



# A multi-channel sensor based on 8-hydroxyquinoline ferrocenoate for probing Hg(II) ion

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## ABSTRACT

A new sensing molecule 8-hydroxyquinoline ferrocenoate (**Fc-Q**) which combines ferrocene and 8-hydroxyquinoline moieties was synthesized and applied as a multi-channel sensor for the detection of Hg<sup>2+</sup> ion. **Fc-Q** can coordinate with Hg<sup>2+</sup> to give colorimetric, fluorescent and electrochemical responses. Upon complexation with Hg<sup>2+</sup> ion, the characteristic absorption peak is red-shifted ( $\Delta\lambda = 45$  nm), the fluorescent intensity is quenched at 303 nm, and the oxidation peak is cathodic shifted ( $\Delta E_{1/2} = -149$  mV). Quantitatively analyzed Hg<sup>2+</sup> ions at the range of ppb level could be achieved by electrochemical response. For the practical application of sensing Hg<sup>2+</sup> in real world water, **Fc-Q** modified screen-printed carbon electrodes were obtained for facile, sensitive, and on-site analysis of Hg<sup>2+</sup>.

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## 1. Introduction

Mercury is widely used in industry, such as coal mining, wood pulping, and chemical manufacturing, and in other products of daily life. It exists in metallic, organic, and inorganic forms [1]. However, it is a widespread pollutant with distinct toxicity, can be easily absorbed and accumulated from the environment by living organisms thus causing brain damage and other chronic diseases [2,3]. Therefore, various procedures for the analysis of Hg<sup>2+</sup> have emerged as a focal point such as cold vapor atomic absorption spectroscopy, hydride generation ICP-MS and ICP-AES, etc. However, most of these methods require the high cost instrumentations [4], and are not appropriate in many situations. Thus the effective colorimetric, fluorescent and electrochemical sensors have received attention due to their high sensitivity and low-cost [5–9]. But the results of these single-channel sensors may be restricted to the interfering substance in the actual samples, such as turbidity and color. Herein, a promising multi-channel sensor is designed to provide identification of Hg<sup>2+</sup> by colorimetric, fluorescent and electrochemical methods [10,11].

Screen-printed carbon electrodes (SPCEs) are devices that are produced by printing carbon inks on various types of plastic or ceramic substrates [12]. Compared to other existing techniques,

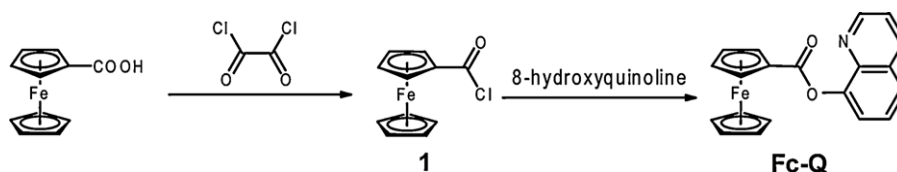
the electrochemical sensor technique based on the SPCEs allows mass production of inexpensive disposable electrodes that can be used as part of an electrochemical instrument for on-site monitoring of trace metals [13–16]. The ability to modify the SPCEs easily is its greatest advantage. Similar to the graphite electrode, the most facile way to modify SPCEs is based on assembling sensing molecules directly onto the working electrode through physical adsorption and non-covalent supramolecular interactions such as  $\pi$ – $\pi$  stacking.

In recent years, the sensing molecules containing ferrocene and analyte recognition sites have received great interest, since ferrocene units could affect the properties of recognition sites and likewise recognition sites can affect the properties of the ferrocene units [17,18]. Furthermore, the traditional receptors, 8-hydroxyquinoline and its derivatives, especially 8-hydroxyquinoline benzoates [19–22], were regarded as versatile and useful molecular optical sensors because of their non-toxicity and excellent selectivity [21]. From this aspect, ferrocene-containing molecules could be applied for the development of multi-channel chemosensors for the detection of cations or anions [10,23–26].

