

# Sol-Gel Derived Carbon Ceramic Electrode Bulk-Modified with Tris(1, 10-phenanthroline-5, 6-dione) iron (II) Hexafluorophosphate and Its Use as an Amperometric Iodate Sensor

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A surface-renewable tris(1, 10-phenanthroline-5, 6-dione) iron (II) hexafluorophosphate (FePD) modified carbon ceramic electrode was constructed by dispersing FePD and graphite powder in methyltrimethoxysilane (MTMOS) based gels. The FePD-modified electrode presented pH-dependent voltammetric behavior, and its peak currents were diffusion-controlled in 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> solution (pH = 0.4). In the presence of iodate, clear electrocatalytic reduction waves were observed and thus the chemically modified electrode was used as an amperometric sensor for iodate in common salt. The linear range, sensitivity, detection limit and response time of the iodate sensor were  $5 \times 10^{-6}$ — $1 \times 10^{-2}$  mol/L, 7.448  $\mu\text{A} \cdot \text{L} / \text{mmol}$ ,  $1.2 \times 10^{-6}$  mol/L and 5 s, respectively. A distinct advantage of this sensor is its good reproducibility of surface-renewal by simple mechanical polishing.

**Keywords** sol-gel, carbon ceramic electrode, tris(1, 10-phenanthroline-5, 6-dione)iron(II), iodate

## Introduction

The sol-gel process provides a versatile method for the fabrication of inorganic and inorganic-organic hybrid materials via the hydrolysis and condensation of suitable metal alkoxides.<sup>1-3</sup> These materials possess notable advantages over other inorganic-organic materials for the encapsulation of various dopants and the development of practical sensors and catalytic supports, which include ease of preparation, high porosity, photochemical and electrochemical stability, and enhanced mechanical and chemical durability. Many studies on silica-modified

electrodes have been reported in the last decade. Recent advances in various fields and applications of sol-gel in electrochemistry were described in several excellent review articles.<sup>4-9</sup> In 1994, Lev *et al.*<sup>10</sup> first introduced a new class of sol-gel carbon ceramic electrodes (CCE), which comprised a dispersion of graphite powder in an organically modified or unmodified silicate porous matrix. The hydrophobicity of these electrodes can be controlled easily using an organically modified sol-gel precursor. An interesting feature of this kind of chemically modified electrodes is that the active section of the electrodes is not clogged upon repeated polishing due to the brittleness of the sol-gel silicate backbone, and thus the electrodes can be renewed by a simple mechanical polish after every use or contamination. Many efforts have been devoted to preparing chemically modified CCEs and using them as sensors for metal ions, glucose, and other important chemical and biological substances.<sup>11-17</sup>

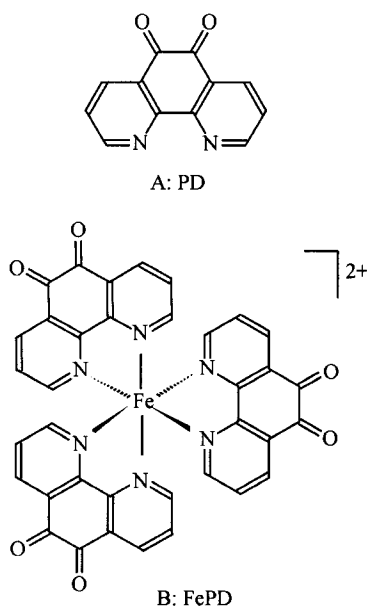
The action of 1, 10-phenanthroline-5, 6-dione [PD, Fig. 1(A)] and its complexes with metal cations as oxidizing agents for organic amines and inorganic reducing agents and for biological reductants such as NADH has attracted considerable interest, and several experimental studies have appeared.<sup>18-22</sup> The electrochemical behavior of a variety of metal complexes of the ligands has also been described.<sup>23-30</sup> In 1985, Goss and Abruna<sup>31</sup> synthesized tris(1, 10-phenanthroline-5, 6-dione)iron (II) hexafluorophosphate [FePD, Fig. 1(B)] and studied its electrochemical and electrocatalytic properties for the

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Received March 26, 2001; revised June 25, 2001; accepted September 18, 2001.

