

Electroactive Properties of 1-propyl-3-methylimidazolium Ionic Liquid Covalently Bonded on Mesoporous Silica Surface: Development of an Electrochemical Sensor Probed for NADH, Dopamine and Uric Acid Detection

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ABSTRACT

A hybrid organic-inorganic porous material was successfully prepared through chemical modification of a non-ordered mesoporous silica, obtained by the sol-gel process, with 1-propyl-3-methylimidazolium groups. The porous material was evaluated as a platform for the development of electrochemical sensors, here probed toward the electrooxidation of NADH (β -nicotinamide adenine dinucleotide), uric acid (UA) and dopamine (DA). The presence of cationic imidazolium groups on the surface of the hybrid silica-based material allowed the electrochemical detection of these biomolecules without any other electron mediator or biomolecular recognition component. Such behavior highlights the potentiality of this material to be applied in the development of new electrochemical sensing devices. Theoretical calculations based on density functional theory emphasizes that the cationic character of imidazolium group provides better oxidation conditions if the solvent effect is minimized.

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1. Introduction

The utilization of ionic liquids (ILs) in electrochemical systems has shown its usefulness in a broad range of applications, including fuel cells [1] solar cells [2,3], lithium batteries [4], electrochemical capacitors [5], electrocatalysis [6] and electrochemical sensors [7–11]. Such possibilities are strongly related to their unique properties, primarily good ionic conductivity, wide electrochemical potential window, high thermal stability, negligible vapor pressure and the ability to dissolve a wide variety of compounds. ILs are generally defined as fluid semi-organic salts composed entirely of organic cations and organic or inorganic anions, with the most common cations containing imidazolium, pyridinium, pyrrolidinium, tetraalkylammonium, tetraalkylsulfonium and tetraalkylphosphonium groups.

From the point of view of electrochemical sensors, several approaches have been used for fabricating IL-modified electrodes [8,9], including carbon paste electrodes with ILs as a binder [12,13], IL droplets or films directly deposited on the electrode surface, IL-gels (usually prepared by mixing them with carbon nanotubes) and

electrodes modified with appended ILs, in which the IL species are chemically attached on the electroactive surface. The great majority of works dealing with such appended ILs are related to carbon-based materials or conventional electrodes, with few examples exploring the possibilities of sol-gel materials, more specifically mesoporous silica-based materials.

The chemical modification of porous silica with ILs and similar cationic charged species have been successfully explored in analytical sciences [14], for instance preparation/purification [15–17] and adsorption processes [18–21], in which is possible to take advantage of the high specific surface areas and pore volumes presented by mesoporous silicas, that simultaneously allow incorporation and accessibility of a huge number of functional groups on the surface and ensure fast diffusion of the target species to the active sites dispersed throughout the porous structure. Besides the characteristics mentioned above, another factor that makes silica an extremely attractive and useful solid support is related to its versatility, directly attributed to several possibilities of manipulating the porous structure and the variety of possible chemical modifications that can be performed on its surface, originating materials with the most diverse functionalities and properties [22–26].

Considering the facts described above, the present work describes the preparation and application of a hybrid mesoporous silica, synthesized via sol-gel methodology, chemically modified

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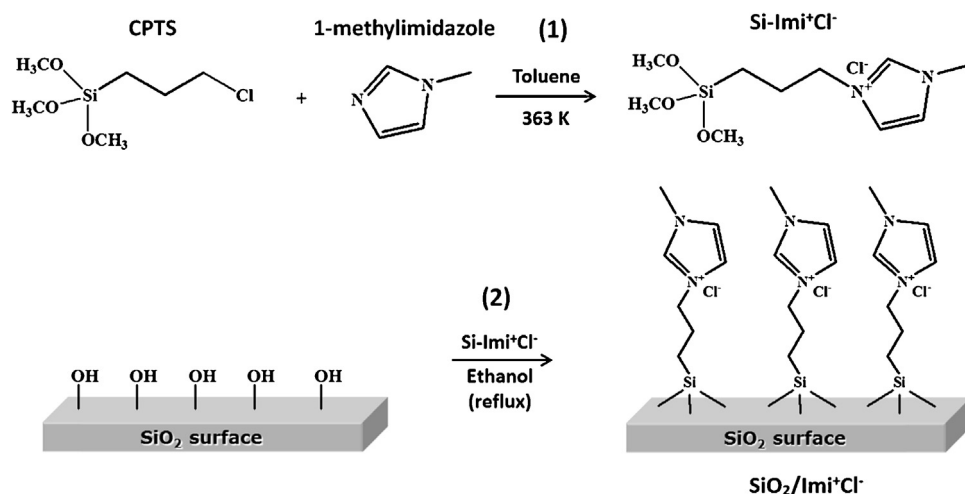


