



Development of a poly(alizarin red S)/ionic liquid film modified electrode for voltammetric determination of catechol



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ABSTRACT

A novel modified electrode for voltammetric catechol determination was fabricated by electropolymerization of alizarin red S (ARS) onto a glassy carbon electrode (GCE) in one kind of room-temperature ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, BMIMBF₄). The polymeric ARS/ionic liquid (PARS/BMIMBF₄) film modified electrode was characterized by using scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and electrochemical methods. The EDX, XPS and FTIR results indicated that PARS/BMIMBF₄ film was successfully obtained. Compared with the GCE modified by electropolymerization of ARS in aqueous solution, the GCE modified by electropolymerization of ARS in BMIMBF₄ showed smoother and more compact morphology for coating and better electroanalytical properties. Given the combined electrochemical activity of PARS and excellent conductivity of BMIMBF₄, the PARS/BMIMBF₄/GCE has been successfully used for catechol determination by differential pulse voltammetry (DPV) with a linear range of 0.10 to 500 μM. The sensitivity and detection limit are 42 nA/μM and 0.026 μM, respectively. The PARS/BMIMBF₄ modified electrode was successfully applied to the determination of catechol in real water samples and may serve as a simple but high-performance sensor for the determination of some environmental pollutants.

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1. Introduction

Alizarin red S (1, 2-dihydroxy-9, 10-anthraquinone-3-sulfonate, ARS) is an anthraquinone dyestuff, which is commonly used to detect metal ions because of its vicinal diols and anthraquinone compositions [1–3]. With the rapid development of electrochemistry [4–9], various kinds of new materials including ARS have been used more frequently than before [10–16]. As an electroactive species, ARS has been employed for the electrochemical detection of some organic molecules [17–19]. ARS has also been successfully deposited onto the surface of glassy carbon electrode (GCE) by electropolymerization [20,21]. The process of electropolymerization of ARS is similar to the radical polymerization of phenol. Having the benzoquinonyl and hydroxyl group in the molecule, polymeric ARS (PARS) can serve as proton

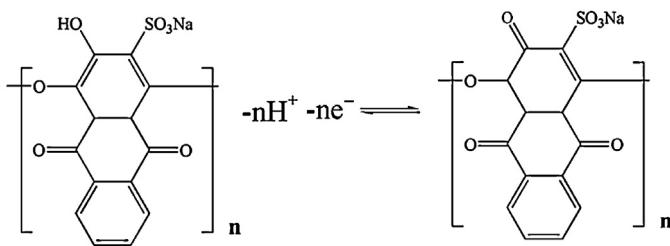
receptor that promotes balanced reaction and enhances charge transfer between electrode and reagent [21]. The mechanism of electrochemical oxidation of PARS on GCE is shown in Scheme 1. However, given its poor conductivity, ARS or PARS is used in combination with other nanomaterials, such as gold nanoparticles [20], graphene [21], multi-walled carbon nanotubes [22], and so on. Such combination process is complicated, thereby limiting the application of ARS or PARS.

Room-temperature ionic liquids (RTILs) have attracted significant attention as a class of organic molten salts with a melting point below 100 °C. RTILs have unique physical and chemical properties, such as negligible vapor pressure and distinctive solubility, wide electrochemical window, and high ionic conductivity [23–25]. Hence, RTILs have been widely used in various applications, including electrodeposition [26,27], extraction [28–30], organic synthesis [31], and electropolymerization [32,33]. The preparation of polymers by electropolymerization in RTILs has been gained attention in recent years. Air- and water-stable RTILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) are

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Scheme 1. Electrochemical oxidation of PARS.

commonly used [34,35]. RTILs can not only support electrolyte but also offer growth medium for the electropolymerization of polymers [32,33]. Polymer films obtained by electropolymerization in RTILs have significantly altered film morphologies and improved electrochemical/physical properties compared with the polymers grown in conventional media. For instance, Erbil et al. [36] have reported a comparative study of polypyrrole in 1-ethyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl) imide or oxalic acid solution. Compared with polypyrrole polymerized in oxalic acid, polypyrrole polymerized in RTILs showed better morphology for coating and better stability for electronic conductivity. Given their wide electrochemical windows and unique solvent capability, RTILs can be used for the electropolymerization of some polymers that can not be synthesized in aqueous solution because of oxygen evolution [37–39].

