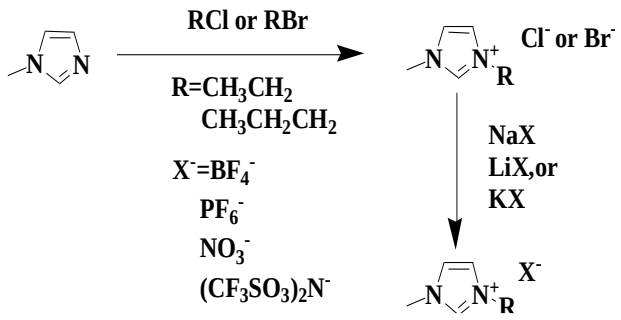


Fig. 35: Illustrative synthesis route of different ionic liquids.

Zhu *et al.* [73] reported selective electrocatalytic reduction of carbon dioxide to carbon monoxide on gold nanoparticles (NPs) (Fig. 36). Among monodisperse 4, 6, 8, and 10 nm NPs tested, the 8 nm Au NPs showed the maximum Faradaic efficiency (FE) (up to 90% at −0.67 V vs reversible hydrogen electrode, RHE). This study provides a new and highly efficient catalytic system for elective electrocatalytic reduction of CO_2 to CO.

Sun *et al.* [74] fabricated the

electrochemical sensor denoted as Nafion/ Mb/ NiO/ GR/CILE. The direct electron transfer of Mb was realized and promoted due to the presence of the NiO/GR nanocomposite on the electrode (Fig. 37). The Mb modified electrode showed an excellent catalytic activity towards the electroreduction of different substrates including trichloroacetic acid and H_2O_2. Besides, the Mb biosensor based on NiO/GR/CILE was constructed with good stability and reproducibility. Carlesi *et al.* [75] developed a method of carbon dioxide-to-methanol via direct electrochemical conversion mediated by IL $[pamin]^+[br]^-$. The results showed that this procedure had good absorption capacity, high ionic conductivity, high chemical–electrochemical stability and enhanced the ability of electrochemical reduction of absorbed CO_2 (Fig. 38).

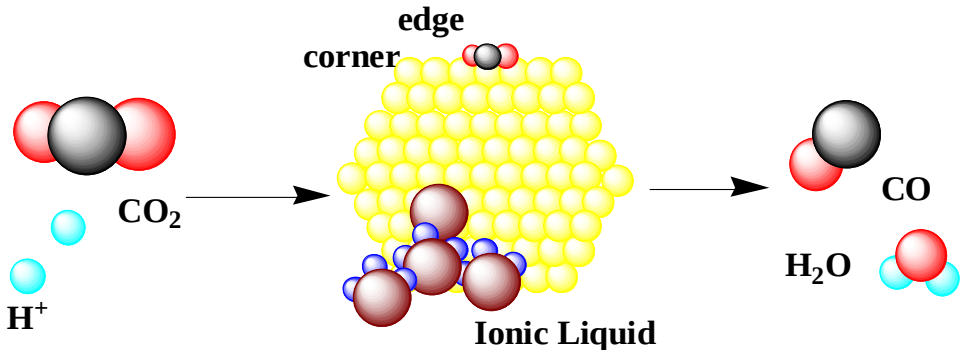


Fig. 36: Electrocatalytic reduction of CO_2 to CO on NPs.