Fig. 1. Schematic illustration of $\text{Si-Imi}^+\text{Cl}^-$ synthesis (1) and the surface functionalization step (2) of mesoporous silica with imidazolium groups.

with cationic 1-propyl-3-methylimidazolium groups. The resulting material, in which the imidazolium groups are attached on the surface, was applied in the construction of a porous carbon ceramic electrode and evaluated as a platform to develop electrochemical sensors, here probed toward the electrooxidation of NADH (β -nicotinamide adenine dinucleotide), uric acid (UA) and dopamine (DA). These molecules play important roles in human's metabolism where NADH is a vital electron carrier (cofactor) in many redox reactions, DA is an important neurotransmitter and UA is the end product of purine (nitrogenous base) metabolism, associated with some diseases when present in abnormal levels.

Theoretical calculations based on density functional theory were performed to reinforce how the imidazolium groups provides high efficiency oxidation conditions for NADH, DA and UA molecules without using any other electron mediator.

2. Experimental

2.1. Synthesis of the materials

A mesoporous silica was prepared according to a procedure described previously [19]: 0.91 mL of HF (48%) was added to 76.0 mL of TEOS (tetraethylorthosilicate, Aldrich, 99%), 76.0 mL of ethanol and 25.0 mL of water. Stirring was carried out for 30 min. The resulting mixture was stored for 15 days at room temperature. The obtained xerogel was ground and the powder was washed with ethanol in a Soxhlet extractor for 12 h and subsequently submitted to a heat treatment at 333 K under vacuum to evaporate all residual solvent. The resulting silica will hereafter designated simply as SiO_2 .

The preparation of the imidazolium-based alkoxy silane was carried out in single step according to the following procedure [27]: in a round bottomed flask with 6.0 mL of dry toluene, 0.30 mmol of 3-(chloropropyl)-trimethoxysilane (Aldrich, 99%) and 0.30 mmol of 1-methylimidazole (Aldrich, 98%) were simultaneously added and the solution was kept under magnetic stirring for 24 h at 333 K under nitrogen atmosphere. After the set time, the reaction mixture was kept under static conditions until the complete separation of the resulting two immiscible liquid phases. The bottom fraction, which corresponds to the $\text{Si-Imi}^+\text{Cl}^-$ product, was then physically separated. This reaction is schematically shown in Fig. 1 (step (1)).

The chemical modification of the silica surface was carried out by the post-grafting procedure (Fig. 1, step (2)), as follows: 1.0 g of the previously synthesized SiO_2 was immersed into 100 mL of 0.02 mol L^{-1} solution of $\text{Si-Imi}^+\text{Cl}^-$ in dry ethanol. This mixture was

kept under reflux for 24 h. The immobilization of the functional groups occurs through condensation reactions between the silanol groups (Si-OH) on the SiO_2 surface and the methoxy groups ($-\text{OCH}_3$) of the $\text{Si-Imi}^+\text{Cl}^-$ alkoxy silane, with alcohol release. The product was then filtered and washed with ethanol in a Soxhlet extractor. Finally, the solid was filtered, washed with ethanol, bidistilled water and dried under vacuum at 323 K. This sample obtained will hereafter be designated as $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$.

2.2. Preparation of the working electrodes

The working electrode was prepared by mixing 0.025 g of $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ and 0.025 g of pure graphite (Aldrich, 99.99%) and then pressing them under 2 tons of pressure (Fig. 2). The resultant pellets (4 mm i.d.) were immersed in pure fused paraffin at 343 K under vacuum until all adsorbed gas in the matrix pores was completely eliminated. The disks were polished with emery paper to remove the paraffin from the surface, and then glued with cyanoacrylate ester glue to the end of a glass tube (4 mm i.d. and 15 cm length), as can be seen in Fig. 2. The electrical contact was made by a copper wire inserted inside the glass tube. In order to improve the connection between the wire and the disk surface, pure graphite powder was added inside the glass tube.