In the present work, the electropolymerization of ARS onto GCE in RTIL (i.e., BMIMBF₄) was introduced for the first time. BMIMBF₄ was successfully mixed in the PARS film. The obtained PARS/BMIMBF₄ film has significantly altered film morphologies and improved electrochemical properties. The proposed PARS/BMIMBF₄ film modified electrode was used for electrochemical determination of catechol.

2. Experimental

2.1. Materials

BMIMBF₄ was supplied by Shanghai Cheng Jie Chemical Co. Ltd. Catechol was obtained from Shanghai SSS Reagent Co. Ltd. All other chemicals were of analytical reagents and used without further purification. All experiments were conducted at room temperature. Deionized water (18.2 MΩ·cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2. Apparatus

The morphology of the modified electrodes was characterized by using scanning electron microscopy (SEM, Hitachi S-4800 microscope, Japan). The elemental composition of the modified electrodes was characterized by using energy dispersive X-ray spectroscopy (EDX, HORIBA EX-350) and X-ray photoelectron spectroscopy (XPS, SHIMADZU/KRATOS AMICUS), respectively. FTIR spectra were recorded with a Nicolet iS 10 infrared spectrometer. The pH measurements were performed at an E-201-C Model pH meter (Shanghai Leici Instrument Factory). All the electrochemical experiments were performed in a conventional three-electrode cell controlled by CHI 660D Electrochemical Work Station (CH Instruments, Inc.). A glassy carbon (GC, 3 mm in diameter, CH Instruments, Inc.) disk and a platinum foil (Shanghai Weiye Instrument Factory) were used as the working and counter electrodes, respectively. Ag/AgCl reference electrode (CH Instruments, Inc.) was adopted in aqueous solution. Ag wire immersed in BMIMBF₄, which was 0.2 V with respect to the Ag/AgCl reference electrode,

was adopted in the BMIMBF₄ media. All potentials were measured with respect to the Ag/AgCl reference electrode.

2.3. Preparation of the modified electrodes

Prior to use, the GCE was polished to a mirror finish using a microcloth with 0.05 μm alumina slurry and then rinsed and ultrasonicated with deionized water. The GCE was immersed in pure BMIMBF₄ containing 0.1 mM ARS by using cyclic voltammetry (CV) from -1.4 to 1.8 V at 100 mV/s for 30 cycles [21]. The obtained PARS/BMIMBF₄/GCE was washed carefully with deionized water. PARS/GCE was also fabricated in 0.1 mM ARS aqueous solution using a similar method for comparison.

2.4. Electrochemical analysis procedure

Unless otherwise stated, 0.1 M phosphate buffer solution (PBS, pH 7.0) was used as the supporting electrolyte for catechol determination. CV and the differential pulse voltammetry (DPV) were adopted. The oxidation peak current of catechol was adopted as a response signal of catechol. CV was performed under the following parameters: initial potential of -0.2 V, final potential of 0.5 V, scan rate of 0.1 V/s. DPV was performed under the following parameters: initial potential of 0 V, final potential of 0.35 V, amplitude of 0.05 V, pulse width of 0.2 s, pulse period of 0.4 s, equilibrium time of 2 s.

