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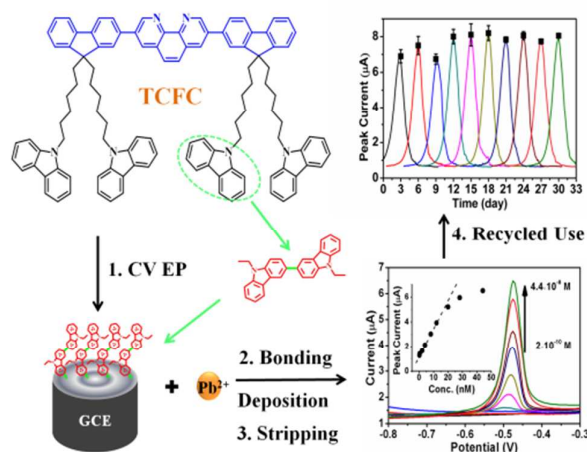
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A novel electro-active compound, 3,8-bis(9,9-bis(6-(9H-carbazol-9-yl)hexyl)-9H-fluoren-2-yl)-1,10-phenanthroline (TCFC) is used to modify glassy carbon electrode (GCE) for the electrochemical detection of  $\text{Pb}^{2+}$ . Phenanthroline unit in the backbone and four electro-active alkyl-linked peripheral carbazole groups as the side chains endow TCFC metal chelated ability and electropolymerized possibility, respectively. By the method of chemical preconcentration/absorption square wave anodic stripping voltammetry (SWASV), TCFC electropolymerized film modified GCE (TCFC/GCE) shows excellent selectivity and sensitivity to  $\text{Pb}^{2+}$ , even in the presence of a large amount of other heavy metal ions (HMIs). The calculated limit of detection (LOD) towards  $\text{Pb}^{2+}$  could be improved to  $1.33 \times 10^{-11}$  M (S/N=3) at an optimum condition. Moreover, the TCFC/GCE is stable under ambient condition (>30 days) and can be recycled used with high sensitivity, which is of great value for practicality. Further, TCFC/GCE can be applied to the determination of  $\text{Pb}^{2+}$  in real water samples.



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## ARTICLE

## Ultrasensitive and Stable Determination of Lead Ion by Phenanthroline-based Electropolymerized Film Modified Glassy Carbon Electrode

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A novel electro-active compound, 3,8-bis(9,9-bis(6-(9H-carbazol-9-yl)hexyl)-9H-fluoren-2-yl)-1,10-phenanthroline (**TCFC**) is used to modify glassy carbon electrode (GCE) for the electrochemical detection of Pb<sup>2+</sup>. Phenanthroline unit in the backbone and four electro-active alkyl-linked peripheral carbazole groups as the side chains endow **TCFC** metal chelated ability and electropolymerized possibility, respectively. By the method of chemical preconcentration/absorption square wave anodic stripping voltammetry (SWASV), **TCFC** electropolymerized film modified GCE (**TCFC/GCE**) shows excellent selectivity and sensitivity to Pb<sup>2+</sup>, even in the presence of a large amount of other heavy metal ions (HMIs). The calculated limit of detection (LOD) towards Pb<sup>2+</sup> could be improved to 1.33×10<sup>-11</sup> M (S/N=3) at an optimum condition. Moreover, the **TCFC/GCE** is stable under ambient condition (>30 days) and can be recycled used with high sensitivity, which is of great value for practicality. Further, **TCFC/GCE** can be applied to the determination of Pb<sup>2+</sup> in real water samples.

## 1. Introduction

Lead ion (Pb<sup>2+</sup>) is nondegradable and can accumulate in bones, muscles, kidney and brain, then result in brain damage, mental retardation, behavioral problems and so on,<sup>1-3</sup> therefore, the sensitive and robust detections of trace Pb<sup>2+</sup> in medicine, environment and biology are exigent.

The electrochemical detection of Pb<sup>2+</sup> has some attractive features, such as high selectivity and sensitivity, intrinsic simple operation, robustness and inexpensiveness.<sup>4,5</sup> Additionally, chemically modified electrode (CME) has its own extraordinary superiority, which can preconcentrate trace heavy metal ions (HMIs) during the accumulation step.<sup>6</sup> Thus, CME has been widely used for the trace HMIs determination. Though considerable efforts have been made to develop CMEs for HMIs sensing,<sup>7-10</sup> the stable and sensitive CME for Pb<sup>2+</sup> detection is still highly needed and deserves to explore.