2.3. Characterization

The amount of organic groups immobilized onto the SiO_2 surface was calculated based on the nitrogen content, determined

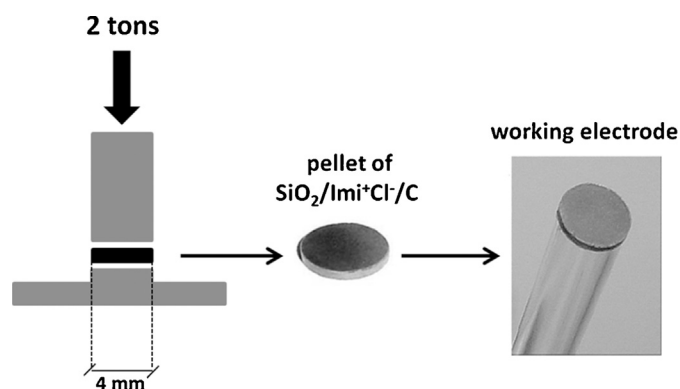


Fig. 2. Scheme of the preparation of the $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ working electrode.

by means of elemental analyses on a Perkin-Elmer 2400 elemental analyzer apparatus. Solid-state nuclear magnetic resonance spectroscopy for ^{13}C (CP/MAS NMR) was performed on a Bruker AC300/P spectrometer. ^{13}C CP/MAS NMR spectra were obtained using pulse sequences with 4 ms contact time, an interval between pulses of 1 s and an acquisition time of 0.041 s. The chemical shifts were calibrated against TMS standard. The specific surface areas were made for the samples outgassed at 353 K for 12 h on a Quantachrome Autosorb 1 instrument. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface areas (S_{BET}).

2.4. Electrochemical measurements

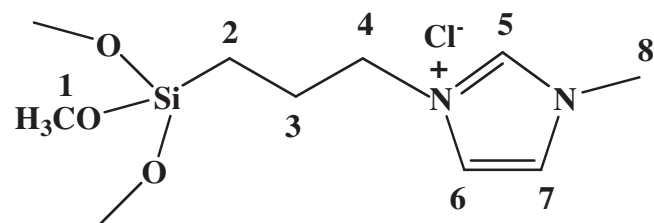
The electrochemical measurements were carried out on an Autolab PGSTAT 20 potentiostat-galvanostat apparatus, using a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as the reference, a platinum foil as the auxiliary electrode and pressed disks of $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ as working electrodes (see item 2.2). All measurements were carried out in 1.0 mol L^{-1} aqueous KCl solution, under room temperature. Differential pulse voltammetry (DPV) was performed with the following parameters: pulse amplitude 50 mV, modulation time 50 ms and scan rate 10 mVs^{-1} .

2.5. Theoretical study

The simulation of an electrochemical system is complex and should consider the electron transference, solvation, surface effects, ionic strength, etc. The computational calculations in this work were carried out in order to achieve a possible indication of the experimental tendencies considering simple quantum chemical properties. Vertical ionization energies and electron affinities were calculated for dopamine, uric acid, NADH and an imidazolium compound. The first ionization and electron affinity energies were calculated simply as the difference between the product and reagent electronic energies considering the removal or addition of an electron. The compact effective core potentials (CEP) developed by Stevens, Basch and Krauss [28] were used along with the well-known B3LYP functional. The anionic character of some compounds suggests the use of a basis set including diffuse functions. Therefore, the CEP-31++G(d,p) basis set was used for all the calculations even for cations. The molecular geometry of the neutral compounds and imidazolium were fully optimized at the B3LYP/CEP-31++G(d,p) level of theory. The compound energies removing or including an electron were calculated using these equilibrium geometries. Further attempts to include solvent effects were done considering two different approaches. The first alternative used only a polarizable continuum model (PCM) [29]. The second option used a combination of PCM and local contributions from one to up four water molecules as local interactions caused by the hydrogen bonds. The only exception was the NADH molecule, which was calculated only in vacuum because of the great number of possible sites capable of having explicit interaction with water molecules. The use of PCM or PCM and water molecules demanded the reoptimization of the geometry of each super-molecule for the calculation of the ionization and electron affinity energies. Similar to the molecules in vacuum, only the neutral compounds and the starting imidazolium had the geometries reoptimized. The ionizations and electron affinities of the solvated compounds were carried out with these optimized super-molecules.