3. Results and discussion

3.1. Characterization of the modified electrode

The surface morphologies of PARS film synthesized in aqueous solution (Fig. 1a) and BMIMBF₄ (Fig. 1b) were characterized by SEM. As shown in Fig. 1a, the PARS film synthesized in aqueous solution was rough and nonuniform. Many granules with irregular shape were dispersed on the film surface. Compared with the PARS film synthesized in aqueous solution, the PARS film synthesized in BMIMBF₄ (Fig. 1b) had smoother and less granular surface. The film synthesized in BMIMBF₄ also uniformly coated the electrode area. Given that the other factors are identical except for the electrolytes of electropolymerization, we hypothesized that the change in morphology is caused by the mix of BMIMBF₄ in the PARS film. To confirm our conjecture, the PARS film synthesized in BMIMBF₄ was characterized by EDX (Fig. 2a). The EDX results showed that C, B, O, N, F, Si and S are the major elements of the PARS film synthesized in BMIMBF₄. Strong C, O, F and S signals and weak N, B and Si signals were detected. The pure PARS backbone only showed C, O and S signals. Thus, F, B and N signals must be contributed by BMIMBF₄. The source of Si might be the Si sealant. The PARS film synthesized in BMIMBF₄ was also characterized by using X-ray photoelectron spectroscopy (XPS) to confirm our conjecture. The results of XPS are consistent with those of EDX, wherein F and N signals which originated from BMIMBF₄ were detected (Fig. 2b). These results illustrated that BMIMBF₄, ARS or PARS were existed on the surface of GCE.

To further clarify the successful electropolymerization of PARS on GCE, FTIR measurements for BMIMBF₄, ARS and PARS obtained from pure water and BMIMBF₄ were carried out and the corresponding results were shown in Fig. 3. The peaks in the band of 1628 cm⁻¹ and 1590 cm⁻¹ which may due to the C=O group with a strong intensity appeared in the spectrum of ARS (Fig. 3, Curve a). Compared with the spectrum of ARS, the peak in the band of 1590 cm⁻¹ disappeared after electropolymerization (Fig. 3, Curve b). Considering the disappearance of the absorption band of 1590 cm⁻¹ for one carbonyl functionality, the formation of PARS with C=O group which almost in the same environment was a reasonable explanation. In addition, the peak in the band of 1155 cm⁻¹

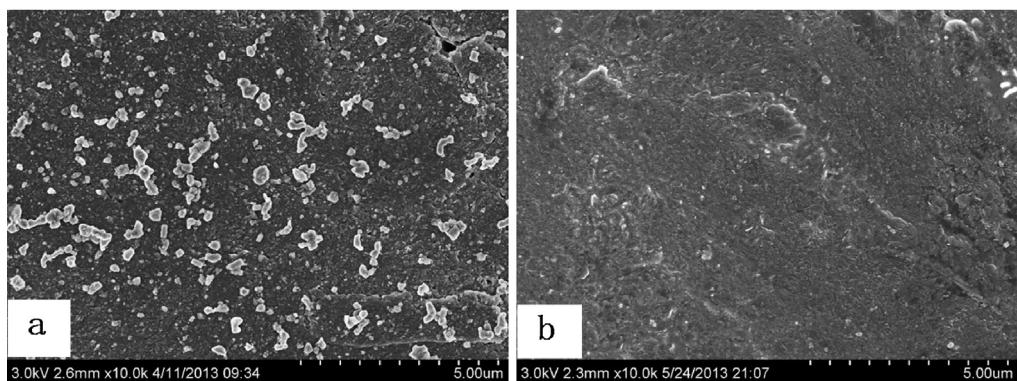


Fig. 1. SEM micrograph of PARS films synthesized in aqueous solution (a) and BMIMBF₄ (b).

which may due to the ether group was observed in the spectrum of PARS (Fig. 3, Curve b). These result further illustrated that PARS can be obtained on GCE by electropolymerization in pure water. On the other hand, the peaks in the band of 3143 cm⁻¹, 3084 cm⁻¹ (C-H stretching vibration of imidazole ring), 1572 cm⁻¹ (stretching vibration of imidazole ring) and 1057 cm⁻¹ (stretching vibration of BF₄⁻) appeared in the spectrum of PARS electropolymerized in BMIMBF₄ (Fig. 3, Curve c), which is similar to that of pure BMIMBF₄

(Fig. 3, Curve d). It demonstrated BMIMBF₄ were existed on the surface of GCE. The result was in accordance with that derived from Fig. 2. In addition, the peaks in the band of 1590 cm⁻¹ and 1155 cm⁻¹ were still existed which indicated that PARS can be obtained on GCE by electropolymerization in BMIMBF₄. The consistency of the spectrum of PARS between Curve b and Curve c proved that there was no chemical interaction between PARS and BMIMBF₄. The possible mechanism was that the imidazolium structure of BMIMBF₄ could interact with the GC electrode through π-π interactions [40]. When PARS films were electrochemical synthesized in BMIMBF₄, BMIMBF₄ was successfully mixed in polymeric ARS film to form PARS/BMIMBF₄ film on GCE.