Within this consideration, we designed and synthesized a new highly sensitive and multi-channel sensor (**Fc-Q**) for Hg<sup>2+</sup>, by facilely appending the redox group ferrocene with an **8-HQ** via esterification reaction (Fig. 1). It is expected that the electron-rich ferrocenyl group could enhance the coordination ability of the **8-HQ** nitrogen atom towards Hg<sup>2+</sup> ion. The obtained molecule was used for the determination of Hg<sup>2+</sup> in CH<sub>3</sub>CN solution through three channels such as UV–vis spectrophotometry, fluorescent spectrom-

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Fig. 1. Synthetic route to **Fc-Q**.

etry and electrochemical method. Furthermore, for the practical application of assaying  $\text{Hg}^{2+}$  in water, we assembled the **Fc-Q** molecules onto the **SPCEs** through non-covalent interaction. This disposable sensor shows the potential utilization for facile, sensitive, and on-site analysis of  $\text{Hg}^{2+}$  in water.

## 2. Experimental

### 2.1. Materials and instruments

Ferrocene-carboxylic acid,  $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ag}(\text{ClO}_4)_2$  were obtained from Aldrich and used without further purification. All solutions were prepared with ultrapure water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) from a Millipore system and/or distilled  $\text{CH}_3\text{CN}$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were acquired in  $\text{CDCl}_3$  on BRUKER AVANCE 500 spectrometer using TMS as an internal standard. HRMS were obtained on HP5989 mass spectrometer. Fluorescence spectra were determined on Varian Cary Eclipse fluorescence spectrometer. UV–vis spectra were measured on Varian Cary 500 spectrophotometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out on a CHI 660 C Electrochemical Workstation. The three-electrode cell comprises a glassy carbon working electrode (diameter = 3 mm), a platinum-wire auxiliary electrode, and an  $\text{Ag}/\text{AgCl}$  reference electrode. All experiments were carried out at room temperature. According to our previous work [4], screen printed electrode was produced on an AT-25P instrument (ATMACHAMP ENT. Corp., China) using polyester screens with appropriate stencil designs. The water sample was collected from Qing-Chun River on campus of our university filtrated with membrane filter ( $0.45 \mu\text{m}$ , Millipore, [www.millipore.com](http://www.millipore.com)).

### 2.2. Synthesis

#### 2.2.1. Synthesis of **Fc-Q**

Ferrocene-monocarbonyl chloride (**1**) was synthesized according to the reported procedure [27]. 8-hydroxyquinoline (0.496 g, 2 mmol) and compound **1** (0.460 g, 2 mmol) were mixed in  $\text{CH}_2\text{Cl}_2$  and stirred for 4 h. The crude products were recrystallized from ethanol and then purified by silica column chromatography (ethyl acetate–petroleum ether (b.p.  $60\text{--}90^\circ\text{C}$ ), 1:5, v/v) to yield orange-red solid (0.632 g, 90%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS),  $\delta$  (ppm): 4.549 (s, 7H), 5.094 (s, 2H), 7.502 (m, 2H), 7.572 (t, 1H), 7.768 (d, 1H), 8.217 (s, 1H), 8.965 (s, 1H).  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 70.935, 71.001, 71.498, 72.430, 77.449, 77.703, 77.957, 122.323, 122.500, 126.476, 126.918, 130.211, 136.649, 148.312, 150.948, 171.123. HRMS (ESI):  $m/z$  [**Fc-Q**] calc. 357.1836, found 357.0453.

### 2.3. Modification of **SPCEs**

The **SPCE** was pretreated in a 0.1 M acetic acid buffer (pH 5.0) containing 0.1 M KCl by applying an anodic potential of 1.700 V for 3 min before use [28]. The **SPCE** was immersed into the **Fc-Q** ethanol solution for about 3 h under stirring. The electrode was rinsed with ethanol, 3 times, and dried at room temperature. Then the **Fc-Q** modified **SPCEs** (**Fc-Q/SPCEs**) were obtained.