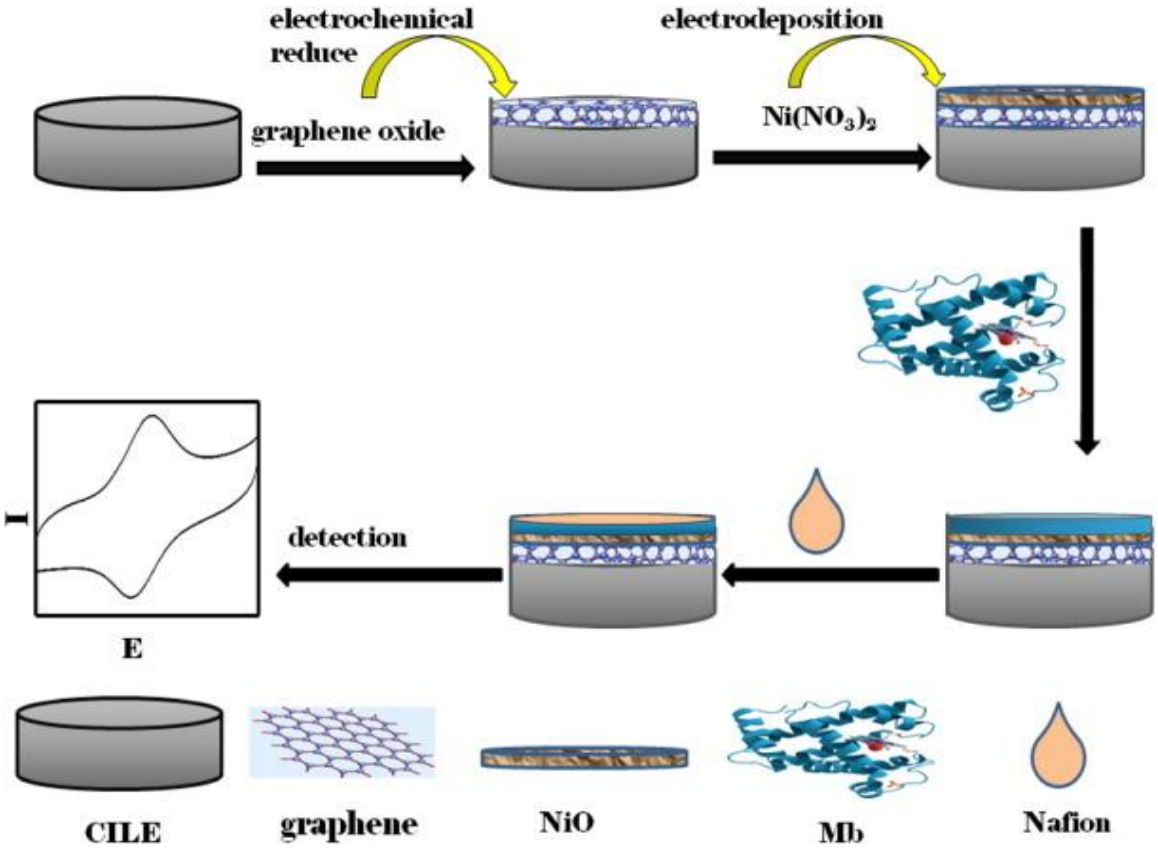
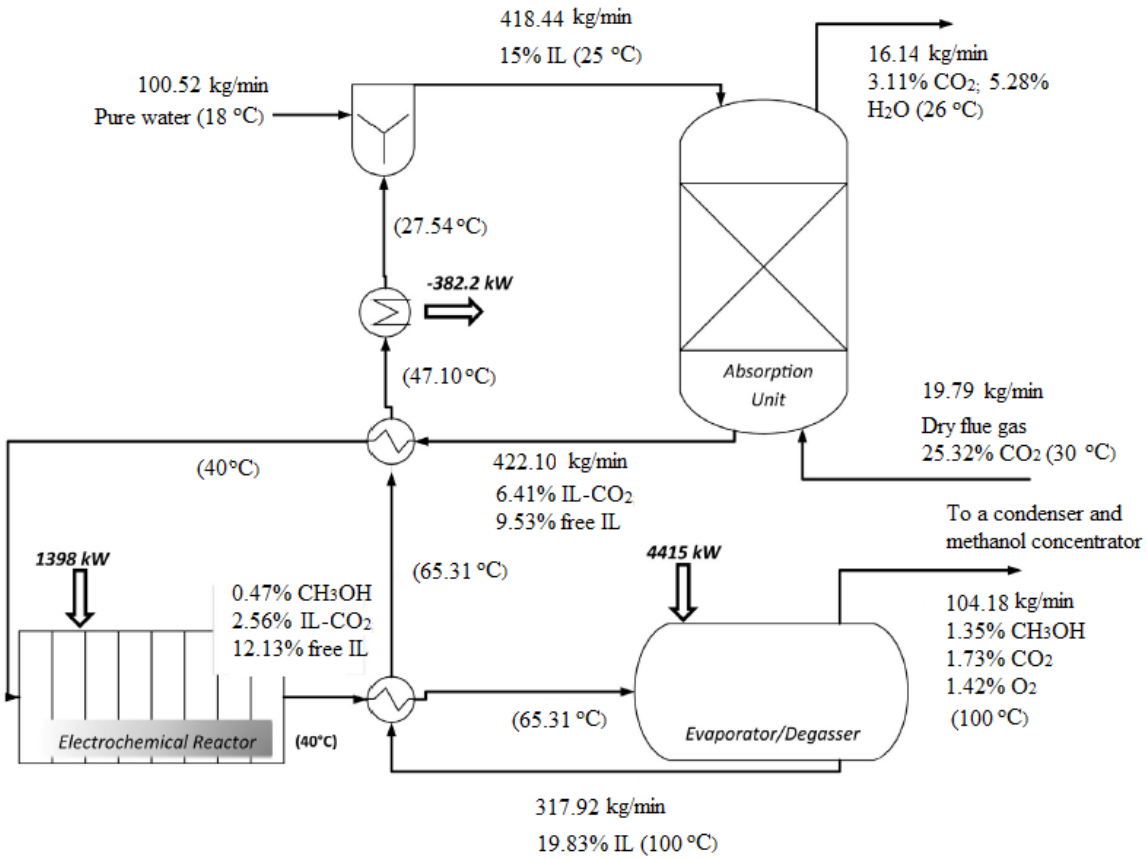
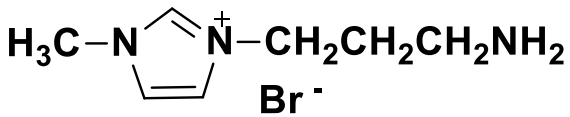