Typical CVs for PARS/GCE synthesized in 0.1 M NaCl, PARS/GCE synthesized in aqueous solution, PARS/BMIMBF₄/GCE and bare GCE were recorded between -0.2 V and 0.5 V in 1 mM [Fe(CN)₆]^{3-/4-} and 0.1 M KCl solution (Fig. 4). The CVs of the bare GCE showed well-shaped reduction-oxidation (redox) peaks. However, compared with the bare GCE, PARS/GCE synthesized in 0.1 M NaCl and PARS/GCE synthesized in aqueous solution had large potential difference between the anodic and cathodic peaks (ΔE_p) at lower peak currents. The difference between the curves (b, c and d) can be attributed to the electrostatic repulsion force between the negatively charged [Fe(CN)₆]^{3-/4-} and PARS film. The amount of PARS which was synthesized in 0.1 M NaCl was more than that synthesized in aqueous solution because of the larger ionic strength. Too thick PARS film hindered the electronic transfer. So PARS/GCE

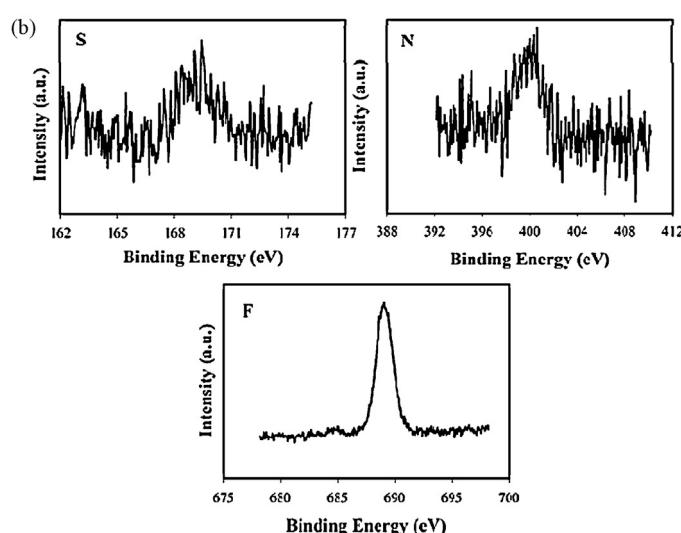
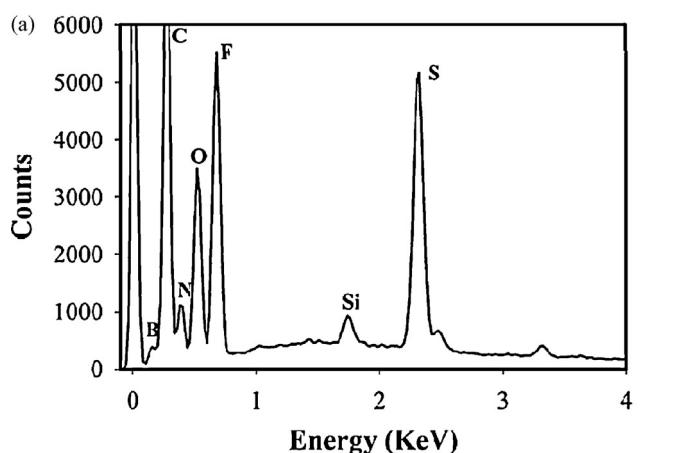


Fig. 2. (a) EDX spectrum and (b) XPS spectrum of PARS films synthesized in BMIMBF₄.