Project supported by the Ministry of Science and Technology of China (No. 2001BA210A04).

first time. Recently, Tobalina *et al.*<sup>32</sup> reported the electrocatalytic oxidation of NADH at FePD-modified carbon paste electrodes. Our interest in FePD stemmed from its strong spontaneous adsorption on graphite and its possible interaction with silanol groups, which means that FePD doped in CCE matrix may not leak out in aqueous solution. In the present paper, FePD and graphite powder were first dispersed in methyltrimethoxysilane (MTMOS) based gels to fabricate surface-renewable FePD-modified CCEs. The chemically modified electrode showed a high electrocatalytic activity toward iodate reduction, and thus was used as an amperometric sensor.



**Fig. 1** Structures of 1,10-phenanthroline-5,6-dione (A) and its iron(II) complex (B).

## Experimental

### Materials

Sodium hexafluorophosphate and high purity graphite powder (average particle diameter, 1–2  $\mu\text{m}$ ) were obtained from Aldrich. MTMOS ( $\geq 97\%$ ) was purchased from ACROS and used without further purification. Other reagents were all of analytical grade and used as received. Ultrapure water obtained from a Millipore Milli-Q water purification system was used throughout the experiments. All experimental solutions were thoroughly deoxygenated by bubbling pure argon through them for at least 15 min.

### Apparatus

IR spectra were recorded on a Bio-Rad FTS-7 infrared spectrophotometer in KBr pellets.  $^1\text{H}$  NMR experiments were carried out at 29  $^\circ\text{C}$  on a Varian Unity-400 spectrophotometer. Chemical shifts were expressed in  $\delta$  using TMS as internal standard. Elemental analysis was performed on a GmbH VarioEL elemental analysis system and a TJA POEMS inductively coupled plasma atomic emission spectrometer. Solution acidities were measured with a Model 620D pH meter (Shanghai, China). A CHI 660 Electrochemical Workstation connected to an IBM-PC compatible computer was used for control of the electrochemical measurements and for datum collection. A conventional three-electrode system was used. The working electrode was an unmodified or FePD-modified CCE. An Ag/AgCl (saturated KCl) electrode was used as a reference electrode and a Pt gauze as a counter electrode. All potentials were measured and reported versus the Ag/AgCl electrode. Electrochemical experiments were performed at room temperature.

### Synthesis of PD and $[\text{Fe}(\text{PD})_3](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$

The following synthetic procedure for PD was based on the report by Paw and Esienberg,<sup>33</sup> and it yielded the product almost quantitatively. A solution of  $\text{H}_2\text{SO}_4$  (40 mL) and  $\text{HNO}_3$  (20 mL) frozen to  $-10$   $^\circ\text{C}$  was in advance added to the mixture of 4.4 g of 1,10-phenanthroline monohydrate and 4.0 g of KBr at  $-10$   $^\circ\text{C}$ . The mixture was slowly heated and then stirred at reflux for 3 h. After cooled, the solution was poured over 500 g ice and neutralized carefully with 40% NaOH aqueous solution until neutral to pH 6.5. The resulting mixture was filtrated to obtain a yellow solid. The filtrate was extracted with  $\text{CHCl}_3$  followed by drying with anhydrous sodium sulfate and removing solvent to give a yellow solid. The total pure solid was obtained with the yield of 94%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 9.13 (d,  $J = 4.0$  Hz, 2H, 2-H and 9-H), 8.51 (d,  $J = 8.0$  Hz, 2H, 4-H and 7-H), 7.60 (q,  $J = 4.0$  Hz, 2H, 3-H and 8-H); IR  $\nu$ : 1688 ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ ; Anal. calcd for  $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2$ : C 68.57, H 2.88, N 15.22; found C 68.52, H, 2.85, N 15.28.

FePD was prepared according to the literature<sup>31</sup> with some modifications. 3.2 equiv. of PD in ethanol was added to 1 equiv. of ferrous sulfate dissolved in water. The formation of the complex was apparent by the imme-

diolate formation of a dark-red solution. The mixture was allowed to stir at room temperature for 30 min and then a proper amount of hydrogen chloride was added. The complex was precipitated as a dark-red solid by the addition of sodium hexafluorophosphate. The solid was collected, washed with water, dried *in vacuo* at 50 °C and confirmed to be  $[\text{Fe}(\text{PD})_3](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ .  $^1\text{H}$  NMR (DMSO)  $\delta$ : 8.76 (d,  $J = 8.0$  Hz, 6H, 4-H and 7-H of three PD ligands), 7.92 (d,  $J = 4.0$  Hz, 6H, 2-H and 9-H of three PD ligands), 7.75 (q,  $J = 4.0$  Hz, 6H, 3-H and 8-H of three PD ligands); IR  $\nu$ : 1698 (C=O), 840 (P—F)  $\text{cm}^{-1}$ ; Anal. calcd for  $\text{C}_{36}\text{H}_{22}\text{F}_{12}\text{FeN}_6\text{O}_8\text{P}_2$ : C 42.71, H 2.19, N 8.30, Fe 5.52, P 6.12; found C 42.65, H 2.23, N 8.32, Fe 5.47, P 6.18.