Fig. 37: Illustrative fabrication procedure of Nafion/Mb/NiO/GR/CILE.



The structure of IL



[pamin]$^{+}$[br]$^{-}$

Fig. 38: Electrochemical reduction of CO_2 to methanol in [pamin][br].

Zhan *et al.* [76] developed a novel electrochemical biosensor by the immobilization of Hb in AFIL–LDH composite film through coprecipitation technique (Fig. 39). The results showed that this modified bioelectrode displayed a good electrocatalytic activity toward the trichloroacetic acid (TCA) reduction with a larger linear range and a lower detection limit. Compared with the previous electrodes, the present ADIL-LDH nanocomposite film have several attractive features such as high conductivity, favorable microenvironment, environmentally benign and good biocompatibility. Zhou and coworkers [77] examined the electrochemical reduction of CO_2 in a series of aqueous solutions of ILs on metal (silver (Ag), copper, platinum and gold) catalyst cathode (Fig. 40). The tests revealed that the chloride containing IL could be the most effective candidate for reduction of CO_2 to CO. The results showed that Ag cathode in [Bmim]Cl with 20wt.% water had excellent synergy in electrochemical reduction of CO_2 to CO with high selectivity (>99%) and efficiency, and with stable area specific activity (ca.2.4 $mA \cdot cm^{-2}$).

$$HbFe(Ⅲ) + e \longrightarrow HbFe(Ⅱ) \quad (1)$$

$$2\ HbFe(Ⅱ) + Cl_3CCOOH + H^+ \longrightarrow 2\ HbFe(Ⅲ) + Cl_2CHCOOH + Cl^- \quad (2)$$

$$HbFe(Ⅱ) + e \longrightarrow HbFe(Ⅰ) \quad (3)$$

$$2\ HbFe(Ⅰ) + Cl_2CHCOOH + H^+ \longrightarrow 2\ HbFe(Ⅱ) + ClCH_2COOH + Cl^- \quad (4)$$

$$2\ HbFe(Ⅰ) + ClCH_2COOH + H^+ \longrightarrow 2\ HbFe(Ⅱ) + CH_3COOH + Cl^- \quad (5)$$

Fig. 39: Electrocatalytic reduction process of TCA.