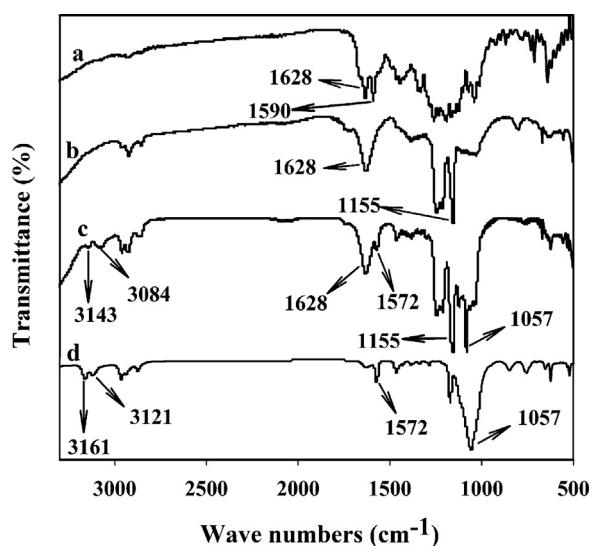


Fig. 3. FTIR spectrum of (a) ARS, (b) PARS synthesized in pure water, (c) PARS synthesized in BMIMBF₄ and (d) pure BMIMBF₄.

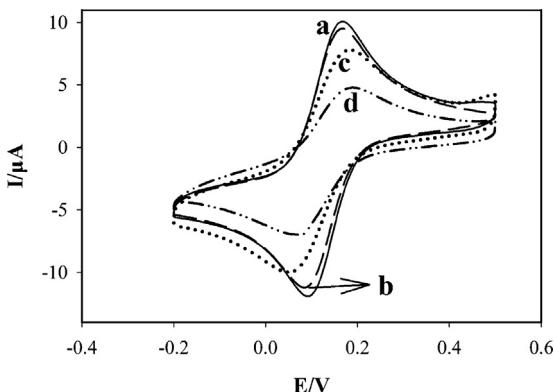


Fig. 4. CVs of (a) bare GCE, (b) PARS/BMIMBF₄/GCE, (c) PARS/GCE synthesized in aqueous solution, (d) PARS/GCE synthesized in 0.1 M NaCl in 1 mM [Fe(CN)₆]³⁻/⁴⁻ and 0.1 M KCl solution in the potential range of -0.2 to 0.5 V. Scan rate: 100 mV/s.

synthesized in 0.1 M NaCl (Fig. 4, Curve d) had lower peak currents. Furthermore, when BMIMBF₄ was mixed in the PARS film, the peak currents increased to a certain degree whereas the ΔE_p value decreased (Fig. 4, Curve b). The presence of BMIMBF₄ was assumed to be critical in accelerating the transfer of the electrons because of its good conductivity.

3.2. Electrochemical behavior of catechol on the PARS/BMIMBF₄ modified GCE

Catechol is highly toxic to humans, animals, plants, and aquatic life at above its concentration limits. Hence, the detection and quantification of catechol have gained significant interest in environmental protection, food safety and human health. Fig. 5 illustrates the potential application of the PARS/BMIMBF₄ film in catechol determination. As shown in Curve a, a pair of broad redox peaks, in which the ΔE_p was 140 mV, was obtained for 0.3 mM catechol on the bare GCE. The ΔE_p value of the PARS/GCE (Fig. 5, Curve b) decreased to 80 mV compared with that of bare GCE. These results indicated that the presence of PARS can improve the electrochemical reversibility of catechol/O-Quinone [41]. The anodic and cathodic peak currents also significantly increased. The ΔE_p value of PARS/BMIMBF₄/GCE decreased to 50 mV (Fig. 5, Curve c), which was considerably smaller than that of bare GCE and PARS/GCE. Furthermore, the anodic and cathodic peak currents on the PARS/BMIMBF₄/GCE showed up to the three fold improvement compared with those on PARS/GCE. These results suggested that BMIMBF₄ not only possessed strong electrocatalytic activity toward

