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Heavy Metal Analysis in Tai Lake Water Sample Based on Vanadium Oxide-Polypropylene Carbonate Modified Electrode

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Heavy metal ions are detrimental risks to human health due to their high toxicity. Electrochemical determination of heavy metal ions is an effective and low cost approach for environmental sample analysis. In this work, we prepared a vanadium oxide polypropylene carbonate for indium tin oxide electrode surface modification. The electrochemical property of the vanadium oxide polypropylene carbonate was studied cyclic voltammetry. The modified electrode showed an excellent performance towards detection of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+}. The concentration measurement of heavy metal ions using proposed electrode are in good agreement with the previous reports. In addition, the proposed electrochemical sensor was applied for heavy metal content analysis of Tai Lake water samples.

Keywords: Heavy metal ions; Vanadium oxide polypropylene carbonate; Tai Lake; Electrocatalysis;

1. INTRODUCTION

Heavy metals are extremely harmful to human health and the environment due to they are not biodegradable, which them highly stable in ecosystem and can accumulate in the food chain [1, 2]. Besides the health issue, the heavy metal ions contamination in water system could result economic and financial damage [3, 4]. Therefore, development of a rapid, sensitive, low-cost, real-time and simple analytical method for trace heavy metal ions determination in water sample is needed. Commonly, the heavy metal ions were determined using atomic spectrometer [5-7]. However, this method is not suitable for real time water sample analysis due to its complex sample preparation procedures and ponderous instruments. On the other hands, the electrochemical approach as an alternative of atomic spectrometer showed an outstanding performance due to its high sensitivity, low cost, quick analysis process and simple preparation procedure [8-13].

Pure commercial electrode such as glassy carbon electrode, indium tin oxide electrode, carbon paste electrode and screen printed electrode only showed acceptable performances towards heavy metal ions electrochemical determination due to the limited catalytic and adsorption properties. In order to overcome this problem, various nanomaterials were prepared for commercial electrode surface modification and enhance their electrochemical performances. For example, Bagheri and co-workers demonstrated a triphenylphosphine-multi-walled carbon nanotube composite modified carbon ionic liquid electrode for trace heavy metal ions detection [14]. Recently, Zhu and co-workers demonstrated a trace heavy metal ions electrochemical sensor based on the graphene nanodots modified porous gold electrode [15]. Cui and co-workers synthesized a nitrogen-doped porous carbon for electrode surface modification and the successfully used for electrochemical determination of Cu (II) [16].

Two aspects were normally considered for designing an advanced electrochemical heavy metal ions sensor. Firstly, the applied electrode modifier should owing a higher electrochemical or electrocatalytic properties, which could enhancing the sensing signal of the electrode [17-19]. For example, Ting and co-workers designed a trace heavy metal ions electrochemical sensor based on the graphene quantum dots functionalized gold nanoparticles [20]. Secondly, the applied electrode modifier should owing a higher surface area which could concentrate the trace heavy metal ions on the electrode surface. For example, Wang and co-workers proposed magnesium silicate hollow spheres with high specific surface, which could adsorb more than 300 mg/g lead ions [21].

In this work, we used conductive polymer film for indium tin oxide electrode surface modification due to its multilayer adsorption nature. Poly(propylene carbonate) (PPC) was chosen in this study because it showed good electrochemical property with excellent adhesiveness. On the other hand, $VO(OC_3H_7)_3$ was also adopted for constructing the electrode surface modifier due to its excellent electrocatalytic activity. Therefore, we proposed a vanadium oxide-polypropylene carbonate composite for trace heavy metal ions analysis. After optimization, the proposed sensor was used for analyzing the real water samples collected from Tai Lake, which is a large freshwater lake in the Yangtze Delta plain, during different seasons. Four species of heavy metal ions including Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} were analysed in detail. Results indicate the heavy metal ions content of the Tai Lake kept a low level through the year. Our work demonstrated the electrochemical sensor could be used for site water quality inspection application.