Electropolymerization (EP) method prompts the electro-active precursors to undergo the oxidative coupling reaction, resulting in direct polymerization on the glassy carbon electrode (GCE). EP has the advantages of controlling morphology and conductivity by judicious selection of the precursors and/or potentiometric conditions. The resulting cross-linking network of the EP film is beneficial for the application in sensing field due to the possible stability and rapid diffusion of analytes. Thus, the electrodes modified by EP materials have the excellent potential to detect HMIs.

In this paper, we reported a novel electro-active material **TCFC** used as the CME modifier to detect Pb<sup>2+</sup>. The chemical structure of **TCFC** is shown in Scheme 1. As can be seen, 1,10-phenanthroline (PHEN) in the backbone could endow

**TCFC** strong metal-chelated capability, which acts as a receptor for the molecular recognition of Pb<sup>2+</sup>. Meanwhile, the alkyl-linked peripheral carbazole groups in side chains, which is well-known electro-active precursor and under anodic oxidation could provide the crossing site (3- and 6-active-sites could form dimers) to get the cross-linking network films. Based on this molecular design, **TCFC** can be coated on GCE (**TCFC/GCE**) by EP method. The **TCFC/GCE** exhibits high sensitivity towards Pb<sup>2+</sup>, and the calculated limit of detection (LOD) towards Pb<sup>2+</sup> can be down to 1.33×10<sup>-11</sup> M, such low LOD has ascend the best level in Pb<sup>2+</sup> sensing publications, which can be attributed to the strong chelated ability of PHEN in **TCFC** and the intrinsic microstructure of EP films.<sup>11</sup> Furthermore, the **TCFC/GCE** is stable under ambient condition and can be recycled used with high sensitivity (continuous measurement for 30 days). The **TCFC/GCE** sensor is also capable to determine the Pb<sup>2+</sup> ions of the real samples without any significant interferes or matrix problems.

## 2. Experimental Section

### 2.1 Chemicals and apparatus

All the reagents and solvents used for the synthesis were purchased from Sigma Aldrich or Acros companies and used as received.

Electrochemical measurements were carried out with CHI 660C electrochemical workstation. Electrochemical impedance spectroscopy (EIS) images were taken by Princeton Applied Research impedance meter (PARSTAT 2273). Fluorescence

spectra were recorded by a fluorescence spectro-photometer (Shimadzu RF-5301PC) equipped with a xenon lamp excitation source.  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCZ 500 spectrometer at 500 MHz using DMSO as solvent at 298 K and tetramethylsilane (TMS) as the internal standard. All aqueous solutions were prepared using Milli-Q water of 18.2 M $\Omega$  (Millipore) resistivity. The pH values were measured by pH meter (METTLER TOLEDO LE438). The 0.1 M acetate buffer solution (pH 4.5) was prepared by adding 0.1 M sodium acetate into 0.1 M acetic acid.  $\text{Pb}^{2+}$  solutions were prepared by diluting the appropriate amount of  $\text{Pb}^{2+}$  stock solution (0.1 M). The indium tin oxide (ITO), used for AFM measurement, were cleaned in an ultrasonic bath with toluene, acetone, ethanol, and deionized water, dried with nitrogen.

## 2.2 Synthesis of TCFC

The synthetic route of TCFC has been reported.<sup>12</sup>

**TCFC:** To a mixture of 3,8-dibromo-1,10-phenanthroline (0.03 g, mmol), and 2-(4, 4, 1, 5, 5 - tetramethyl-1, 3, 2 - dioxaborolan) -9, 9- (N-carbazole- hexyl) fluorene (150 mg, mmol) in 3 mL of toluene with 2 mL of 2.0 M  $\text{Na}_2\text{CO}_3$ , 17.5 mg  $\text{Pd}(\text{PPh}_3)_4$ , was added under nitrogen atmosphere, and the resulting mixture was stirred at 80°C for 72 h. After cooling to room temperature, the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . The precipitated solid was filtrated and purified by chromatography using petroleum ether/dichloromethane as the eluent to afford a white solid 0.06 g (yield: 50 %). **TCFC:**  $^1\text{H}$  NMR (500 MHz, DMSO) :  $\delta$  9.55 (d, 2H), 8.84 (d, 2H), 8.11 (d, 2H), 8.06 (d, 8H), 8.02 (s, 2H), 7.97 (m, 4H), 7.86 (m, 2H), 7.45 (d, 8H), 7.34 (m, 12H), 7.27(m, 2H), 7.1(t, 8H), 4.23 (t, 8H), 2.1 (m, 8H), 1.52 (m, 8H), 1.03 (m, 16H), 0.50 (m, 8H). MALDI-TOF-MS (m/z): 1506.01 [ $\text{M}^+$ ] 1507.3.