#### Fabrication of unmodified and FePD-modified CCEs

Unmodified CCEs were prepared according to the reference method.<sup>10</sup> The FePD-modified CCEs were constructed by the following procedure. 0.75 mL of saturated FePD methanol solution, 0.35 mL of MTMOS, and 0.03 mL of hydrochloric acid (11 mol/L) were ultrasonically mixed for 2 min, then 1.5 g of graphite powder was added and shaken on a vortex agitator for an additional 3 min. The mixture was added to glass tubes with 3 mm inner diameter and 8 cm length, and the length of composite material in the tubes was controlled to be about 0.8 cm. In addition, a little extra mixture had to be retained on the top of the electrodes, and the mixture in the tubes was slightly pressed on smooth plastic paper with a glass stick through the back. After drying at room temperature for 48 h, the electrodes were polished with 600-grit emery paper to remove extra composite material and wiped gently with filter paper. Electric contact was made by silver paint through the back of the electrode.

## Results and discussion

#### Fabrication of FePD-modified CCEs

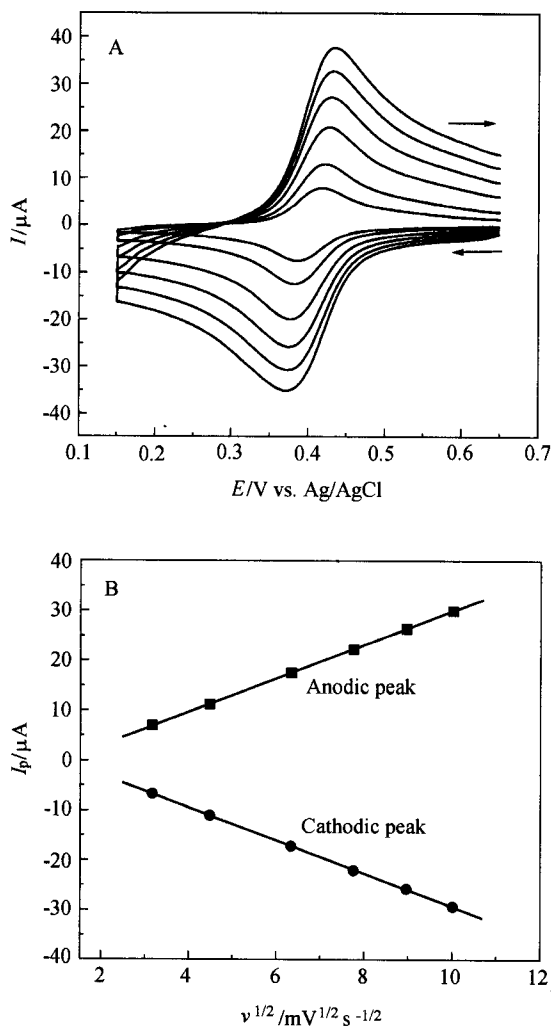
Additional water for the hydrolysis step was provided by air humidity.<sup>10</sup> Base (NaOH or  $\text{NH}_4\text{OH}$ ) or neutral ( $\text{NH}_4\text{F}$ ) catalysts failed to produce rigid monoliths and yielded only silica-covered graphite powder. Large dosages of hydrogen chloride and MTMOS resulted in the rapid gelation before adding graphite powder and the bad

conductivity<sup>34</sup> of the composite, respectively. The Si—C bonds remained unchanged during the hydrolysis and polymerization, and the methyl group remained exposed at the surface of porous silicate network. In the process of fabrication of the FePD-modified CCEs, a little extra mixture was needed to be retained on the top of the electrodes in order to obtain the whole and mirror-like surfaces conveniently when they were first polished. In addition, the composite material became fragile and thus it was difficult to obtain smooth electrode surfaces if the gelation temperature was higher than 60 °C.