## 3. Results and discussion

### 3.1. UV–vis channel for probing $\text{Hg}^{2+}$

The coordination ability of **Fc-Q** with  $\text{Hg}^{2+}$  was investigated by UV–vis absorption spectroscopy in  $\text{CH}_3\text{CN}$  solution. As shown in Fig. 2, the free **Fc-Q** exhibits a maximal absorption at 269 nm, which can be ascribed to  $\pi \rightarrow \pi^*$  transitions, and a low-energy ferrocene absorption band around 450 nm. The significant change was observed in the UV–vis spectra upon the addition of  $\text{Hg}^{2+}$ . With increasing concentration of  $\text{Hg}^{2+}$  in the solution, the absorption band at 269 nm disappeared while two new bands located at 238 nm and 314 nm appeared at the same time. As shown in the inset of Fig. 2, a slight red shift of the peak around 450 nm was observed, which is ascribed to the formation of the **Fc-Q-Hg**<sup>2+</sup> complex [29].

The stoichiometry of the **Fc-Q-Hg**<sup>2+</sup> complex was investigated by measuring the change in absorption at 314 nm in the presence of varying concentrations of  $\text{Hg}^{2+}$  ions. The Benesi–Hildebrand analysis [30] of the absorbance data gives a 1:1 stoichiometry of the **Fc-Q-Hg**<sup>2+</sup> coordination complex. The association equilibrium constant ( $K_{\text{ass}}$ ) is determined to be  $4.98 \times 10^4 \text{ M}^{-1}$ .

The coordination capability of **Fc-Q** with other metal ions has also been studied (see Fig. S1 in supplementary material). The addition of  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  ions induced negligible spectral changes except for  $\text{Cu}^{2+}$ , which confirms the remarkable selectivity of **Fc-Q** towards  $\text{Hg}^{2+}$  (Fig. 3).

### 3.2. Fluorescence channel for probing $\text{Hg}^{2+}$

The coordination of  $\text{Hg}^{2+}$  to **Fc-Q** was also investigated by fluorescence titration in  $\text{CH}_3\text{CN}$ . Fluorescence spectra of the free **Fc-Q** solution exhibits an emission band at 303 nm ( $\lambda_{\text{ex}} = 240 \text{ nm}$ ). Unlike other **8-HQ** based fluorescent sensors, **Fc-Q** does not show an

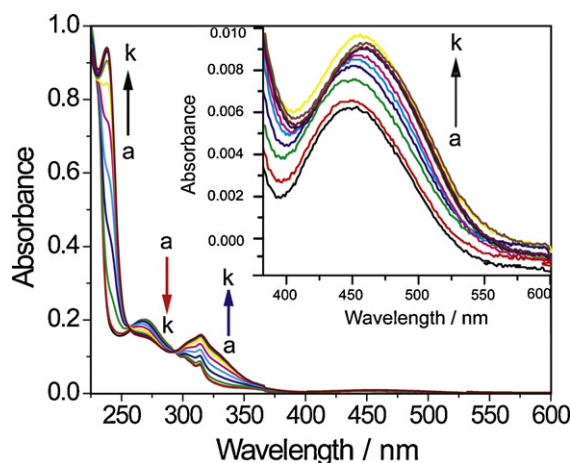
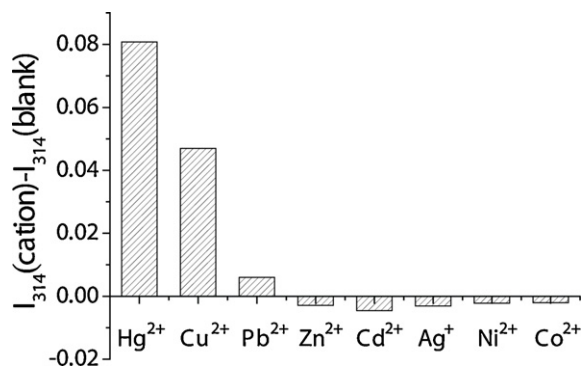