2. EXPERIMENTS

2.1 Materials

Poly(propylene carbonate) (average Mn ~50,000 by GPC), vanadium pentoxide, isopropanol, tetrahydrofuran and lithium perchlorate were purchased from Sigma. 0.1 M acetate buffer solution was prepared by mixing stock solutions of 0.1 M NaAc and HAc. ITO glass (1.1 mm thickness, 100 Ω resistance) was purchased from Suzhou NSG Electronics Co., Ltd. (Suzhou, China). All other reagents were analytical grade used without any purification. Milli-Q water was used through the experiments.

2.2 Preparation of vanadium oxide-polypropylene carbonate

For $VO(OC_3H_7)_3$ preparation, 10 g V_2O_5 was dissolved into 20 mL isopropanol containing 1 mL sulfuric aicd (15 M) and underwent 5 h reflux at 90 °C. After cooling, the solution was extract using tetrahydrofuran and then centrifuged to result tetrahydrofuran. PPC sol was prepared by mixing PPC with lithium perchlorate under stirring. For $VO(OC_3H_7)_3$-PPC composite preparation, prepared $VO(OC_3H_7)_3$ was dispersed into PPC sol under stirring for 2 h.

2.3 Characterization

The morphology of $VO(OC_3H_7)_3$-PPC composite was characterized by a scanning electron microscope (SEM, Quanta 200, FEI Coropration, Holland). A FTIR (Perkin-Elmer Spectrum One) was used for analysing the surface functional groups of the prepared sample.

2.4 Electrochemical determination of trace heavy metal ions

All electrochemical measurements were carried out using a CHI 630A electrochemical analyzer (CH instruments) by a three electrodes system. $VO(OC_3H_7)_3$-PPC composite casted ITO was used as working electrode. A platinum wire and a saturated calomel electrode were used as counter electrode and reference electrode, respectively. Determination of trace heavy metal ions was carried out using Linear sweep voltammetry (LSV) method at 0.1 M acetate buffer solution using scan rate of 50 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried in the frequency of 10^1~10^5 Hz using 5 mM $[Fe(CN)_6]^{3-/4-}$ probe with 0.1 M KCl, dc potential: 180 mV; ac amplitude: 5 mV.

2.5. Tai Lake water sample preparation

Tai Lake water samples were collected from three location, Shihu, Tongli and Yushan, each month in 2015. All water samples were filtrated first for removing the solid impurities. After filtration, 0.5 mL water sample was injected to the 2.5 mL 0.1 M acetate buffer solution for trace heavy metal ions content analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of vanadium oxide-polypropylene carbonate composite

The surface morphology of the prepared $VO(OC_3H_7)_3$-PPC composite was characterized using a SEM. As shown in Figure 1A, the surface of the $VO(OC_3H_7)_3$-PPC composite showed a rough structure, which is different compared with that of previous report [22]. This kind of morphology could exhibit a much higher surface area compared with the smooth surface and allow the target ions adsorption, which consequently enhancing the electrochemical performance of the electrode.

Figure 1B shows the FTIR spectrum of the prepared $VO(OC_3H_7)_3$-PPC composite. The spectrum of $VO(OC_3H_7)_3$-PPC composite displays a series peaks at 1699, 1577, 1365 and 1031 cm^{-1}, which can be assigned to the C═O stretching of COOH groups, C=C vibrations, C—OH stretching vibrations and C—O vibrations from alkoxy groups, respectively. Moreover, an absorbance band was recorded at 722 cm^{-1}, corresponding to C-N vibrations of the nitroso groups. As can be seen from the FTIR spectrum, the $VO(OC_3H_7)_3$ showed a strong interaction with PPC.

