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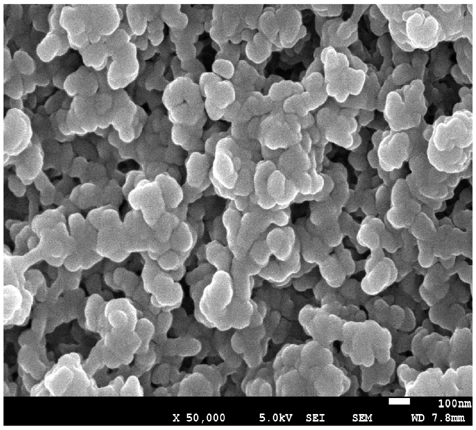
Graphical abstract



A stable and porous nanocomposite of PEDOT/IL with excellent electrocatalytic activity was prepared through a cost-effective electrochemical strategy.

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ARTICLE TYPE

Cost-effective preparation and sensing application of conducting polymer PEDOT/ionic liquid nanocomposite with excellent electrochemical properties

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A conducting polymer based composite material of poly (3, 4-ethylenedioxythiophene) (PEDOT) doped with pure insoluble ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, was prepared through a cost-effective electrodeposition method. A very tiny amount of insoluble IL (less than 15 μL), containing 0.1 M conducting polymer monomer, was drop-coated on a electrode surface and then used for electropolymerization using a homemade electrochemical cell filled with aqueous supporting electrolyte. With this design, the consumption of expensive IL for the preparation of the PEDOT/IL composite was greatly reduced, and thus effectively reduced the cost. The prepared PEDOT/IL composite was found to be highly conductive and stable, and it exhibited a highly nanoporous microstructure and excellent electrocatalytic activity toward the oxidation of dopamine (DA). Based on the excellent stability and electrocatalytic activity of the PEDOT/IL nanocomposite, a highly stable, sensitive and selective DA sensor with a detection limit of about 51 nM was developed.

1. Introduction

Ionic liquids (ILs), a class of organic molten salts at room temperature, are usually composed of organic cations (ammonium, imidazolium, and phophonium, etc.) and anions (Cl^-, BF_4^-, PF_6^-, $AlCl_4^-$ and $(CF_3SO_2)_2N^-$, etc.). At present, there are large numbers of different ILs synthesized from various cations and anions[1, 2]. ILs are known as environmentally friendly organic reagent because of their unique properties such as negligible vapor pressure, high electrochemical and thermal stability, high ionic conductivity, wide potential window, and biocompatibility[3, 4]. Owing to their promising properties, ILs have attracted much attention in the past years, and they have found broad applications, especially practical electrochemical applications in science and technology, such as electrochemical capacitors[5, 6], batteries[7, 8], fuel cells[9-11], and electrochemical sensor[12, 13, 14].

In recent years, conducting polymers have emerged as intelligent materials that can be used for the development of various devices like sensors and actuators due to their unique properties, such as high conductivity, light weight, flexibility, and excellent processability[15]. Conducting polymers are very attractive in electrochemical analysis, as they can be deposited onto electrode with a high degree of geometric conformity and ease of control over the thickness[16]. Among numerous conducting polymeric materials, poly (3, 4-ethylenedioxythiophene) (PEDOT) is one of the most promising candidates, which has been widely used in various electrochemical devices due to its unique properties including high inherent conductivity, narrow electronic bandgap, and biocompatibility[17-19]. However, a big obstacle that restricts the broad application of PEDOT is that, 3, 4-ethylenedioxythiophene (EDOT) has poor solubility in aqueous solution, and its thienyl cation radicals can react with water molecules, which can inhibit EDOT polymerization[20].