## 2.3 Preparation of TCFC/GCE (step1 of Scheme 1)

Firstly, the GCE was polished with different grades of alumina powder (0.05, 0.3 and 1.0  $\mu\text{m}$ ) on nylon cloth, emery paper and chamois, respectively, rinsed with deionized water and then cleaned by ultrasonic bath for 2 min according to the literatures (unless otherwise stated).<sup>13</sup>

Then, cyclic voltammetry (CV) method was used to prepare EP films on GCE by using a standard one-compartment, three-electrode electrochemical cell. Titanium metal and GCE were used as the counter electrode and the working electrode, respectively. The reference electrode was  $\text{Ag}/\text{Ag}^+$  nonaqueous electrode. A mixture of TCFC precursor molecule (0.5  $\text{mg}\cdot\text{mL}^{-1}$ ) and TBAPF<sub>6</sub> with  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (V:V=2:3) were used as the electrolyte solution. The TCFC electro-active precursor was electropolymerized through an oxidation coupling reaction (0 to 0.85 V) to form the cross-linking network film on GCE (TCFC/GCE).

Lastly, the TCFC/GCE was washed with a mixture solution of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (V:V=2:3) to remove the surface electrolyte and precursor, then the prepared TCFC/GCE was dried in a vacuum oven at 40 °C for three hours.

## 2.4. Electrochemical detecting experiments (step2, 3 and4 of Scheme 1)

**Scheme 1** The chemical structure of TCFC and the illustration of the EP and  $\text{Pb}^{2+}$  SWASV detected process using TCFC/GCE.

Electrochemical detecting experiments were carried out in a standard one-compartment, three-electrode electrochemical cell. The TCFC/GCE, Pt wire electrode and the  $\text{Ag}/\text{AgCl}$  (3 M KCl) aqueous electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. Preconcentration of  $\text{Pb}^{2+}$  (step2 of Scheme 1) took place at an open circle condition by dipping the working electrode into  $\text{HAc}/\text{NaAc}$  buffer aqueous (0.1 M, pH 4.5) containing  $\text{Pb}^{2+}$  under vigorous stirring for 300 s and being rinsed with deionized water for three times. Then, these electrodes were immersed in the 10 mL electrochemical cell containing 5 mL  $\text{HAc}/\text{NaAc}$  buffer solution (0.1 M, pH 4.5). Multi potential steps (M-PS) (step3 of Scheme 1) were performed at a potential of -1.2 V for 30 s. After that, SWASV scan (step 4 of Scheme 1) was performed from -1.0 V to 0.4 V by using the following waveform parameters: the scan frequency was 25 Hz, the amplitude was 25 mV and the step increment was 5.0 mV (unless stated otherwise).

In addition, to the aim for the recycled use of TCFC/GCE, the TCFC/GCE was immersed into 2,2',2'',2'''-(ethane-1,2-diylidinitrilo)tetraacetic acid (EDTA) aqueous and scan at 0.4 V for 1 min under vigorous stirring to clean off any remaining traces of  $\text{Pb}^{2+}$  for the next use.

## 2.5 Real world water sample analysis

The real world water samples were taken from the Yitong River (Changchun district in three collection points 1, 2 and 3), the tap water from our laboratory was also tested in the same condition. All water samples were filtered with 0.45  $\mu\text{m}$  and 0.22  $\mu\text{m}$  membrane. After being treated with UV digestion for release of the trace  $\text{Pb}^{2+}$  from the  $\text{Pb}^{2+}$  organic complexes, the samples were analyzed by the standard addition method.

## 3. Results and Discussion

### 3.1. The morphology of the TCFC EP films

The morphology of the TCFC EP films were characterized by atomic force microscope (AFM) and high resolution transmission electron microscopy (HR-TEM) shown in Fig. 1. It can be seen from the AFM images, TCFC could form rough films on the electrode after EP progress, and the roughness is 4.86 nm. And such morphology could improve the contact area between the EP film and  $\text{Pb}^{2+}$ . The HR-TEM images showed the internal structure information of the EP films, which indicated the EP films could form cross-linking cavity microstructure, which benefit the rapid diffusion of  $\text{Pb}^{2+}$ .