In order to inspect a simpler estimate of ionizations and electron affinity tendencies, the HOMO and LUMO energies were calculated at the Hartree-Fock level using the CEP-31++G(d,p) basis set at the equilibrium geometries of the neutral compounds.

Table 1
Solid state ^{13}C and ^{29}Si NMR data of $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ material.



^{13}C	δ/ppm	^{29}Si	δ/ppm
C ₁	54	T ² CSi(OR)(OSi) ₂	-57
C ₂	11	T ³ CSi(OSi) ₃	-65
C ₃	20	Q ² (SiO) ₂ Si(OH) ₂	-89
C ₄	63	Q ³ (SiO) ₃ SiOH	-100
C ₅	140	Q ⁴ (SiO) ₄ Si	-109
C _{6,7}	126		
C ₈	36		

As a final methodological remark, the open shell cations were calculated with the restricted open shell model, while the anions were calculated using the unrestricted alternative, because convergence problems occurred in anion calculations. All the calculations were carried out with the Gaussian/2009 program [30].

3. Results and Discussion

The amount of organic groups on the functionalized material $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ was determined by elemental analyses. Based on the value of N content, the functionalization degree obtained was $N_f = 0.50\text{ mmol g}^{-1}$. The specific surface areas (S_{BET}) determined for SiO_2 and $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ are 342 and $270\text{ m}^2\text{ g}^{-1}$ respectively. The observed decrease in the specific surface area is expected and occurs frequently when porous inorganic materials are modified with organic groups [27]. This behavior suggests that the imidazolium entities are located within the mesopores. Based on the value of the specific surface area and assuming that the organofunctional groups uniformly cover the surface, the average intermolecular distance, l , can be calculated by applying the equation $l = (S_{\text{BET}}/N_f N)^{-1/2}$ where N is the Avogadro' number [31]. The calculated intermolecular distance is $l \sim 1.1\text{ nm}$.

The ^{13}C NMR spectrum for the functionalized silica presents signals with specific chemical shifts (Table 1) of 1-propyl-3-methylimidazolium group, numbered from C₁ to C₈, as in the figure shown in Table 1. Residual ethanol from the synthesis was also observed. ^{29}Si NMR spectrum showed clearly one peak at -65 ppm corresponding to the T³ species (CSi(SiO)₃) and a weak signal at -57 ppm (T² species (CSi(OR)(OSi)₂), confirming that the functional groups are covalently bonded to the silica surface predominantly through T³ configuration [27].

The hybrid $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ material consisting of n-propyl-3-methylimidazolium groups grafted on the surface of mesoporous silica was then applied as an electrochemical sensing platform through the construction of a carbon ceramic electrode (see Fig. 2), aiming to take advantage from the high porosity of silica allied to the electrochemical properties of the imidazolium groups. The electrochemical behavior of $\text{SiO}_2/\text{Imi}^+\text{Cl}^-$ material was probed toward the electrooxidation of NADH, UA and DA using differential pulse voltammetry (DPV) technique. Fig. 3 shows the $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ electrode responses to NADH, UA and DA. As can be seen, the electrode has shown to be active toward the electrooxidation of these molecules with well-defined oxidation peaks. For comparison, a working electrode constituted only by a mixture of SiO_2 and graphite (SiO_2/C) was also