#### Electrochemical behavior of the PQ-modified CCE

In general, transition complexes of PD are chemically more stable and electrochemically more reversible than the PD ligand itself, especially in alkaline media. Fig. 2(A) shows cyclic voltammograms of the FePD-modified CCE in the 0.1 mol/L  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  solution (pH = 0.4) at various scan rates. In the potential range from  $-0.15$  V to  $+0.65$  V, a well-defined redox response for the quinone moiety of FePD doped in CCE matrix was observed. As could be ascertained, instead of two PD-based one-electron reductions for FePD in acetonitrile, in aqueous media the FePD-modified CCE exhibited a reduction wave, which was assigned to the  $2\text{e}^-/2\text{H}^+$  reduction of the quinone moiety to the corresponding catechol.<sup>27,32</sup> Previous studies<sup>32</sup> showed that three PD ligands of FePD were reduced at the same potential, so the total reaction of FePD should be a  $6\text{e}^-/6\text{H}^+$  process. At the scan rate of 10 mV/s, the anodic and cathodic peak potential separation ( $\Delta E_p$ ) is 28 mV. Along with the increase of scan rates, anodic peaks shift positively while cathodic peaks shift negatively, and  $\Delta E_p$  increases gradually. As shown in Fig. 2(B), both anodic and cathodic peak currents are proportional to the square roots of scan rates in the acidic solution (pH = 0.4), suggesting that peak currents are diffusion-controlled in the investigated scan rate range.

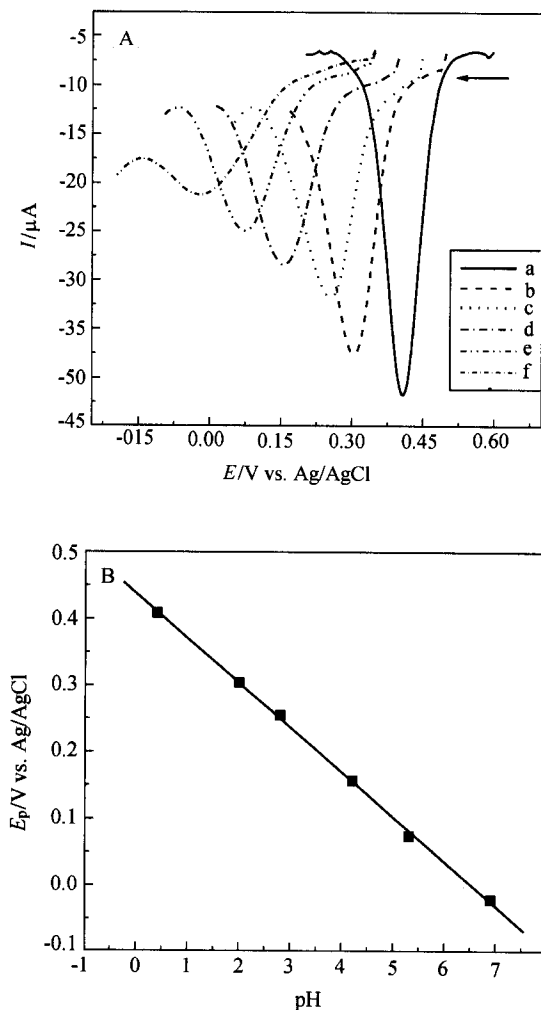
In the present work, square-wave voltammetry was adopted to measure the pH-dependent electrochemical behavior conveniently. Fig. 3(A) presents square-wave voltammograms for the FePD-modified CCE in aqueous solution with different acidities. It can be clearly seen that along with increasing pH, peak potential gradually shift to the more negative potential direction and the peak currents also decrease. Reduction of FePD doped in



**Fig. 2** (A) Typical cyclic voltammograms of the FePD-modified CCE in 0.1 mol/L  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  aqueous solution ( $\text{pH} = 0.4$ ) at different scan rates. From inner curve to outer curve; 10, 20, 40, 60, 80 and 100  $\text{mV}/\text{s}$ , respectively. (B) The dependence of (a) anodic and (b) cathodic peak currents on the square roots of scan rates.

the CCE matrix is accompanied by the evolution of protons from solution to the electrode wetting section to maintain charge neutrality. Along with the increase of pH, slower diffusion rate of protons should be the reason for the current decrease, and the more negative reduction potentials can be elucidated by the Nernst equation. Plots of peak potential versus pH for the FePD-modified CCE show good linearity in the pH range from 0.04 to 6.8, as shown in Fig. 3 (B). Slopes in this pH range are  $-69 \text{ mV}/\text{pH}$  which is close to the theoretical value  $-60 \text{ mV}/\text{pH}$  expected for the  $6\text{e}^-/6\text{H}^+$  redox process at room tem-

perature. In addition, the peak currents are not proportional to proton concentrations, which may be caused by the effect of sol-gel-derived methylsilicate matrix.