**Fig. 1** The AFM (A), the three-dimensional (B) and HR-TEM images (C) of TCFC EP film.

### 3.2. Electrochemical impedance spectra and cyclic voltammograms of the different electrodes

As we known, CV and EIS have been widely used for the characterization of modified electrodes, which provides clear information about electron transfer kinetics of the redox probes,<sup>13</sup> thus, CV and EIS were measured to characterize the bare GCE, TCFC/GCE and TCFC/GCE with Pb<sup>2+</sup>, respectively. As can be seen from the Fig. 2A, for the bare GCE in the solution of 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> dissolved in 0.1 M KCl, an obvious amperometric response could be observed. After the modification with TCFC by EP method, the TCFC/GCE presented a tremendous decrease in the amperometric response. The results indicated TCFC has been deposited onto GCE.

The Nyquist plot of the bare GCE was showed in the inset of Fig. 2B, the semicircle diameter at high frequencies is corresponding to the electron transfer resistance ( $R_{ct}$ ), and the linear part at low frequencies corresponds to the diffusion process.<sup>13, 14</sup> The equivalent circuit diagram can be written as:

$$R_s(Q(R_{ct}W))$$

where  $R_s$  is the solution resistance,  $Q$  corresponds to the double-layer capacitance of the electrodes/electrolyte interface, and  $W$  stands for Warburg resistance, respectively.

After the modification, TCFC layer on GCE produced an interior resistance ( $R_i$ ) except  $R_{ct}$  as shown in Fig. 2B, its equivalent circuit diagram can be denoted as:

$$R_s(Q_1R_i)(Q_2R_{ct})$$

The  $R_{ct}$  value on the bare GCE is 337  $\Omega$ . The  $R_i$  and  $R_{ct}$  values on the TCFC/GCE before detecting Pb<sup>2+</sup> are  $9.5 \times 10^5$  and  $4.9 \times 10^5$   $\Omega$ , respectively, and those after detecting Pb<sup>2+</sup> are  $2.7 \times 10^5$  and 5051  $\Omega$ , respectively. Obviously, the  $R_i$  and  $R_{ct}$  values on the TCFC/GCE before detecting Pb<sup>2+</sup> are larger than those after detecting Pb<sup>2+</sup>, this is maybe caused by the embedding of Pb<sup>2+</sup> into EP layer increasing its conductivity.

**Fig. 2** Cyclic voltammograms (A) and Nyquist plots (B) of the bare GCE, TCFC/GCE in 0.1 M KCl containing 5.0 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> before and after detection of  $10^{-6}$  M Pb<sup>2+</sup>. Inset: Nyquist plot of the bare GCE.

### 3.3 Optimization of the deposition condition

**Fig. 3** The effect of deposition potential (A) and deposition time (B) on the stripping peak current of  $4.0 \times 10^{-6}$  M Pb<sup>2+</sup> at TCFC/GCE in NaAc/HAc buffer solution (0.1 M, pH 4.5). (C) The effect of different pHs on the stripping peak current of  $4.0 \times 10^{-6}$  M Pb<sup>2+</sup> at TCFC/GCE; (D) The influence of different ion strength of NaAc/HAc buffer solution (pH 4.5) on the stripping peak current of  $4.0 \times 10^{-6}$  M Pb<sup>2+</sup> at TCFC/GCE.

For the electrochemical measurement, optimizing deposition condition is usually a simple and effective way to enhance the sensitivity, thus, the influence of deposition potential and deposition time on the stripping signal for Pb<sup>2+</sup> were firstly studied and shown in Fig. 3. As can be seen from Fig. 3A, for the TCFC/GCE (in 0.1 M HAc/NaAc, pH 4.5) exposed to Pb<sup>2+</sup> ( $4.0 \times 10^{-5}$  M), the stripping peak current of Pb<sup>2+</sup> exhibited a notable increasing trend with the negative shift of deposition potential. The maximal peak-height could be observed at  $-1.8$  V. Considering the increasing possibility of hydrogen evolution reaction at more negative potentials, which might damage the deposition of Pb<sup>2+</sup> at the electrode surface, the deposition potential of  $-1.2$  V was chosen as the optimum potential for Pb<sup>2+</sup>.