Fig. 2. Absorption titration spectra of **Fc-Q** ( $1.0 \times 10^{-5} \text{ M}$ ) in  $\text{CH}_3\text{CN}$  with increasing concentration of  $\text{Hg}^{2+}$  ion (a) 0, (b)  $5.0 \times 10^{-5} \text{ M}$ , (c)  $1.5 \times 10^{-4} \text{ M}$ , (d)  $2.0 \times 10^{-4} \text{ M}$ , (e)  $2.5 \times 10^{-4} \text{ M}$ , (f)  $3.0 \times 10^{-4} \text{ M}$ , (g)  $3.5 \times 10^{-4} \text{ M}$ , (h)  $4.0 \times 10^{-4} \text{ M}$ , (i)  $4.5 \times 10^{-4} \text{ M}$ , (j)  $5.0 \times 10^{-4} \text{ M}$  and (k)  $5.5 \times 10^{-4} \text{ M}$ . The inset shows a magnification of the 375–600 nm region.

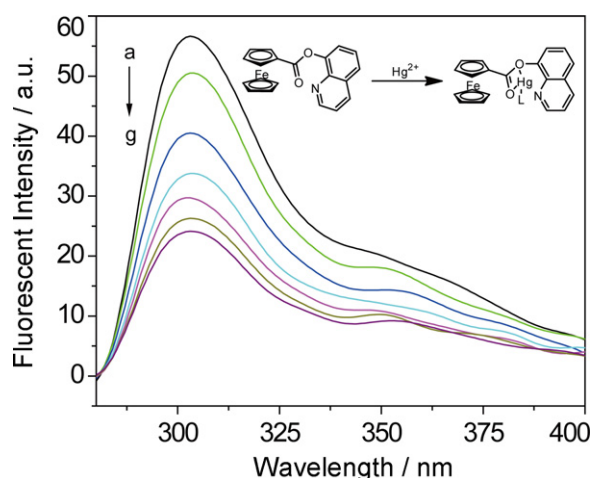


**Fig. 3.** Responses of **Fc-Q** to the different metal ions in  $\text{CH}_3\text{CN}$  solution. The absorbance was measured at 314 nm. The concentration of **Fc-Q** and tested metal ions were  $1.0 \times 10^{-5}$  M and  $5.0 \times 10^{-5}$  M, respectively.

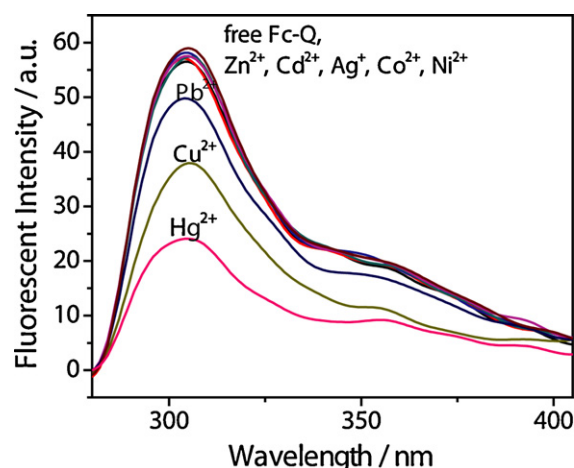
enhanced fluorescence turn on following metal ions binding, it displays as an on-off type sensor. As shown in Fig. 4, due to the blockage effect of the ester group, **Fc-Q** exhibits weak fluorescent emission. Upon the addition of  $\text{Hg}^{2+}$ , the emission band at 303 nm decreases gradually. As shown in the inset of Fig. 4, the formation of **Fc-Q-Hg** $^{2+}$  probably enhances the intramolecular charge transfer (ICT), which is associated with the heavy-atom effect [31]. Among the other tested metal ions ( $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ag}^+$ ),  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  showed less quenching effect than  $\text{Hg}^{2+}$  (Fig. 5).