In order to solve the above problem, polymerization of EDOT in organic solvents, especially ILs has been adopted. It has been reported that conducting polymers could be polymerized with ILs so as to combine the unique properties of conducting polymers with ILs[21], and also to improve performance and lifetime of conducting polymers[22]. Moreover, EDOT can also be well dissolved in ILs. All these advantages make ILs an ideal media for the preparation of conducting polymers, and currently the electropolymerization of conducting polymers including polypyrrole[23], polythiophene[24], polyphenylene[25, 26] have been attempted. However, for the electrochemical polymerization of conducting polymers doped with ILs, in many cases the electropolymerization solutions are just pure ILs added with conducting polymer monomers (especially for water insoluble ILs), which requires considerably a large volume of pure ILs (normally 500-5000 μL for each electrochemical polymerization). As pure ILs, though commercially available, are very expensive, the cost for the preparation of these composite materials is really high.

Here, we successfully electrodeposited a composite material of PEDOT doped with IL, using a tiny amount of insoluble IL which can greatly reduce the cost of experiments. In the experimental design, 10-15μL IL containing EDOT monomer was drop-coated on a electrode surface, and then this working electrode, together with a reference electrode and an auxiliary electrode, were put in an aqueous solution of 0.1 M KCl to form a three-electrode system for electropolymerization. The prepared PEDOT/IL composite was found to be highly stable and conductive, and it showed excellent electrocatalytic activity toward the oxidation of dopamine (DA), an important indicator for many serious diseases such as Parkinson's disease, HIV infection, and Schizophrenia. It is known that in biological samples, ascorbic acid (AA) and uric acid (UA) are coexisted with DA, and their oxidation potentials are close to each other, which makes their simultaneous determination highly difficult[27-30]. While with this PEDOT/IL based sensing system, the assay of DA can be easily achieved with satisfying sensitivity and selectivity, and ultrahigh stability.

2. Experimental

2.1 Matarials

3, 4-ethylenedioxythiophene (EDOT), water-insoluble ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (electrochemical grade, >97% purity), DA, AA and UA were purchased from Aladdin Reagents (Shanghai, China). All other reagents were of analytical grade. Phosphate buffered saline (PBS, pH 7.4, containing 0.9% NaCl) was used as buffer for all related experiments. All aqueous solutions were prepared using millipore water produced by a Milli-Q water purifying system.

2.2 Apparatus and Measurements

Electrochemical experiments were performed with a CHI760D electrochemical workstation (Shanghai CH Instruments Co., China). A conventional three-electrode system was used, with an Ag/AgCl (3 M KCl) electrode as the reference electrode (RE), a platinum wire electrode as the auxiliary electrode (AE), and a bare or modified glassy carbon electrode (GCE, 3.0 mm in diameter) as the working electrode.

The electrochemical impedance spectroscopy (EIS) experiments were recorded in 5.0 mM $[Fe(CN)_6]^{4-/3-}$ solution containing 0.1 M KCl within a frequency range of 0.1 Hz to 100 kHz. The alternating current (AC) perturbation was set at 5 mV and the direct current potential was set at 0.20 V. The stability of the PEDOT/IL films was measured in PBS (0.2 M, pH 7.4) by cyclic voltammetry (CV) with potential scanning between -0.2 V and 0.5 V at a scan rate of 100 mV s^{-1}. The electrocatalytic oxidation of DA was examined using CV and amperometry (i-t curve) in stirring PBS, with the potential set at 0.2 V. Simultaneous detection of DA, AA and UA was performed by differential pulse voltammetry (DPV) in a potential range of -0.4 V to 0.8 V with an amplitude of 50 mV and a pulse width of 0.05 s in PBS (0.2 M, pH 7.4).

Scanning electron microscope (SEM) was performed with a JEOL JSM-7500 F SEM instrument (Hitachi High-Technology Co., Ltd., Japan). Fourier transform infrared spectroscopy (FTIR) was performed with the BRUKER TENSOR 70 spectrometer (Bruker Optics, Germany).