The dependence of the deposition time was also investigated from 60 s to 480 s. Fig. 3B shows the relationship between the peak currents and deposition time for  $4.0 \times 10^{-5}$  M Pb<sup>2+</sup> at  $-1.2$  V in 0.1 M NaAc/HAc (pH 4.5). As can be seen in Fig. 3B, the peak currents increased with the increase of the deposition time, and after 300 s, a saturation section was appeared, so a deposition time of 300 s was chosen as the optimum deposition time for the following experiments.

pH is also an important factor in HMIs sensing, hereby, we carried out the experiment to explore the influence of pH to the detection of Pb<sup>2+</sup>. As we can see from Fig. 3C, different pHs (Na<sub>2</sub>HPO<sub>4</sub>/Citric Acid: pH=2.0; NaAc/HAc: pH=3.5, 4.5 and 5.5; PBS; pH=7.0; and Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>: pH=8.5) were investigated. Based on the achieved intensity, NaAc/HAc (pH 4.5) was selected as the optimized buffer solution.

As a parameter of pH, ion strength can influence the binding process of TCFC/GCE with Pb<sup>2+</sup>, thus, the effect of the ion strength is also studied shown as Fig. 3D, which indicates the peak current decreased slowly with the increase of ion strength. From that we can easily get that the binding ability of TCFC to Pb<sup>2+</sup> decreases with the increase of ion strength. On this consideration, 0.1 M ion strength was chosen as the optimized condition.

### 3.4 Electrochemical detection of Pb<sup>2+</sup>



**Fig. 4** (A) The cyclic voltammograms of the **TCFC/GCE** recorded in acetate buffer (pH 4.5, 0.1 M) with (square dots) and without (circle dots)  $4.0 \times 10^{-6}$  M  $\text{Pb}^{2+}$ ; (B) The SWASV curves of **TCFC/GCE** recorded in NaAc/HAc buffer solution (0.1 M, pH 4.5) with  $1.0 \times 10^{-8}$  M  $\text{Pb}^{2+}$  and  $1.0 \times 10^{-6}$  M  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ .

Furthermore, due to the designed metal-chelated unit, PHEN, in **TCFC** molecule, the chelated behavior of **TCFC/GCE** was also studied by CV (Fig. 4A). As can be seen, before the exposure of  $\text{Pb}^{2+}$ , the CV of the bare **TCFC/GCE** was nearly a straight line (circle dot line). After the accumulation of  $\text{Pb}^{2+}$  and being rinsed with deionized water for three times to remove the adsorptive  $\text{Pb}^{2+}$  and other electrolyte, significant oxidation peak and reduction peak ( $-0.4$  V and  $-0.65$  V) appear in the CV curves, which indicated the chelation of  $\text{Pb}^{2+}$  to **TCFC** molecule.

**TCFC/GCE** shows excellent selectivity to  $\text{Pb}^{2+}$  even in the presence of a large amount of other HMIs. Fig. 4B is the SWASV curves of **TCFC/GCE** detecting  $\text{Pb}^{2+}$  ( $1.0 \times 10^{-8}$  M) with disturbing metal ions of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ( $1.0 \times 10^{-6}$  M). As can be seen, though the concentrations of disturbing metal ions were 100 times higher than that of  $\text{Pb}^{2+}$ , an intense stripping signal of  $\text{Pb}^{2+}$  can be clearly observed compared with other HMIs, which indicates the high selectivity of **TCFC/GCE** to  $\text{Pb}^{2+}$ .

To ascertain the value of LOD, further investigations using SWASV was carried out under the same experimental conditions as in Scheme 1. Firstly, the SWASV performance of the bare GCE with  $2.0 \times 10^{-10}$  M  $\text{Pb}^{2+}$  in NaAc/HAc buffer solution (0.1 M, pH 4.5) was measured, and no peak was observed. Then, the **TCFC/GCE** was tested. Fig. 5 shows the SWASV of **TCFC/GCE** with different  $\text{Pb}^{2+}$  concentration ranged from  $2.0 \times 10^{-10}$  M to  $4.4 \times 10^{-8}$  M. The insert shows an amplification of SWASV curves with ultralow  $\text{Pb}^{2+}$  concentration of  $2.0 \times 10^{-10}$ – $1.2 \times 10^{-9}$  M. The corresponding calibration plot (Fig. 5B) revealed that the peak current increases linearly in the range of  $\text{Pb}^{2+}$  from  $2.0 \times 10^{-10}$  M to  $1.2 \times 10^{-8}$  M ( $R^2=0.9908$ ). The final calculated LOD is  $1.3 \times 10^{-11}$  M, which is comparable to the previously reports shown in Table 1.<sup>13, 15-21</sup>

