



# Poly(zwitterionic liquids) functionalized polypyrrole/graphene oxide nanosheets for electrochemically detecting dopamine at low concentration



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## ABSTRACT

Poly(3-(1-vinylimidazolium-3-yl)propane-1-sulfonate) (PVIPS), a novel kind of poly(zwitterionic liquids) (PZILs) containing both imidazolium cation and sulfonate anion, was successfully modified on the surface of polypyrrole/graphene oxide nanosheets (PPy/GO) by covalent bonding. The obtained novel PZILs functionalized PPy/GO nanosheets (PVIPS/PPy/GO) modified glassy carbon electrode (GCE) presented the excellent electrochemical catalytic activity towards dopamine (DA) with high stability, sensitivity, selectivity and wide linear range (40–1220 nM), especially having a lower detection limit (17.3 nM). The excellent analytical performance is attributed to the strongly negative charges on the surface of modified GCE in aqueous solution, which is different from conventional poly(ionic liquids) modified GCE. DA cations could be quickly enriched on the electrode surface by electrostatic interaction in solution due to the existence of  $-\text{SO}_3^-$  groups with negative charge at the end of pendant groups in zwitterionic PVIPS, resulting in a change of the electrons transmission mode in the oxidation of DA, that is, from a typical diffusion-controlled process at conventional poly(1-vinyl-3-ethylimidazole bromide) (PVEIB)/PPy/GO modified GCE to a typical surface-controlled process.

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## 1. Introduction

In the past few years, poly(ionic liquids) (PILs), as a new kind of functional material, have become a research focus, because they combine the unique properties of ionic liquids (ILs) (such as low flammability and toxicity, enhanced ionic conductivity, high polarity, good chemical stability, etc.) [1] with the macromolecular architecture, and presented the intrinsic polymer properties with new functions and expanded the application of ILs in various fields [2]. For instance, hierarchically structured nanoporous PILs membranes were coated onto the surface of an optical fiber, resulting in a device with high pH-sensing performance in terms of the response rate and the sensitivity [3]; ILs groups can be introduced on the surface of polymer microspheres by a copolymerization of polymerizable ILs monomers and styrene, which facilitated the formation of novel K-birnessite hierarchical hollow microspheres bearing excellent performance for the removal of the anionic organic dye from aqueous solution [4]; noble metal nanoparticles functionalized carbon nanotubes were synthesized by PILs as a kind of

effective stabilizer or modifier and showed good performance in methanol electrooxidation [5]; especially, the performance of electrochemical devices was significantly improved by the introduction of PILs: glucose oxidase was immobilized on PILs functionalized carbon nanotubes or graphene by electrostatic interaction and the modified electrodes exhibited excellent direct electrochemical response for glucose [6–7]; nonenzymatic sensor for hydrogen peroxide was improved by Ag nanoparticles electrodeposited on PILs stabilized graphene [8].

Recently, our group have reported that the imidazolium-type PILs, poly(1-vinyl-3-ethylimidazole bromide) (PVEIB), functionalized polypyrrole nanotubes (PVEIB/PPyNTs) presented the excellent sensitivity and good stability for the simultaneous detection of dopamine (DA) and ascorbic acid (AA) [9], especially, PVEIB functionalized polypyrrole/graphene oxide nanosheets (PVEIB/PPy/GO) exhibited an excellent electrochemical catalytic activity towards DA with good stability, high sensitivity and selectivity as well as wide linear range in the present of AA with high concentration [10]. The graphene-based electrodes can provide excellent capability in ultrasensitive electrochemical detection of single nucleotide polymorphisms of DNA [11] and early detection of leukemia [12–13] using differential pulse voltammetry (DPV). PVEIB as a kind of cationic-type PILs effectively improved the transmission mode of electrons and resulted in the different electrocatalytic performance towards the oxidation of DA and AA. However, the detection