2.3 Electrodeposition of PEDOT/IL nanocomposites

GCE was polished with 1.0, 0.3, 0.05μm alumina slurries in sequence and ultrasonically washed in distilled water, ethanol and distilled water for about 2 min, respectively. Then the polished electrode was electrochemically pretreated in PBS according to a previous report[31]. For the preparation of the PEDOT/IL nanocomposite, a small volume (about 10-15 μL) of electrodeposition solution (pure insoluble IL added with 0.1 M EDOT) was dropped on the surface of the GCE to cover the whole electroactive area, and then it was assembled into a three electrode system for further electropolymerization, using a homemade electrochemical cell filled with 0.1 M KCl as the supporting electrolyte, as shown in Fig. 1. The homemade electrochemical cell was made of centrifuge tube (4mL), whose bottom was cut so as to insert the working electrode (sealed with Parafilm). The electrochemical polymerization was carried out by CV deposition with the potential scanning between -0.5 V and 1.2 V at a scan rate of 100 mV s^{-1} for 2 cycles. The obtained PEDOT/IL modified electrodes were washed with acetonitrile and then dried in air, and stored at room temperature until use. For comparison, PEDOT conducting polymer without IL was prepared similarly through the electrochemical polymerization in 0.02 M EDOT solution containing 0.2 M $LiClO_4$.

3. Result and discussion

3.1 Preparation and characterization of PEDOT/IL nanocomposite film

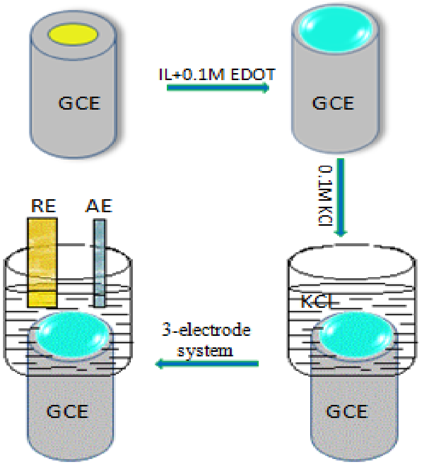

Fig. 1. Schematic illustration of the homemade electrochemical cell.

For the electropolymerization of EDOT in IL with a traditional three electrode system, all the electrodes (including the reference electrode, the auxiliary electrode and the working electrode) were soaked in the IL (acting as supporting electrolyte), which seriously caused the waste of expensive IL as a result of a considerably large volume requirement of IL. To save the consumption of IL, we have changed the traditional mode. Firstly, we dropped the expensive reagent-insoluble IL containing 0.1 M EDOT only on the surface of the electrode, and then assembled the three electrode system by soaking the reference electrode and the auxiliary electrode into 0.1 M KCl which covered the surface of working electrode as the supporting electrolyte. Lastly, we prepared the PEDOT/IL nanocomposite by electrodeposition with the new three electrode system. The principle scheme of the homemade electrochemical cell was shown in Fig. 1, and with this design, the consumption of IL can be greatly reduced.

In this electropolymerization system, as the surface of the working electrode is fully covered by the insoluble but highly conductive IL (dissolved with EDOT), and the only electroactive molecule under the applied potential range is EDOT, the electrochemical polymerization of EDOT will happen at the GCE surface and lead to the formation of PEDOT/IL composite. The morphology of PEDOT/IL composite electrodeposited on the GCE was characterized using SEM. As shown in Fig. 2A, a uniform film was presented at the electrode surface, indicating successful electrodeposition of the PEDOT/IL composite. Clearly, the PEDOT/IL composite showed a highly porous morphology, consisting of many interconnected ginger-like dots, with a size in the range of about 50-100 nm (Fig. 2B), which greatly increased the specific surface area of the modified electrode.