### 3.3. Electrochemical channel for probing $\text{Hg}^{2+}$

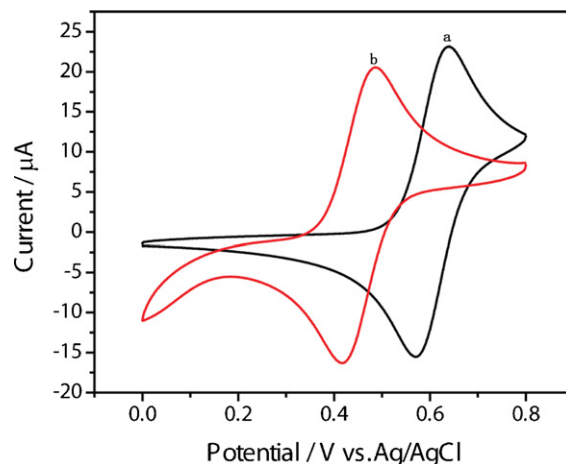
Electrochemical methods, in particular, are extremely attractive from a practical standpoint because the signals can be easily read out on-site. Within the **Fc-Q** structure, the electronic density and the redox property of ferrocene could be influenced by the coordination with  $\text{Hg}^{2+}$ . The cyclic voltammogram of **Fc-Q** in  $\text{CH}_3\text{CN}$  solution exhibits a reversible one-electron electrochemical process of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) with the redox peaks separation around 65 mV. As expected, **Fc-Q** shows an obvious change in the redox behavior upon the addition of  $\text{Hg}^{2+}$  ion. As shown in Fig. 6, the addition of 1 equiv.  $\text{Hg}^{2+}$  induces a significant negative shift of  $\text{Fc}/\text{Fc}^+$  ( $\Delta E_{1/2} = -149$  mV). It may be ascribed to the presence of the positively charged  $\text{Hg}^{2+}$  ion which could increase the electron den-



**Fig. 4.** Fluorescence titration spectra of **Fc-Q** ( $1.0 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}$  solution with increasing concentration of  $\text{Hg}^{2+}$  (a) 0, (b)  $5.0 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-4}$  M, (d)  $2.0 \times 10^{-4}$  M, (e)  $2.5 \times 10^{-4}$  M, (f)  $3.0 \times 10^{-4}$  M and (g)  $3.5 \times 10^{-4}$  M. Excitation wavelength: 240 nm. The inset was the proposed binding mechanism of **Fc-Q** with  $\text{Hg}^{2+}$  ion.



**Fig. 5.** Fluorescence spectra of **Fc-Q** in  $\text{CH}_3\text{CN}$  in the presence of different metal ions. The concentration of **Fc-Q** and metal ions were  $1.0 \times 10^{-5}$  M and  $5.0 \times 10^{-5}$  M, respectively.  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ . Excitation wavelength was 240 nm.

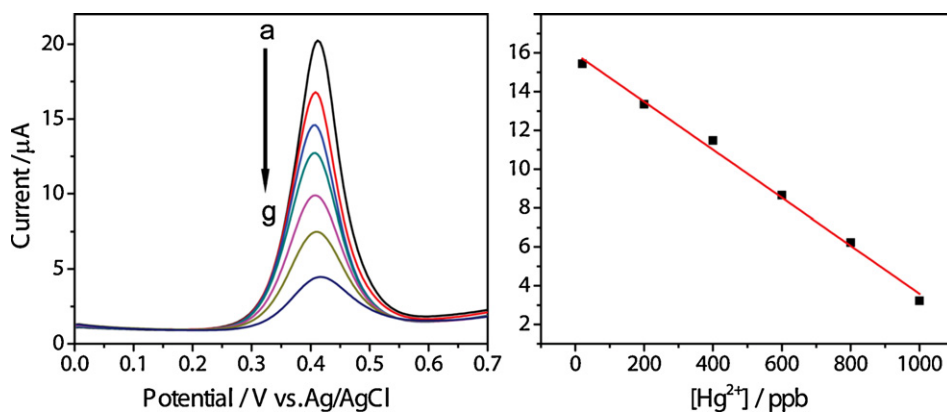


**Fig. 6.** Cycle voltammetry in  $\text{CH}_3\text{CN}$  of free **Fc-Q** (a) and after the addition of  $\text{Hg}^{2+}$  (b) [**Fc-Q**] = 1 mM. 0.15 M [(n-Bu) $_4$ N]ClO $_4$  was used as supporting electrolyte. Scan rate: 100 mV/s.