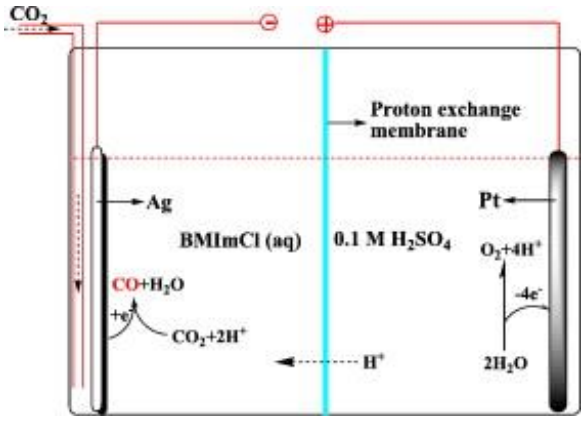


Fig. 40: Electrocatalytic reduction of CO_2 to CO in ILs.

Bouden *et al*. [78] investigated the electrochemical immobilization of redox active molecule based IL onto glassy carbon electrode (Fig. 41). They found that the electrochemical reduction of [NO_2PhEImMFc][TFSI] in acidic media containing sodium nitrite could lead to the in situ formation of the corresponding diazonium, in the vicinity of the electrode, and subsequently the grafting of redox based IL onto the electrode surface. The features of the [NO_2PhEImMFc][TFSI] electrode include: high sensitivity, good reproducibility, electrochemical reversible wettability, and high activity. Rama *et al*. [79] studied the electrochemical behavior of Eu(III) in [C_6mim]NTf_2, in the presence and absence of TBP and DHOA (Fig. 42). The cyclic voltammogram of Eu(III) in C_6mimNTf_2 exhibited a prominent quasi-reversible reduction wave, culminating in a peak at−0.84 V (Vs Fc/Fc+) was due to the reduction of Eu(III) to Eu(II). The ionic liquid [C_6mim]NTf_2 based-electrochemical system shown excellent stability and catalytic efficiency.

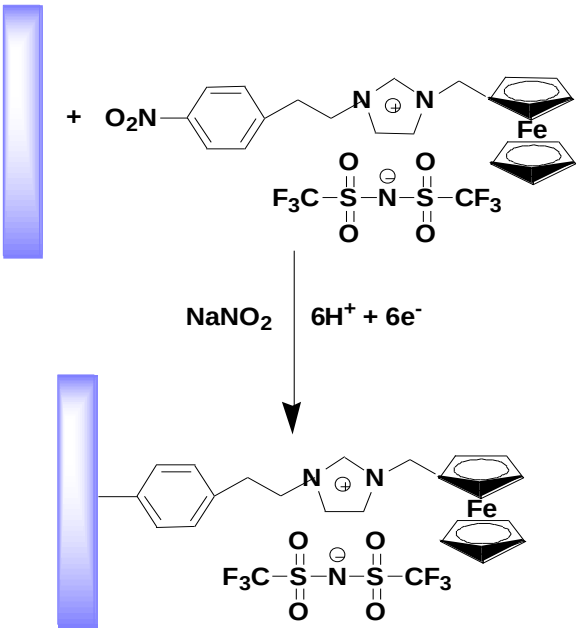


Fig. 41: Electrochemical reduction of [NO_2PhEImMFc][TFSI].

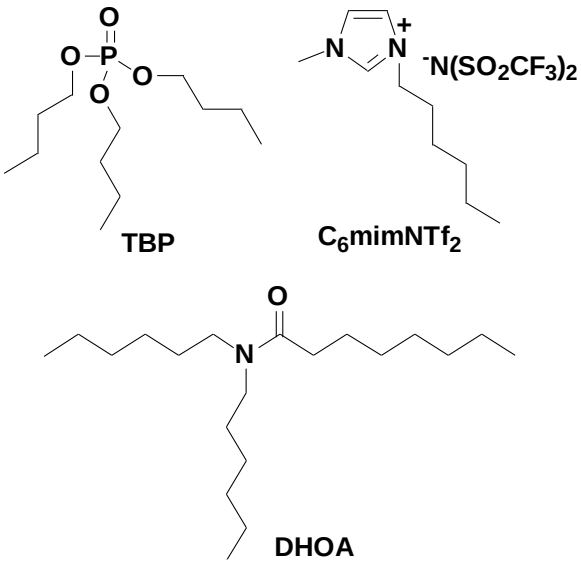


Fig. 42: Structure of the extractants and IL.