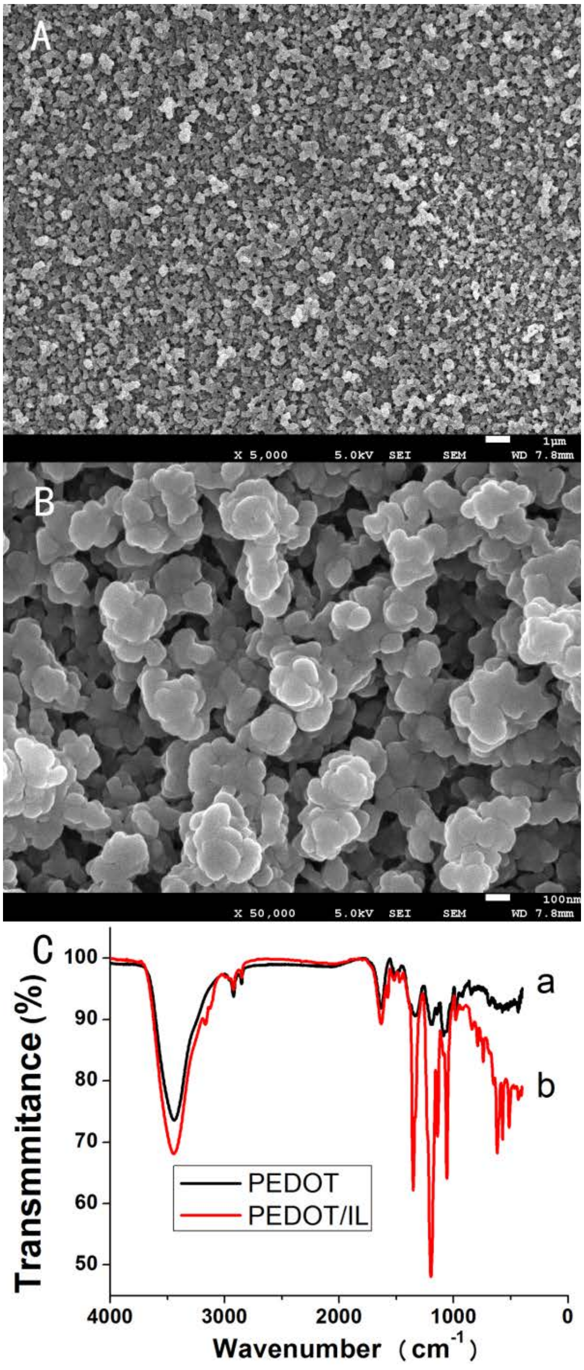

Fig. 2. SEM images of the PEDOT/IL nanocomposite with a lower (A) and higher magnification (B) and FTIR spectra (C) of the PEDOT film (curve a) and PEDOT/IL film (curve b)

The PEDOT/IL composite was also characterized with Fourier transform infrared (FTIR) spectroscopy (Fig. 2C). For the FTIR spectra of the PEDOT (curve a, Fig. 2C), bands at 1198 cm^{-1}, 1575 cm^{-1} and 1635 cm^{-1} are originated from the stretching modes of C-O-C, C-C and C=C bonds in thiophene rings[32-34], which also can be seen in the FTIR spectra of the PEDOT/ IL (curve b, Fig. 2C). Moreover, the O=S=O and C-F bonds of the anionic group of IL showed stretching vibration peaks at 1352 cm^{-1}, 1141 cm^{-1}, and 1059 cm^{-1} (curve b). All the above characteristic peaks demonstrated the successful formation of the PEDOT/IL composite.

The interface properties of PEDOT/IL modified electrodes were further characterized with Faradaic EIS in the presence of a redox probe (Fig. 3). In the Nyquist plots, the semicircle diameter of the impedance spectra can be used to estimate the electron transfer resistance (R_{et}). Clearly, the R_{et} of the PEDOT/IL modified electrode (curve b) was significantly lower than that of the bare GCE (curve a), which may be ascribed to the excellent electronic conductivity and the large specific surface area of the PEDOT/IL nanocomposite.