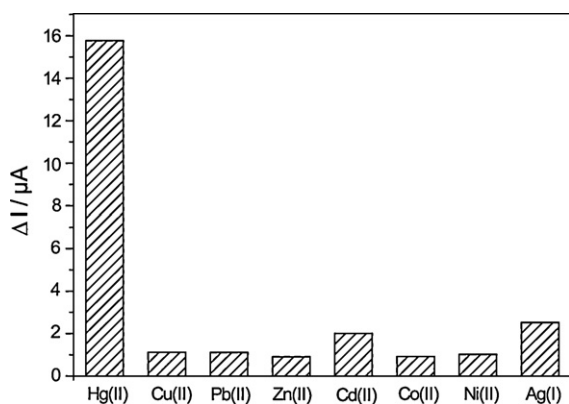
sity at the ferrocenyl redox center of **Fc-Q** [32]. The electrochemical responses to other tested metal ions were also investigated (see Fig. S2 in supplementary material).

In order to further examine the coordination capability of **Fc-Q** in aqueous solution, differential pulse voltammetry (DPV) measurement as a sensitive electrochemical technique has been carried out to study the electrochemical properties of **Fc-Q** coordination with  $\text{Hg}^{2+}$  in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (4:1, v/v) solution. As shown in Fig. 7, the DPV peak current decreases with increasing concentration of  $\text{Hg}^{2+}$  ion. This is caused by the slow diffusion of **Fc-Q** to the electrode after the interaction with  $\text{Hg}^{2+}$  [33]. The linear correlation between the peak current and the concentration of  $\text{Hg}^{2+}$  allows the quantitative analysis of  $\text{Hg}^{2+}$  at ppb levels. The interaction of **Fc-Q** with other metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ) in  $\text{CH}_3\text{CN}$  aqueous solution was also investigated. As shown in Fig. 8, the significant change can only be observed upon the addition of  $\text{Hg}^{2+}$  ( $\Delta I = 15.771$   $\mu\text{A}$ ). The other ions cause negligible changes and have no interference to the determination of  $\text{Hg}^{2+}$  (see Fig. S3 in supplementary material). The anions, such as  $\text{Cl}^-$ ,  $\text{Ac}^-$ , and  $\text{ClO}_4^-$ , also have no interference.

The selectivity of **Fc-Q** towards different metal ions has been investigated in UV-vis, fluorescent and electrochemical channels. As summarized in Table 1, although **Fc-Q** give no measurable



**Fig. 7.** (Left) DPV of **Fc-Q** (1 mM) upon the addition of  $\text{Hg}^{2+}$  in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (4:1 v/v). (a) 0, (b) 20 ppb, (c) 200 ppb, (d) 400 ppb, (e) 600 ppb, (f) 800 ppb, (g) 1000 ppb. (Right) The calibration curve of the peak current and the concentration of  $\text{Hg}^{2+}$ . 0.15 M [(n-Bu) $_4$ N] $\text{ClO}_4$  was used as the supporting electrolyte.