Yu *et al*. [80] reported ther synthesis of B and N co-doped graphene (B,N-G) samples via chemically grafting ionic liquid (IL), followed by thermal annealing (Fig. 43). The workers found that chemically grafting via IL is an efficient strategy for inhibiting and avoiding the agglomeration and restacking of graphene oxide (GO) sheets to a great degree in comparison to that of physically mixed IL and GO, further leading to efficient doping. The B,N-G-1200 annealed at 1200 °C derived from IL-grafted GO as CE has demonstrated the best electrochemical performance for triiodide reduction, yielding a power conversion efficiency of 8.08%. The synergetic effects of co-doped B and N, which is superior to 6.34% of Pt CE. Berenguer *et al*. [81] explored the electrochemical behavior of screen printed graphite electrodes (SPGEs) in $[C_6mim][PF_6]$ by studying electrochemical parameters of Fc, BQ, AQ, TC and BZ-3 (Fig. 44). Their reductive cyclovoltammograms provided valuable information and comparison of the electrochemical reduction of the C=O functional group in model molecules of different size, solubility and π-aryl aromaticity.

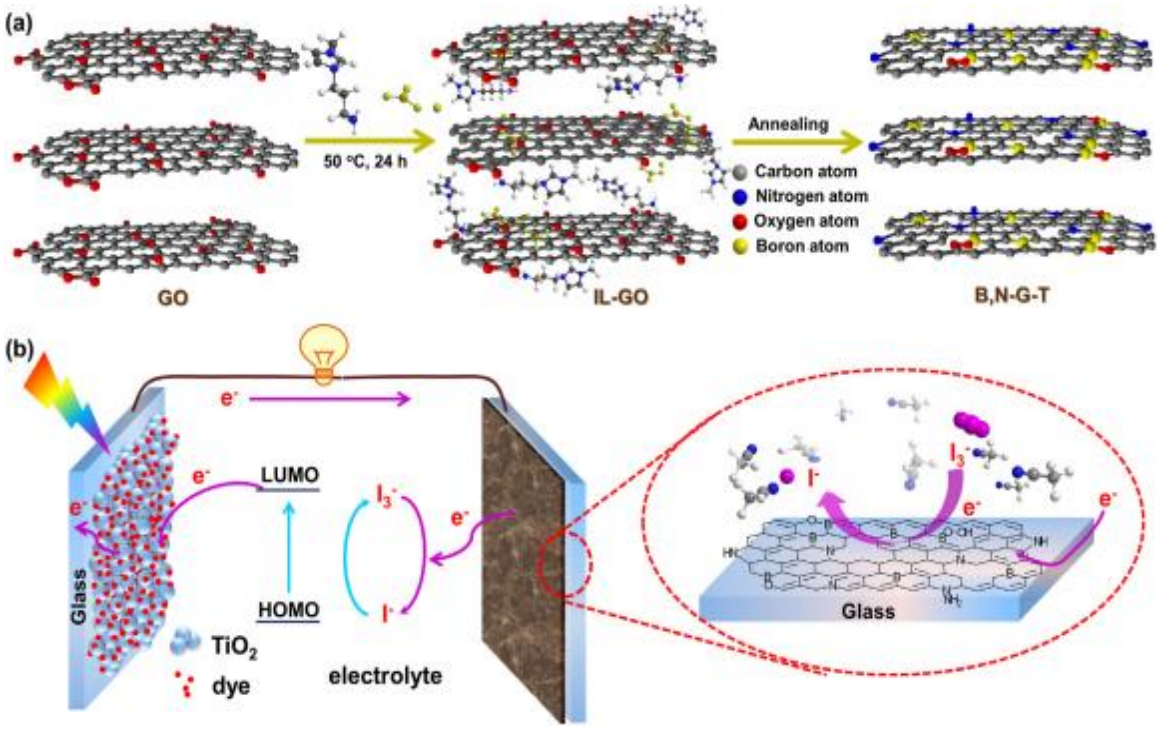


Fig. 43: Illustration of synthesis process (a) and catalytic mechanism (b) for chemically grafting GO to B,N-G.

