Electrochimica Acta 193 (2016) 321–343

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Ionic Liquid-Carbon Nanomaterial Hybrids for Electrochemical Sensor Applications: a Review

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A R T I C L E I N F O

*Article history:*
Received 3 December 2015
Received in revised form 8 February 2016
Accepted 8 February 2016
Available online 10 February 2016

*Keywords:*
ionic liquids
nanomaterials
Electrochemical Sensor
carbon nanotube
graphene

A B S T R A C T

During the last decade, ionic liquids (ILs) have received a considerable attention in different fields of nanotechnology applications. Their unique physicochemical properties have been highly utilized in electrochemistry, commonly in the form of IL-carbon nanomaterial (IL-CNM) hybrids. The synergistic combination of both components results in significant improvement for numerous electrochemical applications, including energy storage devices and sensor electrodes. The need for high surface area, excellent electrical conductivity, high sensitivity, and catalytic activity was the key behind the extent of ILs usefulness and numerous applications. This review aims to provide an overview of the synthetic routes for electrochemical sensor fabrication based on IL-CNM hybrids. The differences in sensing performance between the electrode designs are also discussed. ILs can affect the structure and surface chemistry of CNMs, including carbon nanotube, graphene, and fullerene. IL-CNM-modified solid electrode was the most common and effective design used in academic research. However, the inclusion of biological components and metallic nanoparticles significantly affects electrode performance. The electrochemical techniques used for detection have varied based on several considerations related to electrode design and targeted analyte. They also play an important role in determining the sensor sensitivity and detection limit.

## Contents

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http://dx.doi.org/10.1016/j.electacta.2016.02.044
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**Abbreviation**

Cation

| | |
|---|---|
| EMIm | 1-ethyl-3-methylimidazolium |
| BMIm | 1-butyl-3-methylimidazolium |
| OMIm | 1-octyl-3-methylimidazolium |
| $BPy_4$ | butyl-pyridinium |
| APMIm | 1-(3-Aminopropyl)-3-methylimidazolium |
| iBMIm | 1-isobutyl-3-methylimidazolium |
| DBIm | 1,3-dibutylimidazolium |
| DPIm | 1,3-dipropylimidazolium |
| BPIm | 3-butyl-1-[3-(N-pyrrolyl)propyl]imidazolium |
| $C_6MIm$ | 1-hexyl-3-methylimidazolium |
| BMPy | 1-Butyl- 3-methylpyridinium |
| B4MPy | 1-butyl-4-methylpyridinium |
| HPy | 1-hexylpyridinium |
| $P(C_6)_3C_{14}$ | trihexyltetradecyl phosphonium |
| BPIm | 3-butyl-1-[3-(N-pyrrolyl)propyl]imidazolium |
| VEIm | 1-vinyl-3-ethyl imidazolium |
| BMP | 1-butyl-1-methyl-pyrrolidinium |
| BIm | 1-butylimidazole |
| HeMIm | 1-(2′-hydroxylethyl)-3-methylimidazolium |
| SBMIm | 1-(4-sulfonylbutyl)-3-methylimidazole |
| MP | N-methyl-piperidinium |
| OPy | octylpyridinium |
| CMMIm | 1-carboxymethy-3-methylimidazolium |
| AMIm | 1-(2-acryloyloxy-ethyl)-3-methyl-imidazol-1-ium |
| HPAA | 3-hydroxypropanaminium acetate |
| $Py_{1,4}$ | 1-butyl-1-methylpyrrolidinium |
| BPy | N-butylpyridinium |

Anion

| | |
|---|---|
| TFSI | bis(trifluoromethylsulfonil)imide |
| FSI | bis(fluorosulfonyl)imide |
| TFA | trifluoroacetate |
| $PF_6$ | hexafluorophosphate |
| $BF_4$ | tetrafluoroborate |
| TFS | trifluoromethanesulfonate |
| Ala | alanine |
| HS | hydrogen sulfate |
| Cys | 2-amino-3-mercaptopropionic acid (L-cysteine) |
| ES | ethyl sulfate |