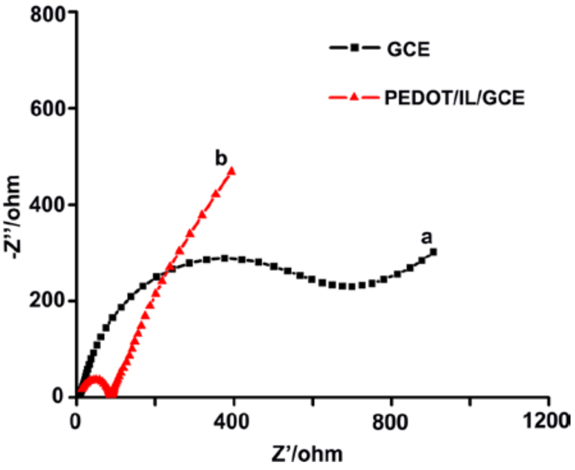

Fig. 3. Nyquist plots of the EIS for the bare GCE (a) and the PEDOT/IL/GCE (b).

3.2 DA sensing using cyclic voltammetry

The voltammetric behavior of DA on the bare GCE and the PEDOT/IL modified GCE was examined using CV. As shown in Fig. 4, there was no significant redox response for both electrodes in PBS (0.2 M, pH 7.4) (Fig. 4, curve a and c). However, in the presence of 0.5 mM DA, a couple of small redox peaks, with the reduction and oxidation peak potential at about 0.102V and 0.205V, and a peak separation (ΔEp) of 0.103V was observed at the bare GCE (Fig. 4, curve b). While on the PEDOT/IL modified GCE, a couple of sharp redox peaks with the reduction and oxidation peak potentials at about 0.125V and 0.180V, and a peak separation (ΔEp) of 0.55V was observed (Fig. 4 curve d). Compared with the bare GCE, the redox reaction of DA at the PEDOT/IL modified GCE exhibited much bigger redox peak currents and smaller peak separation, indicating excellent catalytic activity of the PEDOT/IL toward the oxidation of DA.

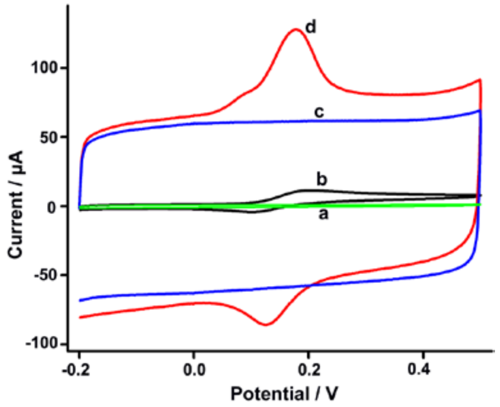

Fig. 4. CV curves of the bare GCE (curves a and b) and the PEDOT/IL/GCE (curves c and d) in PBS (0.2 M, pH 7.4) without (curves a and c) and with (curves b and d) the addition of 0.5 mM DA. The scan rate for the CV was 100 mV s^{-1}.

3.3 Electrochemical properties of the PEDOT/IL/GCE

For the practical application of conducting polymer materials, the stability is crucial in most cases. In order to investigate the stability of the PEDOT/IL nanocomposite, the PEDOT/IL modified electrode was tested in PBS (0.2 M, pH 7.4) using CV between -0.2 V and 0.5 V, with duration over 10,000 cycles, as shown in Fig. 5A. The charge storage capacity of the PEDOT/IL modified electrode was evaluated by CV curves, as the charge storage capacity was proportional to the CV curve covered area. Interestingly, the charge storage capacity of the PEDOT/IL modified electrode was able to retain 98.5 % of its initial value after 10,000 cycles (Fig. 5B), implying ultrahigh stability of the PEDOT/IL composite. To further investigate the durability of the catalytical activity of the PEDOT/IL composite, the CV response of the PEDOT/IL/GCE in PBS (0.2 M, pH 7.4) containing 0.5 mM DA was monitored after different CV scanning cycles, as shown in Fig. 6. It is clear that both the oxidization and reduction peak currents of DA can be maintained even after 10,000 CV cycles. Thus, the excellent stability of the PEDOT/IL/GCE ensures reliable application of this material for the detection of DA.