Wang *et al*. [82] investigated the direct electrochemistry of cytochrome *c*(cyt-*c*) entrapped in agarose hydrogel on Au, EPPGE and GC in two ILs (Fig. 45). The results showed that a good quasi-reversible redox behavior of cyt-*c* could be found after adding DMF in agarose-cyt-*c* film, electrochemical performance of cyt-*c* is the best when the water content is 5.2% and 5.8% for [Bmim][Br] and [Bmim][BF_4] respectively. Compared with the previous systems, the present electrocatalytic system has some attractive features such as high conductivity, excellent electro-catalytic activity green and high reaction rate. Wang *et al*. [83] prepared the multiwalled carbon nanotube (MWCNT)/IL/gold nanoparticle hybrid materials by a chemical route that involved functionalization of MWCNT with ILs followed by deposition of Au (Fig. 46). They found the hybrid material had good catalytic behavior toward oxygen electroreduction, relative to glassy carbon electrode. The results showed that the ionic liquids modified MWCNT with Au could play a key role in increasing the electrocatalytic activity of MWCNT. Chen *et al*. [84] investigated the electrochemical reduction of carbon dioxide (CO_2) to carbon monoxide (CO) with propylene carbonate (PC)/Bu_4NClO_4 in ionic liquid [Bmim][Cl] (Fig. 47). The results showed that a good electrochemical performance of [Bmim][Cl] could be found for CO_2 reduction.

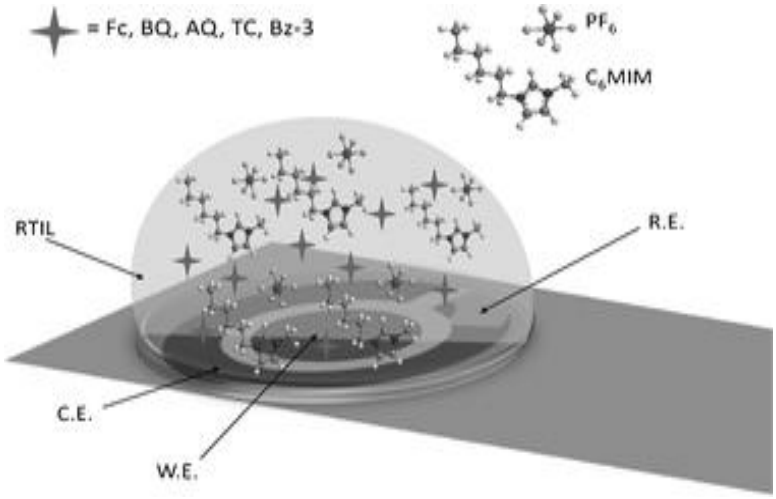


Fig. 44: Illustrative electrochemical behavior ofSPGEs in [C_6mim][PF_6].