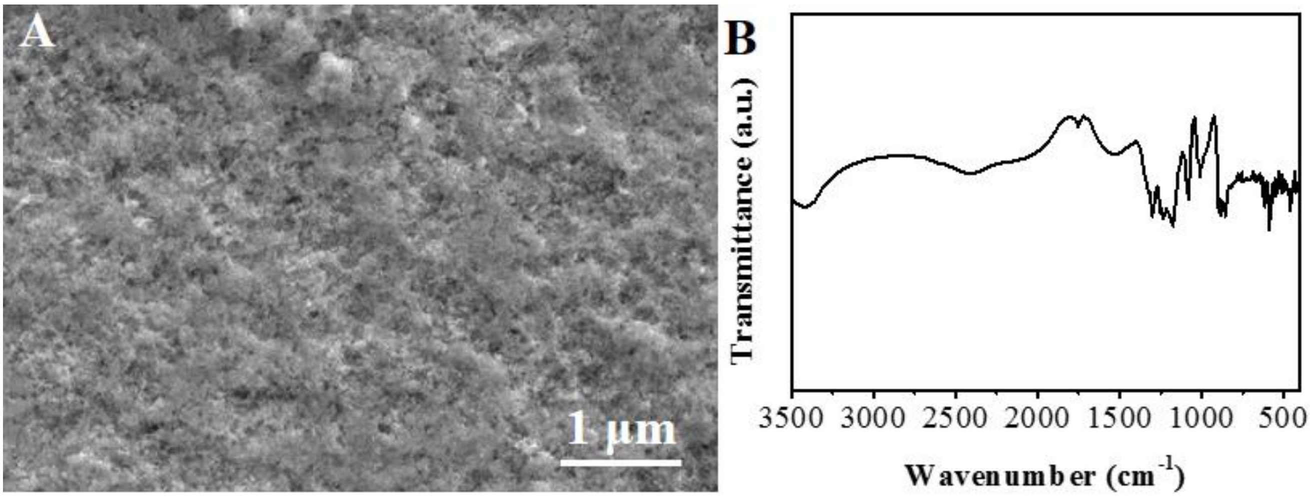

Figure 1. (A) SEM image and (B) FTIR spectrum of $VO(OC_3H_7)_3$-PPC composite.

3.2 Electrochemical property of vanadium oxide-polypropylene carbonate composite

Cyclic voltammetry and electrochemical impedance spectroscopy have been widely used for investigating the electron transfer kinetics of the electrode before and after surface modification. Figure 2A shows the CV profiles of bare ITO and $VO(OC_3H_7)_3$-PPC/ITO in a 5 mM $[Fe(CN)_6]^{3-/4-}$ with 0.1 M KCl. An decrease in the amperometric response was observed at $VO(OC_3H_7)_3$-PPC/ITO compared with that of the bare ITO, suggesting the surface modification of $VO(OC_3H_7)_3$-PPC/ITO was successful. The interface properties of the $VO(OC_3H_7)_3$-PPC composite modified electrode was further analyzed using EIS. Figure 2B shows the Nyquist plots of the bare ITO and $VO(OC_3H_7)_3$-PPC/ITO in a 5 mM $[Fe(CN)_6]^{3-/4-}$ probe with 0.1 M KCl. It can be seen that the both profiles showed two sections involving a semicircle followed with a straight line. The semicircle and line could represent to the electron-transfer resistance at high frequencies and low frequencies, respectively. In comparison of Nyquist plots of the bare ITO and $VO(OC_3H_7)_3$-PPC/ITO, a smaller semicircle was observed at bare $VO(OC_3H_7)_3$-PPC/ITO, suggesting the decrease in the electron-transfer resistance after surface modification. Based on the both characterizations, the enhanced electrochemical properties of the $VO(OC_3H_7)_3$-PPC/ITO were confirmed.