**Fig. 3** (A) Square-wave voltammograms of the FePD-modified CCE in aqueous solutions with various acidities. (a)  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  aqueous solution ( $\text{pH} = 0.4$ ); (b) glycine buffer solution ( $\text{pH} = 2.0$ ); (c) glycine buffer solution ( $\text{pH} = 2.8$ ); (d) acetate buffer solution ( $\text{pH} = 4.2$ ); (e) phosphate buffer solution ( $\text{pH} = 5.3$ ); (f) phosphate buffer solution ( $\text{pH} = 6.8$ ). Increment; 4  $\text{mV}$ ; frequency; 10  $\text{Hz}$ ; scan rate; 40  $\text{mV}/\text{s}$ . (B) Relationship between peak potential and pH for the FePD-modified CCE.

#### *Electrocatalytic oxidation of iodate*

The determination of iodate in common salt is of particular importance since the content of iodate has a straightforward influence on human health. Trace quality

of iodate was usually determined by spectrophotometric and fluorescent quenching techniques, but seldom by electrochemical methods.<sup>35,36</sup> Although the amperometric response of the FePD-modified CCE in pH 0.4 aqueous solution is enhanced compared with that in high pH solutions, the steady electrocatalytic response of iodate in such a high acidic solution can not be achieved until pH > 2.0. Therefore, pH 2.2 glycine buffer solution was selected as media for the electrocatalytic reduction of iodate. As is known, the electrochemical reduction of iodate requires a large overpotential, and no obvious response was observed in the potential range from +0.6 V to -0.05 V at an unmodified CCE in pH 2.2 glycine buffer solution [shown in Fig. 4(A)]. In this work, the FePD-modified CCE showed an electrocatalytic activity toward iodate reduction. As shown in Fig. 4(B), adding iodate to the electrolyte cell caused a dramatic change in the cyclic voltammograms with an increase in

cathodic current and a concomitant decrease in anodic currents, indicating that iodate was electrocatalytically reduced by the reducing product from FePD. At present, a confirmed mechanism of the electrocatalytic reduction of iodate at the FePD-modified CCE is unknown.

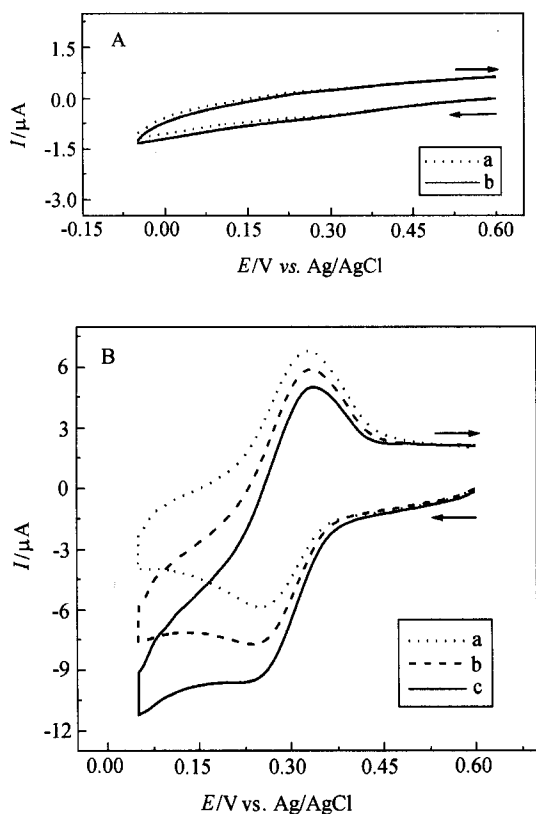
#### Amperometric sensing and interference

On the basis of the voltammetric results described above, it is possible to use the FePD-modified CCE as amperometric iodate sensor. According to the potential dependence of electrocatalytic reduction currents at steady-state conditions, the optimum electrode potential was selected at +0.23 V versus Ag/AgCl for amperometric measurement in order to obtain constant and high sensitivity. A typical hydrodynamic amperometry [Fig. 5(A)] was obtained by successively adding iodate to continuously stirred pH 2.2 glycine buffer solution. The electrode response time was less than 5 s. The fast response is attributed to the thin wetting section controlled by methyl group and the short penetration depth of iodate. Fig. 5(B) shows the calibration graph for iodate at the modified electrode. The electrode response was linear for iodate within the concentration range  $5 \times 10^{-6}$ — $1.0 \times 10^{-2}$  mol/L, and the sensitivity is  $7.448 \mu\text{A} \cdot \text{L}/\text{mmol}$  (correlation coefficient of 0.999). The detection limit was  $1.2 \times 10^{-6}$  mol/L when signal-to-noise was 3.