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limit of DA using PVEIB/PPy/GO modified glassy carbon electrode (GCE) was unsatisfactory for detecting the very low concentration of DA in the extracellular fluid [14]. PVEIB and DA often showed strong electropositivity in buffer solution with suitable pH value, which may seriously influence the detection of DA at nanomolar level concentration due to the electrostatic repulsion between PVEIB and DA. In the family of ILs, zwitterionic liquids (ZILs) are electronically neutral with a positive and a negative charge chemically bonded in the same group, which are significantly different from conventional ILs and expected to attract many attentions in several aspects [15], especially as proton transfer media in fuel cell application [16–17], because of their high ion density, unique ionic conductivity and simple preparation [18–19]. Poly(zwitterionic liquids) (PZILs) can be synthesized by the combination of ZILs groups with the macromolecular architecture, which may present promising application in electrochemical sensors and biosensors, but to our knowledge, by far, no related reports have been seen.

Herein, poly(3-(1-vinylimidazolium-3-yl)propane-1-sulfonate) (PVIPS), a novel kind of PZILs containing both imidazolium cation and sulfonate anion, were successfully modified on the surface of polypyrrole/graphene oxide nanosheets (PPy/GO) by covalent bonding. The obtained novel PZILs functionalized PPy/GO nanosheets (PVIPS/PPy/GO) modified GCE presented the excellent electrochemical catalytic activity towards dopamine (DA) with high stability, sensitivity, selectivity and wide linear range (40–1220 nM), especially having a lower detection limit (17.3 nM), attributed to the strongly negative charge on the surface of modified GCE in aqueous solution which is different from conventional poly(ionic liquids) modified GCE, due to the existence of  $-\text{SO}_3^-$  groups with negative charge at the end of pendant groups in zwitterionic PVIPS.

## 2. Experimental section

### 2.1. Materials

Pyrrrole (Py) ( $\geq 98.0\%$ ), 1,3-propane sultone ( $\geq 99.5\%$ ) and bromoethane ( $\geq 98.0\%$ ) are chemical grade, which were purchased from Sinopharm Chemical Reagent Co., Ltd. N-vinyl imidazole was purchased from Yancheng Medical Chemical Factory (China), which were distilled under vacuum before use. High-purity graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. All the other reagents are analytical grade and were used without further purification, such as  $\text{KMnO}_4$  (Tianjin Baishi Chemical Co., Ltd,  $\geq 99.5\%$ ),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 99.0\%$ ),  $\text{H}_2\text{SO}_4$  ( $\geq 98.3\%$ ),  $\text{KOH}$  ( $\geq 85.0\%$ ), chloroform ( $\geq 98.0\%$ ), uric acid (UA) ( $\geq 99.0\%$ ) and  $\text{NaCl}$  ( $\geq 99.5\%$ ) (Sinopharm Chemical Reagent Co. Ltd.), L-ascorbic acid (AA) ( $\geq 99.7\%$ ),  $\text{H}_3\text{PO}_4$  ( $\geq 98.0\%$ ),  $\text{Na}_2\text{HPO}_4$  ( $\geq 99.0\%$ ) and  $\text{NaH}_2\text{PO}_4$  ( $\geq 99.0\%$ ) (Tianjin Yongda Chemical Reagent Co., Ltd.),  $\text{H}_2\text{O}_2$  (Shenyang Xinhua Reagent Factory,  $\geq 30.0\%$ ),  $\text{NaNO}_3$  (Tianjin Bodi Chemicals Co., Ltd.,  $\geq 99.0\%$ ), dimethyl formamide (DMF) (Tianjin Beilian Fine Chemicals Development Co., Ltd.,  $\geq 99.5\%$ ), ethanol (Tianjin Damao Chemical Factory,  $\geq 99.7\%$ ), dopamine hydrochloride (DA) (Alfa Aesar,  $\geq 99.0\%$ ), 1,4-dibromobutane ( $\geq 98.0\%$ ), 2,2-azobisisobutyronitrile (AIBN) ( $\geq 98.0\%$ ), L-Tryptophan (Trp) ( $\geq 99.0\%$ ), Serotonin hydrochloride (SER) and Epinephrine hydrochloride (Ep) ( $\geq 98.0\%$ ) (Aladdin reagent (Shanghai) Co., Ltd.).