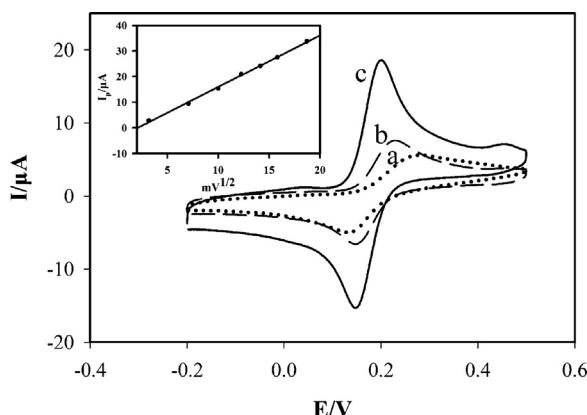


Fig. 5. CVs of (a) bare GCE, (b) PARS/GCE and (c) PARS/BMIMBF₄/GCE in 0.1 M PBS (pH 7.0) containing 0.3 mM catechol. Scan rate: 100 mV/s. Insert: linear relationship of square root of scan rate versus oxidation current response of 0.3 mM catechol.

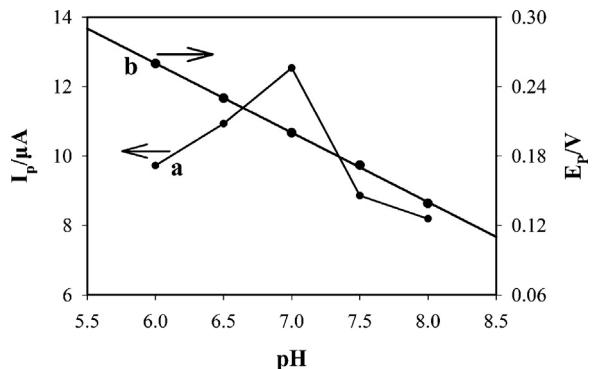


Fig. 6. Effect of pH on (a) the oxidation current response and (b) oxidation peak potential of 0.3 mM catechol in 0.1 M PBS on PARS/BMIMBF₄/GCE.

the redox reaction but also promoted the electron-transfer rate on the surface of the electrode. The relationship between scan rate and catechol response was also investigated. The anodic peak currents of catechol were proportional to the square root of the scan rate from 10 to 300 mV s⁻¹ (the inset in Fig. 5). This result indicated that the electrooxidation reactions of catechol at PARS/BMIMBF₄/GCE were typical diffusion-controlled processes.

3.3. Optimization for catechol determination on PARS/BMIMBF₄/GCE

3.3.1. Effect of electropolymerization cycles

The voltammetric response of catechol was dependent on the thickness of the PARS/BMIMBF₄ film, which was determined by the electropolymerization cycles of ARS. The relationship between the electropolymerization cycles and peak current was investigated. The peak current of 0.3 mM catechol on PARS/BMIMBF₄/GCE gradually increased after 10 to 30 cycles and then peaked after 30 cycles. The peak current decreased continuously when the number of cycles was further increased. Such phenomenon may be associated with the increased thickness of the PARS/BMIMBF₄ film, which resulted in the obstruction of electron-transfer on the electrode surface. Based on the above analysis, the optimized electropolymerization cycles are chosen as 30 cycles.

3.3.2. Effect of pH values

The pH value of the supporting electrolyte is an important factor that affects the voltammetric response of catechol. Curve a in Fig. 6 shows the dependence of anodic peak currents on PARS/BMIMBF₄/GCE in 0.1 M PBS containing 0.3 mM catechol from pH 6.0 to 8.0. The anodic peak current gradually increased from pH 6.0 to pH 7.0. The maximum current was observed at pH 7.0. However, the anodic peak current decreased when pH was increased from pH 7.0 to 8.0. Thus, pH 7.0 was deemed optimum. In addition, the peak potential shifted negatively and linearly as the solution pH increased from pH 6.0 to 8.0 (Fig. 6, Curve b). The slope value of the E_p/pH plots was -60 mV/pH for catechol. This value indicated that an equal number of electrons and protons (two electrons and two protons) were involved in the electrochemical redox processes of catechol based on the Nernst Equation. Scheme 2 shows the oxidation mechanism of catechol on the PARS film coated GCE. The electrode gained two electrons from ARS and yielded the respective oxidation product (PARS) after ARS was scanned in the positive direction between -1.4 V and 1.8 V on the bare GCE. When catechol diffused to the surface of GCE, the PARS that already lost its electrons was inclined to take the corresponding electrons from catechol by oxidizing it to O-quinone and returning to its original ARS.