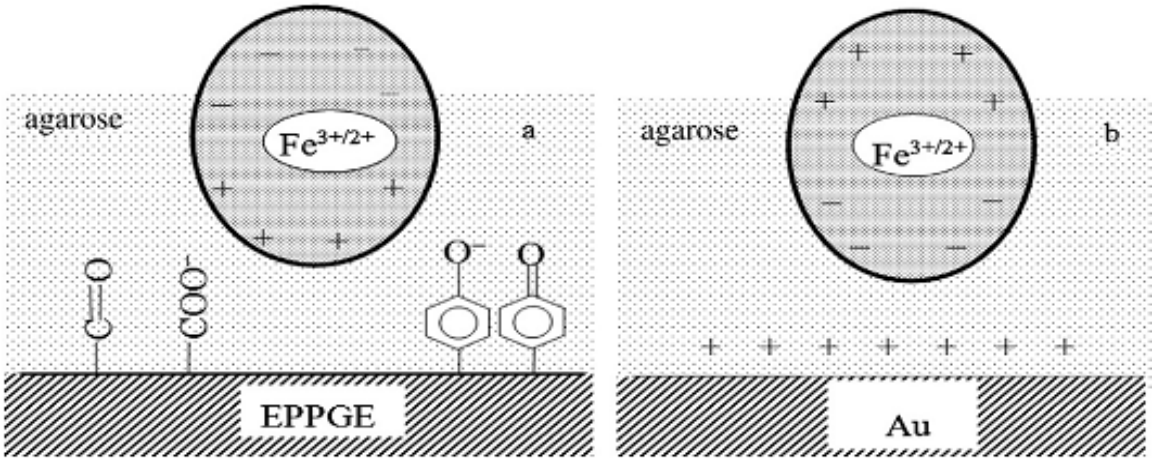


Fig.45: Electro-reduction of trichloroacetic acid and t-BuOOH in ILs.

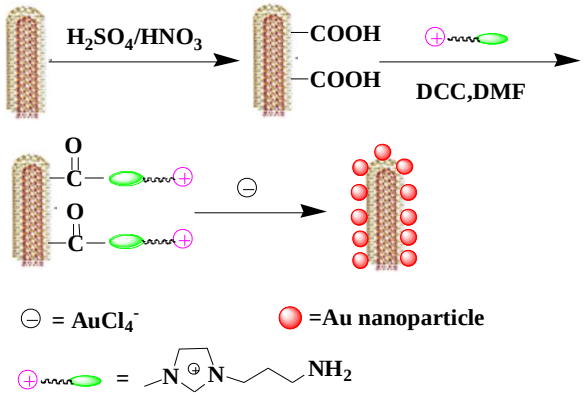


Fig. 46: Oxygen electro-reduction using MWCNT/IL/Au hybrids in IL.

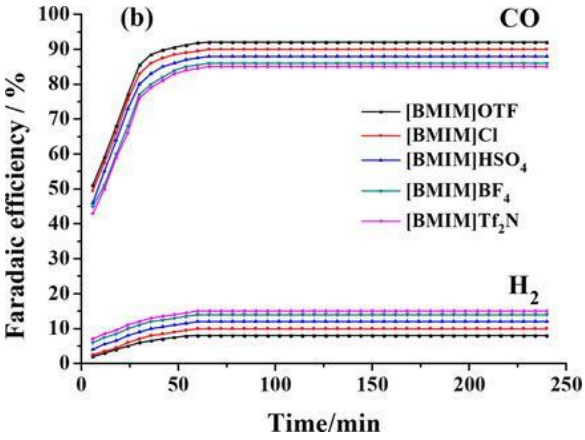


Fig. 47: Electrochemical reduction of CO_2 to CO in propylene carbonate/ tetrabutylammonium perchlorate.

Conclusion

In summary, various ionic liquids having highly promising future prospects in the field of electrochemistry have been outlined in this review. Many of their applications in fields of oxidation and reduction possess great electrochemical importance. It is to be expected that in future the scope and diversity of electrochemical applications in ionic liquids will be further increased, the possibilities of ionic liquids to reduce environmental pollution and to make better use of synthetic building blocks will be expanded. The toxic electrolytes that has been often used in classical electrochemistry will be more and more replaced by ionic liquids. Compared with the traditional electrochemical systems, the summarized present electrochemical oxidation and reduction ILs-based systems have several attractive features such as green, high catalytic activity, environmentally benign and safe. This review provides a new insight into design and application of sustainable and efficient electrochemical oxidation and reduction systems via the combination of electrochemistry and electrocatalytic activities of ionic liquids. Moreover, we do believe that ionic liquids with selectively functionalized anions and cations will greatly broaden the future scopes and applications in different fields of electrochemical science.

Acknowledgements

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