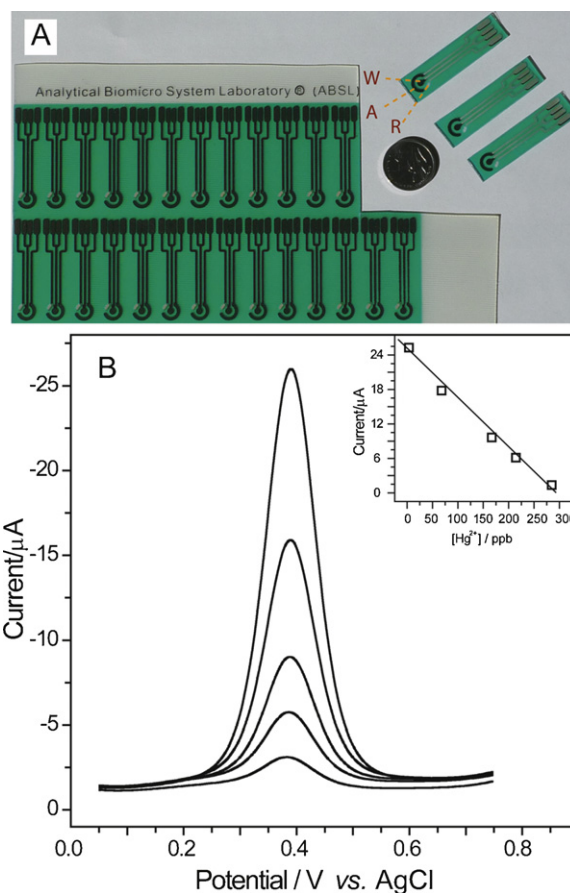


**Fig. 8.** Change of peak current (DPV) of **Fc-Q** in the presence of different metal ions.

response to some other ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ) in one or two channels, only  $\text{Hg}^{2+}$  induces the most significant change in all three channels. **Fc-Q** sensing molecule based on the multi-channel sensor could be selected as a sensitive and selective probe for  $\text{Hg}^{2+}$  determination.

### 3.4. Electrochemical determination of $\text{Hg}^{2+}$ in water by **Fc-Q/SPCEs**

In order to examine the capability of **Fc-Q** sensor to measure  $\text{Hg}^{2+}$  in real water sample, **Fc-Q** was assembled onto the screen-printed carbon electrodes (SPCEs, as shown in Fig. 9A) through non-covalent interactions to fabricate the disposable **Fc-Q/SPCE** sensors, which could be provided for on-site environmental analysis [4]. DPV was applied to characterize the fabricated **Fc-Q/SPCEs** by testing  $\text{Hg}^{2+}$  in the range of 0–300 ppb. As shown in Fig. 9B, the DPV response peak at 0.385 V from ferrocene moiety decreased upon addition of  $\text{Hg}(\text{ClO}_4)_2$  into 0.10 M PBS solution (pH = 7.0) to form the coordination of **Fc-Q** with  $\text{Hg}^{2+}$ . The decreasing ratio of DPV peak current ( $i_p$ ) is proportional to the addition of  $\text{Hg}^{2+}$



**Fig. 9.** (A) The photograph of the fabricated SPCEs, and (B) DPVs of **Fc-Q/SPCE** upon the addition of  $\text{Hg}^{2+}$  in water.

**Table 1**  
UV–vis, fluorescent and electrochemical multi-channel response to different metal ions.

Channel response	$\text{Hg}^{2+}$	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Ag}^+$
Electrochemistry	●	●	●	●	●	●	●	●
Fluorescence	●	●	●	○	○	○	○	○
UV–vis	●	●	●	○	○	○	○	○

●: represent high response; ○: represent medium response; ○: represent no response.

concentration ( $C_M$ ). The calibration equation was calculated by the least-squares method as  $i_p = -0.087 C_M + 24.7$ , ( $R = 0.9847$ ). The detection limit is 5 ppb calculated as three times standard deviation of blank/slope of the calibration curve.

The recovery studies were carried out in real water samples with  $\text{Hg}^{2+}$ , the results are shown in Table 2. The average recovery is >94% in all cases in our experiments. On the basis of these results, it could be affirmed that no interference of the matrix composition to the measurement was observed.



**Table 2**Recovery test for Hg<sup>2+</sup> in spiked samples.

Sample	Added (ppb)	Found <sup>a</sup> (ppb)	Average recovery (%)	RSD (%)
Tap water	50.0	47.2	94.4	3.2
	40.0	42.4	106.0	2.8
	60.0	57.9	96.5	3.1
River water	50.0	47.1	94.2	3.4
	40.0	41.9	104.8	2.9
	60.0	58.3	97.1	3.2

<sup>a</sup> The average value of five determinations.

#### 4. Conclusion

In summary, **Fc-Q** was designed and synthesized to develop a high sensitive and selective multi-channel sensor for determination of Hg<sup>2+</sup> ions, which combined the advantages of UV–vis, fluorescent and electrochemical measurements together. The **SPCEs** modified with **Fc-Q** were successfully used to detect Hg<sup>2+</sup> in real water sample. The results of the recovery studies indicate the matrix composition has no interference with the detection of Hg<sup>2+</sup>.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.talanta.2011.02.024](https://doi.org/10.1016/j.talanta.2011.02.024).

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