Table 1

Comparison of response characteristic on different modified electrodes.

Electrodes	Linear range (μM)	Detecting limit (μM)	References
Palygorskite-modified CPE	5–100	0.57	[42]
MWCNT ^a -Polypyrrole-HRP ^b -Au	1.6–8	0.93	[43]
GO ^c -mesoporous MnO ₂ /GCE	0.03–1	0.01	[44]
Polydopamine-rGO ^d /GCE	1–230	0.74	[45]
Au-C ^e /GCE	1–100	0.15	[46]
CNTs/ionic liquid/GCE	0.18–35	0.06	[47]
MWNTs-P3MT ^f /GCE	0.5–150	0.05	[48]
Co ₃ Fe ₂ –xO ₄ – β -CD ^g /GCE	1–200	0.12	[49]
Activated GCE	0.5–200	0.11	[50]
MWNTs/beta-cyclodextrin/CILE ^h	0.7–1000	0.08	[51]
PARS/BMIMBF ₄ /GCE	0.1–500	0.026	Present work

^a Multiwalled carbon nanotube^b Horse radish peroxidase^c Graphene oxide^d Reduced graphene oxide nanocomposite^e Graphene^f Poly (3-methylthiophene)^g β -cyclodextrin-cobalt ferrite nanocomposite^h Carbon ionic liquid electrode

3.4. Calibration Curve

The calibration curve of the catechol sensor was derived from the DPVs obtained on the PARS/BMIMBF₄/GCE in 0.1 M PBS (pH 7.0) under the optimum conditions (Fig. 7). The peak current (I_p) was proportional to the concentration of catechol from 0.1 μM to 500 μM [$I_p (\mu\text{A}) = 0.13 + 0.042 C (\mu\text{M})$] with a correlation coefficient of 0.9989. The sensitivity of the PARS/BMIMBF₄/GCE to catechol was 42 nA/ μM . The detection limit of catechol was calculated to be 0.026 μM ($s/n = 3$).

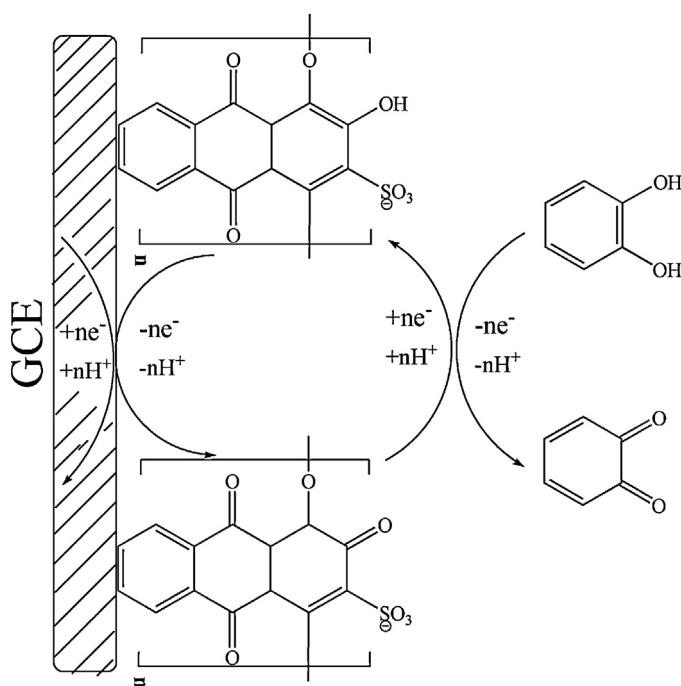
In order to show the novelty and superiority of our work, the response characteristics of the PARS/BMIMBF₄/GCE were compared with other sensors in previously published works. As shown in Table 1, most of the materials that modified the electrode were carbon materials and nanocomposite. It is a novel method to modify the electrode by electropolymerization of ARS in RTILs. Above all, the proposed PARS/BMIMBF₄/GCE had wider linear dynamic range

and lower detection limit than most of the materials used in other works for catechol determination.