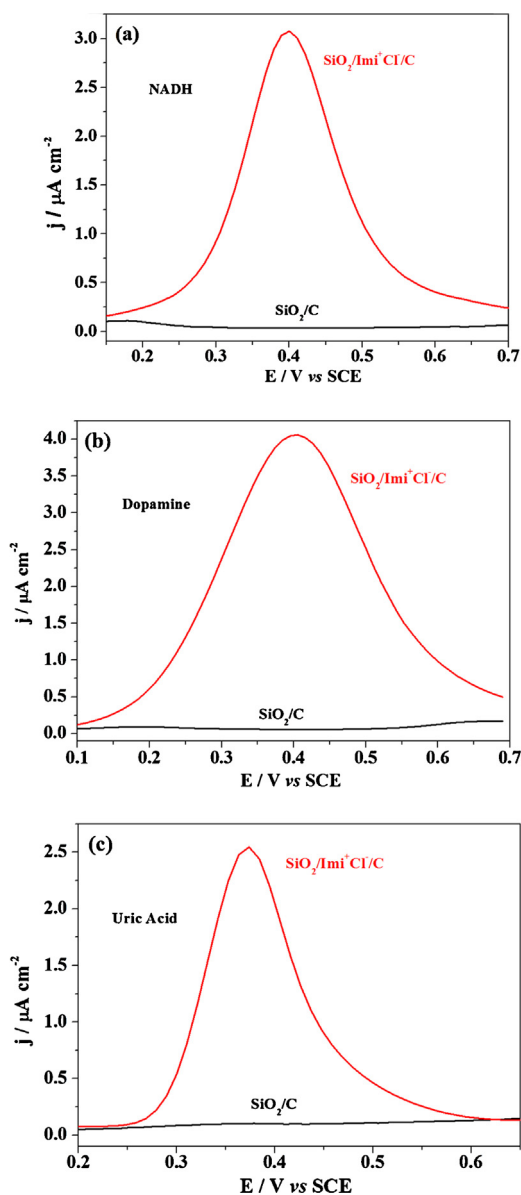


Fig. 3. Differential pulse voltammetry observed for SiO_2/C (dotted line) and $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ (black line) for: (a) $[\text{NADH}] = 0.04 \text{ mmol L}^{-1}$, (b) $[\text{DA}] = 0.04 \text{ mmol L}^{-1}$ and (c) $[\text{UA}] = 0.08 \text{ mmol L}^{-1}$. Supporting electrolyte: $\text{KCl } 1.0 \text{ mol L}^{-1}$, $T = 298 \text{ K}$, $\text{pH } 6.5$.

tested under the same conditions and showed no electroactivity, with no faradaic currents observed in the studied potential range.

The voltammetric responses at $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ electrode (Fig. 4 (a), (b) and (c)) for successive addition of the analytes show a remarkable increase of the anodic peak currents (oxidation process), signaling good electrochemical responses with changes in the concentration of the probe molecules.

In all cases it is observed that the proposed electrochemical sensor showed linear responses in the studied concentration ranges (Fig. 4 (a'), (b') and (c')), with the respective linear correlation coefficients (r) and the sensitivities (α) of the $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ electrode toward the probe molecules, as follows: NADH , $r = 0.999$, $\alpha = 34.96$; UA , $r = 0.996$, $\alpha = 23.18$ and DA , $r = 0.998$, $\alpha = 43.72$.

This behavior emphasizes that the hybrid imidazolium silica-based substrate can act as a suitable platform for the development of new electrochemical sensing devices.

Table 2

Ionization (IP), negative HOMO, electron affinity (EA) and LUMO energies calculated at the B3LYP/CEP-31++G(d,p) in vacuum and considering solvent effect using PCM and PCM+water molecules (data in eV).

Molecule	IP	$-\epsilon_{\text{HOMO}}$	EA	ϵ_{LUMO}
Imidazolium	13.97	13.95	3.28	-2.03
Imidazolium + PCM	7.77	9.97	1.39	1.08
Imidazolium + H_2O + PCM	7.67	9.88	1.28	1.07
Imidazolium + $2\text{H}_2\text{O}$ + PCM	7.59	9.78	1.28	1.05
Imidazolium + $3\text{H}_2\text{O}$ + PCM	7.51	9.69	1.31	1.04
Imidazolium + $4\text{H}_2\text{O}$ + PCM	7.46	9.60	1.21	1.01
Dopamine	7.65	8.11	-0.27	0.97
Dopamine + PCM	5.92	8.24	1.10	1.18
Dopamine + H_2O + PCM	5.74	8.06	1.32	1.18
Dopamine + $2\text{H}_2\text{O}$ + PCM	5.83	8.14	1.33	1.17
Dopamine + $3\text{H}_2\text{O}$ + PCM	5.85	8.15	1.32	1.16
Uric Acid	8.31	8.86	2.11	0.54
Uric Acid + PCM	6.13	8.62	1.37	1.32
Uric Acid + H_2O + PCM	6.19	8.67	1.44	1.30
Uric Acid + $2\text{H}_2\text{O}$ + PCM	6.22	8.70	1.52	1.30
Uric Acid + $3\text{H}_2\text{O}$ + PCM	6.21	8.68	1.49	1.28
Uric Acid + $4\text{H}_2\text{O}$ + PCM	6.20	8.68	1.47	1.27
NADH	7.20	7.97	0.34	0.79