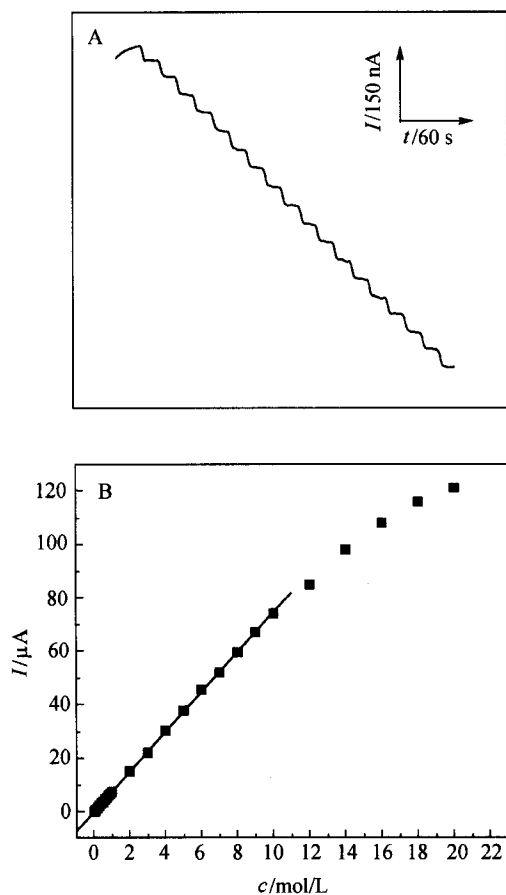
Interference effects were investigated by testing the response of the modified electrode to  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  because these species exist in common salt samples. Our experiments showed that 1000-fold excess of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , 200-fold excess of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , and 50-fold excess of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{As}^{3+}$  and  $\text{F}^-$  did not interfere in the determination of iodate. Therefore, the FePD-modified CCE is used as amperometric sensor for iodate in common salt. The results of six replicate analyses were a mean of  $44.10 \mu\text{g}/\text{g}$  with a relative standard deviation (RSD) of 0.8% compared to  $39.95 \mu\text{g}/\text{g}$  obtained by a standard titration method.<sup>37</sup> It can be seen that the agreement between the two methods is satisfactory.

#### Stability and repeatability of surface renewal

The hydrophobic MTMOS monomer results in the electrode wetting in aqueous solutions to be controlled.



**Fig. 4** (A) Cyclic voltammograms of the unmodified CCE in pH 2.2 glycine buffer solution containing (a) 0 or (b) 1 mmol/L iodate. (B) Cyclic voltammograms of the FePD-modified CCE in pH 2.2 glycine buffer solution containing (a) 0, (b) 0.5 or (c) 1 mmol/L iodate. Scan rate; 10 mV/s.



**Fig. 5** (A) Amperometric response for the FePD-modified CCE to the successive increments of 5  $\mu\text{mol/L}$  iodate in pH 2.2 glycine buffer solution. Applied potential: +0.23 V; stirring rate; 1000 rpm. (B) Calibration curve for iodate.

Hence, a bulk modified electrode can be polished using an emery paper and a fresh surface exposed whenever needed. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is fouled. Indeed, ten successive polishings of a FePD-modified CCE resulted in a RSD of 5.2%. In addition, no obvious current decrease was found when the electrode was immersed in a pH 2.2 glycine buffer solution for 15 d. We think that the high stability of the FePD-modified CCEs is related to the stability of the silicate matrix, the limited wetting section controlled by methyl group, the possible interaction between the quinone moiety of FePD and silanol groups,<sup>31</sup> and mainly the strong adsorption of FePD on graphite.<sup>27,32</sup>

## Conclusions

FePD-modified CCEs have been fabricated by the sol-gel method and their performance has been evaluated under steady-state and dynamic conditions. The chemically modified electrodes showed a high catalytic activity toward iodate reduction and thus used as an amperometric iodate sensor. The hydrophobic, organically modified backbone of the electrode rejects water and leaves only a thin active layer at the outermost section exposed to the analyte, which makes surface renewal by mechanical polishing possible. In addition, the sensor has other advantages, such as simple preparation, fast response, good chemical and mechanical stability.

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