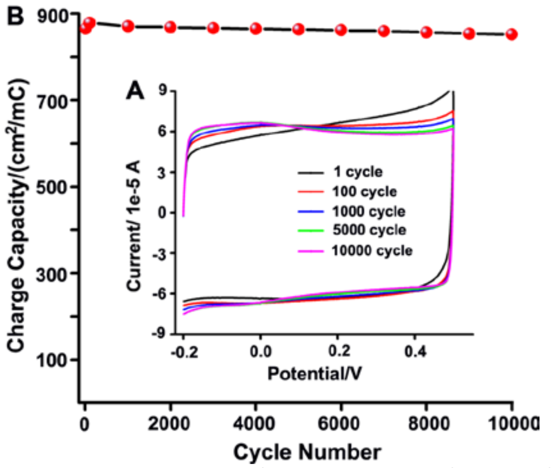

Fig. 5. The charge storage capacity of the PEDOT/IL modified GCE after different CV cycles measured in PBS (0.2 M, pH 7.4) between -0.2 V and 0.5 V at a scan rate of 100mVs^{-1} (B). Inset A, CV responses of the PEDOT/IL/GCE in PBS (0.2 M, pH 7.4) at different CV cycles between -0.2 V and 0.5 V at a scan rate of 100mV s^{-1}.

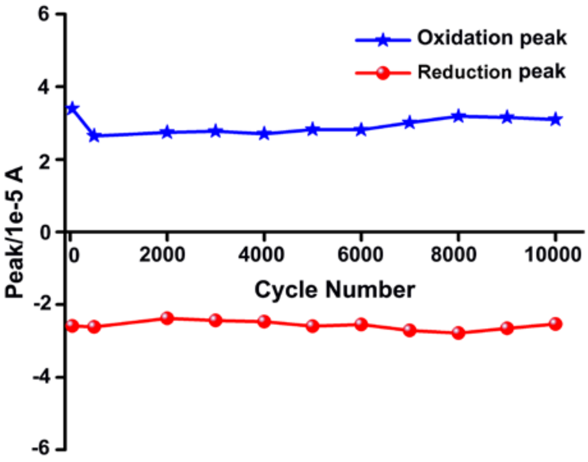

Fig. 6.CV responses of the PEDOT/IL modified GCE in PBS (0.2 M, pH 7.4) containing 0.5 mM DA after different CV cycles. The PEDOT/IL modified GCE was scanned for different CV cycles between -0.2 V and 0.5 V at a scan rate of 100 mVs^{-1}.

3.4 Amperometric detection of DA

The Amperometric response of DA was measured in PBS (0.2 M, pH 7.4) on the PEDOT/IL modified GCE at a constant potential of 0.2 V, which was the oxidation potential of DA (Fig4 curve d). As shown in Fig. 7, the amperometric i-t curve of DA showed that the PEDOT/IL modified GCE responded quickly to the successively addition of various concentrations of DA in stirring PBS. The well-defined steady-state current response indicated that the PEDOT/IL/GCE can detect a very low concentration of DA (Inset b) with a very fast response time (< 4 s, Inset c). The linear response range of this DA sensor was from 0.2 to 312 µM, and the regression equation of the calibration curve was I (µA) = 0.094 + 45.35 c (R^2=0.9995) (Inset a). The detection limit was calculated to be 51 nM based on a signal-to-noise ratio of 3, which is lower than that of many related DA assays[35-38].