4. Theoretical explanation of UA, DA and NADH oxidation

The calculated ionization, electron affinity, HOMO and LUMO energies are summarized in Table 2.

The general tendency of the first ionization potential in vacuum for the three compounds follows the tendency: uric acid > dopamine > NADH. The HOMO energies provide similar tendency larger by approximately 0.6 eV than the respective ionizations calculated at the B3LYP/CEP-31++G(d,p) level. The cationic character of imidazolium provides large ionization energy and similar to the negative of the respective HOMO energy. The electron affinity of imidazolium, as expected, is the largest one, as well as the negative LUMO energy. This large electron affinity justifies the high electrochemical acceptor when compared to the other compounds not requiring the presence of gold or other metal to mediate the oxidation of the organic compounds.

The solvent effect provides significant changes in the ionization and electron affinity energies (see Table 2). The ionization of the solvated imidazolium is significantly reduced from 13.97 eV to approximately 7.5 eV. However, solvated imidazolium still presents the largest ionization energy with respect to the other solvated compounds. The negative of the HOMO energies yield the same tendency, but do not present significant changes when comparison is made between the compounds in vacuum and solvated. On the other hand, the electron affinity of solvated imidazolium achieves similar values when compared to the other solvated compounds.

Combining all these theoretical information, it can be suggested that the favorable oxidation process in mesoporous silica electrodes modified with cationic imidazolium groups are favored because of its high electronic acceptor capability. The calculations shown in Table 2 suggest that the oxidation process is more effective whether the solvent effect is minimized. Possibly the electron transfer occurs by close contact between the organic compounds and the electrode surface after elimination of the solvation shell. This suggestion is reinforced by the high electron affinity of imidazolium (3.28 eV) in vacuum and the ionization energies in vacuum of dopamine (7.65 eV) and NADH (7.20 eV), which present similar qualitative tendency with the experimental oxidation potential (dopamine $\cong 0.41 \text{ V}$ and NADH $\cong 0.40 \text{ V}$). The higher ionization potential of uric acid (8.31 eV) in vacuum than dopamine and NADH cannot justify the lowest oxidation potential, as observed in the experimental data. In order to explain this particular behavior of uric acid, it can be suggested that this compound is not completely free of the solvent effect during the oxidation