### 2.2. Preparation of PVIPS/PPy/GO nanosheets

The reaction procedure for preparation of PVIPS/PPy/GO was similar to that of the poly(1-vinyl-3-ethylimidazole bromide) functionalized polypyrrole/graphene oxide nanosheets (PVEIB/PPy/GO) according to our previous work [10]. 3-(1-vinylimidazolium-3-yl)propane-1-sulfonate (VIPS) was synthesized by the substitution reaction of N-vinyl imidazole and 1,3-propane sultone. In a typical procedure, 150 mg of VIPS and 25 mg AIBN were dissolved in 20 mL of ethanol. 30 mg of polymerizable vinyl imidazolium-type ILs modified PPy/GO (ILs/PPy/

GO) (synthesized according to our previous work [10]) were added into the above solution and dispersed after ultrasound for 5 min. Then, the mixture was removed to an oil bath and the reaction was carried out under refluxing for 4 h with balloon protection filled with  $\text{N}_2$  at  $68^\circ\text{C}$ . The products were collected by centrifugation, and then washed and redispersed with ethanol and water for several times to remove unreacted chemicals and outgrowths. Finally, the obtained black powders were dried in vacuum at  $45^\circ\text{C}$  for 24 h.

### 2.3. Preparation of PVIPS/PPy/GO nanosheets modified GCE

A PVIPS/PPy/GO suspension was prepared by mixing obtained PVIPS/PPy/GO nanosheets (1 mg) with ethanol (1 mL).  $2\ \mu\text{L}$  of the suspension was dropped onto clean GCE surface to form a film and then evaporating the solvent in the environment. The modified GCE was used as the working electrode. Otherwise, GO modified GCE, PPy/GO modified GCE and PVEIB/PPy/GO modified GCE were also prepared for the comparison.

### 2.4. Characterizations and apparatus

The images of PVIPS/PPy/GO were obtained by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements, respectively. SEM measurements were performed on a Hitachi SU-8010 electron microscope with primary electron energy of 10 kV. TEM experiments were performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The zeta-potential data of the products were obtained by using a Zeta-Plus4 instrument (Brookhaven Corp., USA). Fourier transform infrared spectroscopy (FTIR) Spectra of KBr powder-pressed pellets were recorded on a Perkin Elmer Spectrum one FTIR spectrometer (Perkin-Elmer Corp., USA). Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB 250 using Al as the exciting source. Transmission spectra were recorded on a TU-1900 UV/visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). An SDT Q600 Simultaneous DSC-TGA Instrument (TA Corp., USA) was used to investigate the thermal stability of PVIPS/PPy/GO in the temperature range from room temperature to  $700^\circ\text{C}$  under condensed  $\text{N}_2$  at a rate of  $10.0^\circ\text{C}/\text{min}$ . The electrochemical performance of PVIPS/PPy/GO was investigated by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with a CHI660E Electrochemical Station (Shanghai CHENHUA instrument Co., Ltd.). In a three-electrode system, a modified GCE, a platinum wire and an Ag/AgCl electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The measurements were performed in 0.05 M phosphate buffer solution (PBS) ( $\text{pH} = 7.0$ ,  $20^\circ\text{C}$ ) with 0.05 M NaCl.

Dopamine can be self-polymerized into polydopamine under some conditions. Except for the influence of solution pH value on the oxidation of dopamine, the oxygen content in solution and the lighting conditions during the reaction can also have some effects on the self-polymerization of dopamine. In our experiments, each solution in the experiment was treated with nitrogen to remove the oxygen content from it, so the oxygen would have little impact on all the electrochemical response of DA in the testing system. Meanwhile, all the experiments were carried out in dim lighting conditions as much as possible. So both the oxygen content in solution and the lighting conditions should have little influence on the self-polymerization of dopamine.

### 2.5. Data processing and error analysis

In order to get the reliable and practical results, the experiments were carried out for many times to ensure the reliability of the sample data. At the same time, the error analysis in analytical chemistry field was also used in the data processing based on the obtained sample data. For example, 10 sets of data of the oxidation peak current corresponding to the oxidation of DA were obtained under the same

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