## 1. Introduction

The inclusion of positive and negative ions combined together in a liquid form is the main characteristic of ILs. However, an arbitrary definition has been frequently used to describe IL as a molten salt which has a melting point below $100\,^{\circ}C$ [1]. The boundary between ILs and molten salts was justified by the rapid improvement in many fields of liquid salt applications below this temperature. As common with normal salts, IL can include various types of cations, and anions. It is a combination of large organic cation such as imidazolium, pyridinium, or phosphonium, and a relatively small anion, which can either be a single atom like $Cl^-$ and $Br^-$, or larger complex like ethyl sulfate, tetrafluoroborate, or hexafluorophosphate. ILs have unique properties compared to conventional solvents, including low volatility, high electric conductivity, and low toxicity, which make them considered to be green media [2]. Their high solvation ability, along with the good thermal and ionic conductivity, attracted interest in utilizing them in chemical and electrochemical synthesis [3]. Other applications in electrochemical devices, lubricants composite materials, polymers, and nanoparticles were established [4]. In the field of electrochemical analysis, novel electrochemical sensors and biosensors were introduced in the form of modified electrodes [5].

CNMs have increasingly attracted attention due to their structural and physical properties. They can exist in different dimensionalities of $sp^2$ bonded graphitic carbon [6]. The most common types of CNMs found in various studies and especially in the field of electrochemical sensor applications are represented in Fig. 1.

Zero-dimensional form, seen as an irregular sheet of graphene curled up into a sphere through the incorporation of pentagons in its structure, represents fullerene particles ($C_{60}$). The size of fullerene may range from 30–300 carbon atoms. Graphene has the structure of a two-dimensional block of $sp^2$ carbon sheets. Conceptually, rolling up one or more graphene sheets results in single or multi layered graphene tubes, known as single wall carbon nanotube (SWCNT) or multi wall carbon nanotube (MWCNT) [6–8].

CNMs offer distinctive features in the field of sensor applications. The ability of CNMs to be modified in different ways has led to enhancement of their usability and improvement in the level of exploitation of their electronic properties and sensitivity.

Various analytes were successfully detected using CNMs based sensors. While CNM based sensors have beaten traditional sensing technologies in performance, seeking for better sensitivity, reusability, reversibility, and real applicability is still challenging [9–12].

CNM-modified electrodes became a common solution to address the overvoltage limitations of ordinary electrodes and enhance the redox activity of analytes [13,14]. CNMs proved to promote electron transfer reactions at the electrode surface due to the presence of edge plane defects in their structure. In addition, CNMs can reduce the surface fouling associated with the accumulation of the reaction products [7,15].

Carbon paste electrodes (CPEs) have become a popular tool in electroanalytical community. They consist basically of carbon particles (commonly graphite) and organic liquid for binding purposes. Fabrication of CPEs with inclusion of CNMs has resulted in drastically improved electrocatalytic performance, reduced overvoltage effect, and sometimes better redox reversibility compared to ordinary CPEs [16–18]. However, since chemical modification of CNMs can add new functionalities, functionalized

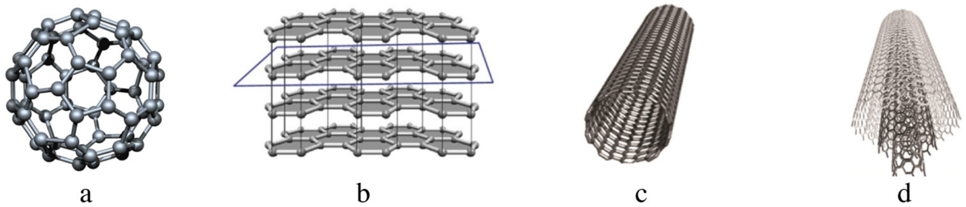

**Fig. 1.** Common types of CNMs, (a) $C_{60}$, (b) graphene, (c) SWCNT and (d) MWCNT.