**Fig. 5** (A) The SWASV responses of **TCFC/GCE** towards  $\text{Pb}^{2+}$  at different concentration ( $2.0 \times 10^{-10}$ – $4.4 \times 10^{-8}$  M) dissolved in HAc/NaAc buffer solution (0.1 M, pH 4.5). Insert: the

amplification of SWASV curves of the ultralow  $\text{Pb}^{2+}$  concentration ( $2.0 \times 10^{-10}$ – $1.2 \times 10^{-9}$  M); (B) The calibration linear curve of Fig. 5A. Insert: the enlarged calibration curve of the ultralow  $\text{Pb}^{2+}$  concentration ( $2.0 \times 10^{-10}$ – $1.2 \times 10^{-9}$  M); (Deposition potential:  $-1.2$  V; deposition time: 300 s; quiet time: 1.0 s; frequency: 25.0 Hz; pulse amplitude: 25 mV)

Table 1. The merits of comparable methods for  $\text{Pb}^{2+}$  determination.

### 3.5 The stability and recycled use of **TCFC/GCE**

The stability of **TCFC/GCE** was evaluated by the repeated serial measurements each day, which was performed continuously for 30 days. To remove the chelated  $\text{Pb}^{2+}$  in the **TCFC/GCE** and gain the original SWASV window between  $-1.0$  V to  $0.4$  V, the **TCFC/GCE** was cleaned in EDTA aqueous at a M-PS potential of 0 V for 3 min with vigorous stirring, then, dried with  $\text{N}_2$  and placed in a vacuum oven at a temperature of  $40$  °C for 2 h before being exposed in air for each measurement. Fig. 6 displays the SWASV responses of **TCFC/GCE** towards  $\text{Pb}^{2+}$  at a concentration of  $4.4 \times 10^{-8}$  M within 30 days. As can be seen that the current response of **TCFC/GCE** did not change considerably even after 30 days under ambient circumstances. It is demonstrated that the intrinsic characteristic of PHEN of the **TCFC/GCE** can repeatedly entrapped  $\text{Pb}^{2+}$ , which is of great value for practical sensors.

**Fig. 6** The SWASV responses of **TCFC/GCE** towards  $\text{Pb}^{2+}$  at a concentration of  $4.4 \times 10^{-8}$  M within 30 days. Results are presented as mean  $\pm$  SD (error bar) of triplicate experiments.

Furthermore, in order to illustrate its accuracy in practical analysis, the comparison between **TCFC/GCE** and inductively coupled plasma mass spectrometry (ICP-MS) for  $\text{Pb}^{2+}$  detection in real samples (Yitong River and the tap water in our laboratory) were carried out. The results are shown in Table 2, as can be seen, for the Yitong River sample, the concentrations of  $\text{Pb}^{2+}$  were measured as  $66.1 \pm 1.5$ ,  $55.3 \pm 1.8$  and  $23.0 \pm 1.7$  nM, respectively. The obtained values showed good agreement with the certified values performed by ICP-MS with good precision. The **TCFC/GCE** was also applied successfully for the determination of  $\text{Pb}^{2+}$  in tap water. The value of  $\text{Pb}^{2+}$  was detected as  $15.0 \pm 1.5$ . To compare the results, the tap water was also analyzed using ICP-MS, the result show that  $17.3 \pm 1.2$  was present in the tap water, indicating that the **TCFC/GCE** can be

applied to the determination of Pb<sup>2+</sup> in real water samples.

Table 2. Comparison of the results obtained by the TCFC/GCE and ICP-MS for determination of Pb<sup>2+</sup> in real water samples

## Conclusions

In summary, an innovative material TCFC was used to modify GCE by EP method, further this TCFC/GCE was applied to detect ultratrace Pb<sup>2+</sup> with excellent performance, which might be due to the strong metal ion chelate ability of PHEN unit in TCFC and the intrinsic cross-linking network of the EP films. The TCFC/GCE showed a better linear ( $R^2=0.9908$ ) response to Pb<sup>2+</sup> ranged from  $2.0 \times 10^{-10}$  to  $1.2 \times 10^{-8}$  M with a calculated LOD of  $1.33 \times 10^{-11}$  M ( $S/N=3$ ). Moreover, the TCFC/GCE can be stable and recycled used with high sensitivity even after 30 days, what's more, the final results suggest that TCFC may be a promising competitor for detecting Pb<sup>2+</sup> in real water samples.

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## Notes and references

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