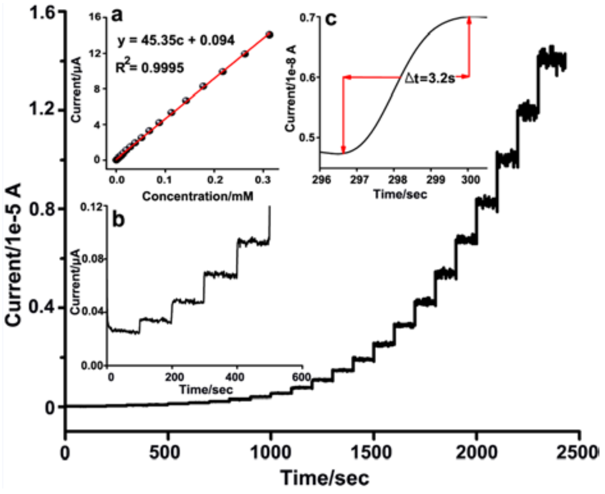

Fig. 7 Amperometric responses of the PEDOT/IL modified GCE in stirring PBS (0.2 M, pH 7.4) at an applied potential of 0.2 V to various concentrations of DA from 0.2 µM to 312 µM. Inset a, the linear calibration curve of currents and DA concentrations; Inset b and c, the enlarged curves of amperometric response of DA

3.5 Simultaneous detection of DA, AA and UA

The overlap of the oxidation potentials of DA, AA and UA made their simultaneous detection very difficult for many electrochemical sensors. Based on the excellent electrocatalytic activity of the PEDOT/IL nanocomposite toward the oxidation of DA, the developed electrochemical sensor can easily distinguish DA, AA and UA, as shown in Fig. 8. Clearly, the oxidation peaks of DA, AA and UA are mixed at the bare GCE (curve a), while at the PEDOT/IL/GCE, their DPV oxidation peaks are well separated (curve b, -0.06 V for AA, 0.15 V for DA and 0.26 V for UA). Therefore, owing to the electrocatalytic activity of the PEDOT/IL nanocomposite, the PEDOT/IL modified electrode can be used for the simultaneous detection of DA, AA and UA effectively.

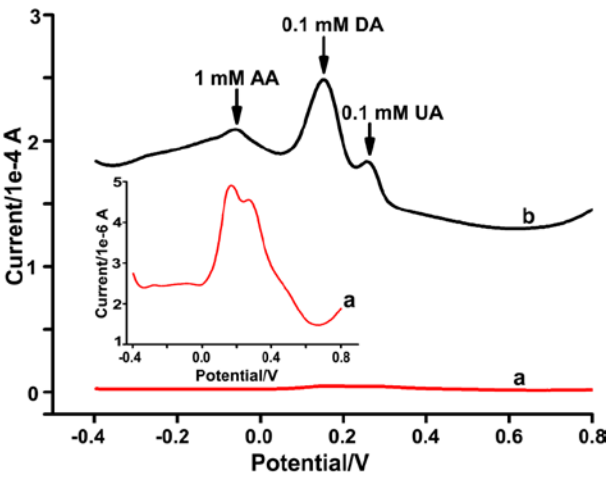

Fig.8. DPVs of bare GCE (a) and the PEDOT/IL modified GCE (b) in PBS (0.2 M, pH 7.4) containing 0.1 mM DA, 1 mM AA and 0.1 mM UA. Inset is the enlarged figure of curve a.

4. Conclusion

In summary, a highly stable conducting polymer nanocomposite of PEDOT/IL was prepared using a cost-effective method. Through a novel design of the three electrode system, a very small amount of IL (less than 15 µL) containing EDOT can be used for the effective electrodeposition of PEDOT/IL, which greatly reduced the cost. The prepared PEDOT/IL exhibited a highly nanoporous microstructure, and excellent stability and catalytic activity toward the oxidation of DA. The PEDOT/IL based electrochemical sensor can be used for the detection of DA with satisfying selectivity and sensitivity. It is expected that this method may be extended to the cost-effective preparation of other composite materials based on different conducting polymers and ILs.

Acknowledgements

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