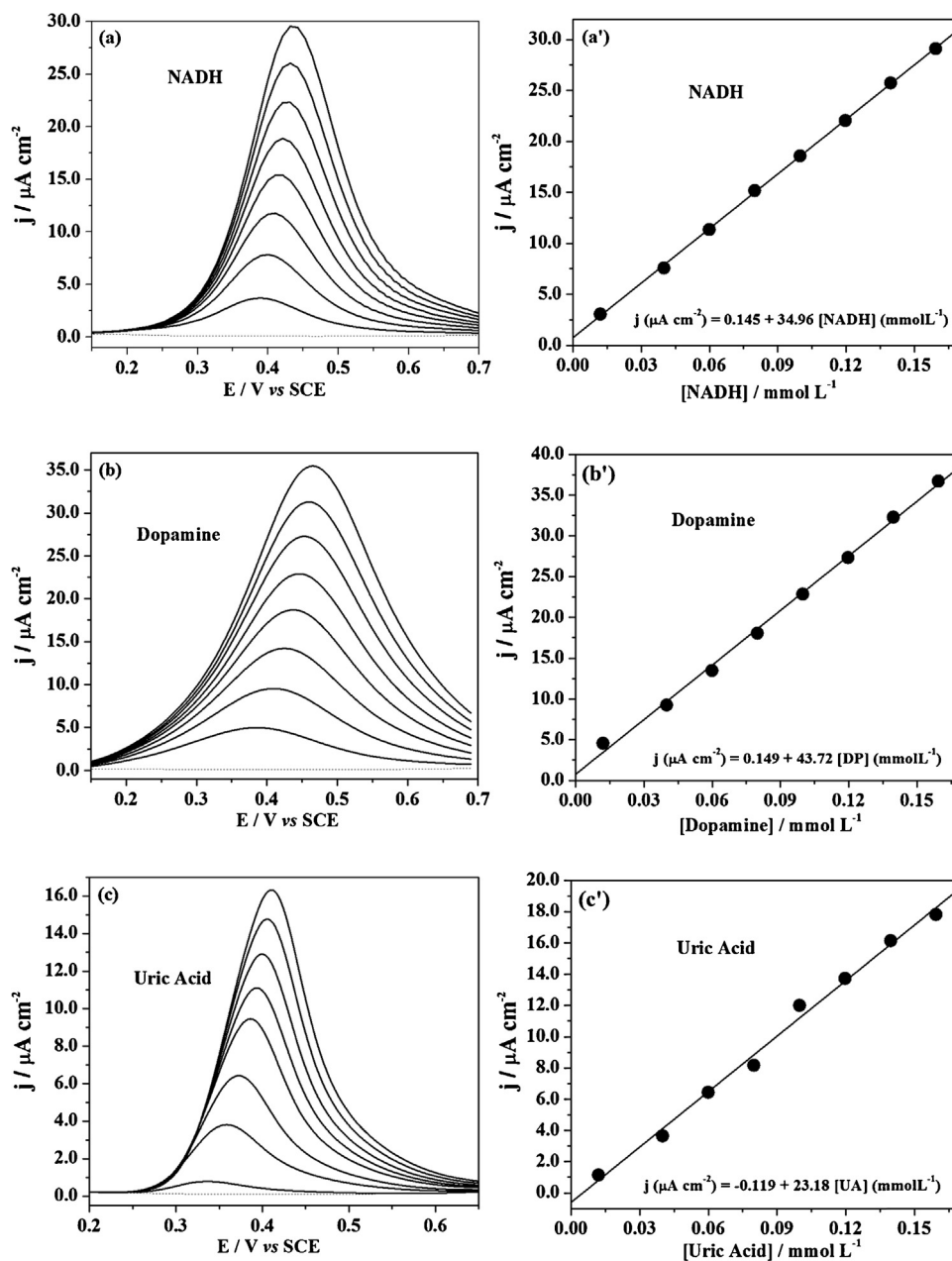


Fig. 4. Differential pulse voltammetry observed for $\text{SiO}_2/\text{Imi}^+\text{Cl}^-/\text{C}$ for different concentrations of (a) NADH, (b) DA and (c) UA and the respective plots of current density versus concentration in (a'), (b') and (c'). KCl 1.0 mol L⁻¹, T = 298 K and pH 6.5.

process, which provides a significant reduction of its ionization potential (6.20 eV), and consequently a lower oxidation potential ($\cong 0.38$ eV) when compared with dopamine ($\cong 0.41$ V) and NADH ($\cong 0.40$ V).

5. Conclusions

In this work, a novel platform for electrochemical sensors based on the combination of 1-propyl-3-methylimidazolium cationic groups supported on mesoporous silica was described. The organic entities were chemically bonded to the silica surface by a post-grafting procedure.

The robustness of the synthesized hybrid materials allowed the construction of carbon ceramic electrodes, successfully applied as a platform for electrochemical sensors. The electrochemical

properties were evaluated toward the electrooxidation of NADH, uric acid and dopamine.

Theoretical calculations based on density functional theory and the HOMO and LUMO energies emphasize that the oxidation process in mesoporous silica electrodes with cationic imidazolium groups are favored because of its high electronic acceptor capability. Solvent effect tends to minimize the acceptor tendency of the imidazolium group, suggesting that the electron transfer is more effective when the solvation shell is eliminated.

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