3.5. Repeatability, Reproducibility and selectivity

The repeatability of PARS/BMIMBF₄/GCE was investigated by detecting a certain amount of catechol in 0.1 M PBS for one electrode in 30 measurements. The relative standard deviation (RSD) of the anodic peak current was 2.2% for catechol determination. The reproducibility of the developed method was also evaluated by using five different PARS/BMIMBF₄/GCEs and the obtained RSD was 4.5%. Therefore, PARS/BMIMBF₄/GCE showed good repeatability and reproducibility.

The selectivity of the PARS/BMIMBF₄/GCE for catechol determination was investigated by adding various foreign species into PBS (pH 7.0) containing 400 μM catechol. Moreover, 100-fold Cu²⁺, Na⁺, K⁺, Fe³⁺, SO₄²⁻, Cl⁻, NO₃⁻, 5-fold ascorbic acid, uric acid, phenol, hydroquinone, and 20-fold glucose did not affect the determination of catechol (< 5% of current change). These results indicated good selectivity of the proposed electrochemical sensor.



Scheme 2. Electrochemical oxidation mechanism of catechol on PARS/BMIMBF₄/GCE.

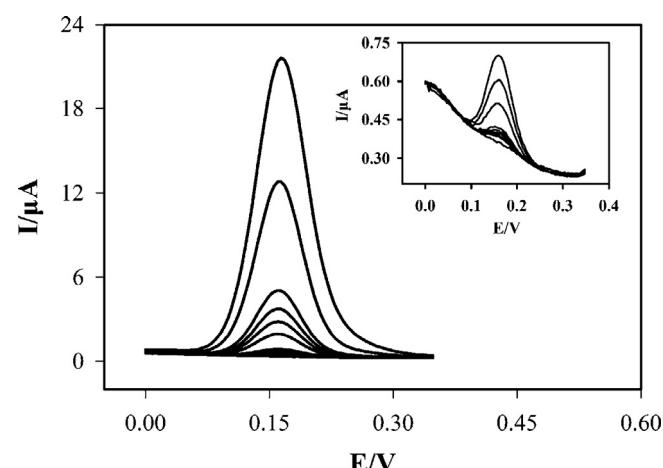


Fig. 7. DPVs of catechol at different concentrations (from 0.1 μM to 500 μM) in 0.1 M PBS on PARS/BMIMBF₄/GCE (pH 7.0). Scan rate: 100 mV/s. Inset: DPVs of catechol at different concentrations (from 0.1 μM to 7 μM) in 0.1 M PBS on PARS/BMIMBF₄/GCE.

Table 2

Recovery results for catechol in real water samples.

Sample	Catechol added (μM)	Catechol found (μM)	Recovery (%)
Tap water	20	20.5	102.5
	40	39.0	97.7
	60	64.8	108
Yellow River water	20	21.9	109.5
	40	41.3	103.3
	60	60.8	101.3
Lake water	20	21.9	109.0
	40	39.8	98.8
	60	59.5	99.2

3.6. Practical application of PARS/BMIMBF₄/GCE

PARS/BMIMBF₄/GCE was used for catechol determination in real water samples to evaluate the potential applications of the proposed method. The recovery experiments were performed. In brief, known amounts of standard catechol solutions were added to the real water samples followed by analysis using the standard addition method. The obtained values were listed in Table 2. The recovery values for the different types of real water samples ranged from 97.1% to 107.4%. These results indicated that the fabricated electrode may serve as an electrochemical sensor for catechol determination.

4. Conclusions

A simple and novel method of fabricating an effective electrode for catechol determination was established by electropolymerization of ARS in BMIMBF₄. EDX, XPS and FTIR results demonstrated that BMIMBF₄ was successfully mixed into the PARS film. Compared with the PARS/GCE and bare GCE, the obtained PARS/BMIMBF₄/GCE exhibited significantly enhanced electrocatalytic performance for catechol determination. The detection limit of catechol was 0.026 μM. In addition, the PARS/BMIMBF₄/GCE showed excellent repeatability, reproducibility, selectivity and had been applied for real water samples determination. The fabricated electrode may serve as an electrochemical sensor for catechol determination.

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