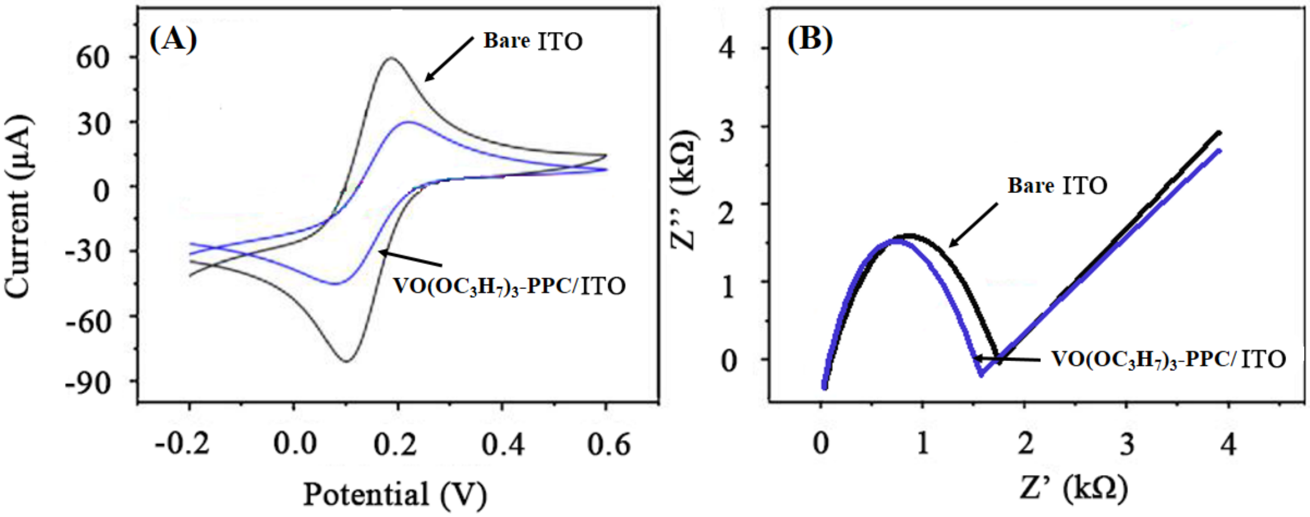

Figure 2. Cyclic voltammograms and Nyquist diagrams of electrochemical impedance spectrum of bare ITO and $VO(OC_3H_7)_3$-PPC/ITO in the solution of 5 mM $Fe(CN)_6^{3-/4-}$ with 0.1 M KCl.

3.3 Electrochemical determination of trace heavy metal ions using $VO(OC_3H_7)_3$-PPC/ITO

Species of Cu^{2+} was used as an example for optimizing the $VO(OC_3H_7)_3$-PPC/ITO for trace heavy metal ions detection. Figure 3A shows the stripping voltammograms of 0.5 μM Cu^{2+} on bare ITO and $VO(OC_3H_7)_3$-PPC/ITO in acetate buffer solution. It can be seen that no obvious peak was observed at bare ITO while the $VO(OC_3H_7)_3$-PPC/ITO exhibited a well-defined peak at -0.13 V, suggesting the $VO(OC_3H_7)_3$-PPC/ITO exhibited an excellent electrochemical performance toward Cu^{2+}. In order to obtain a high sensitive electrochemical performance with $VO(OC_3H_7)_3$-PPC/ITO to trace heavy metal ions, several electrochemical determination parameters were optimized. Figure 3B shows the effect of the buffer solution pH from 3.0 to 7.0 on determination performance. It can be seen that the current response was increased from 3.0 and reached to the maximum at 5.0. Further increasing pH value results a decreasing of current response. Therefore, pH 5.0 was chosen for further study. The accumulation step is a simple method was applied for enhance the sensitivity of electrochemical sensor. Figure 3C shows the influence of the accumulating potential on the current response. In order to avoid the influence of the determination of other trace heavy metal ions, the accumulation potential was chosen above -1.0 V. In this study, the accumulation potential was investigated from -1.0 to -1.5 V. As shown in the figure, the current response increased from -1.0 V to -1.2 V and then kept a stable performance after further increase accumulation step. Therefore, -1.2 V was used as optimum condition for accumulation. Moreover, the effect of accumulation time on $VO(OC_3H_7)_3$-PPC/ITO was also studied. Figure 3D shows the current response along with the increasing of accumulation time. It can be seen that the current response increased dramatically from 0 s to 70 s and then reached the saturation. Therefore, the accumulation time was chose as 70 s.

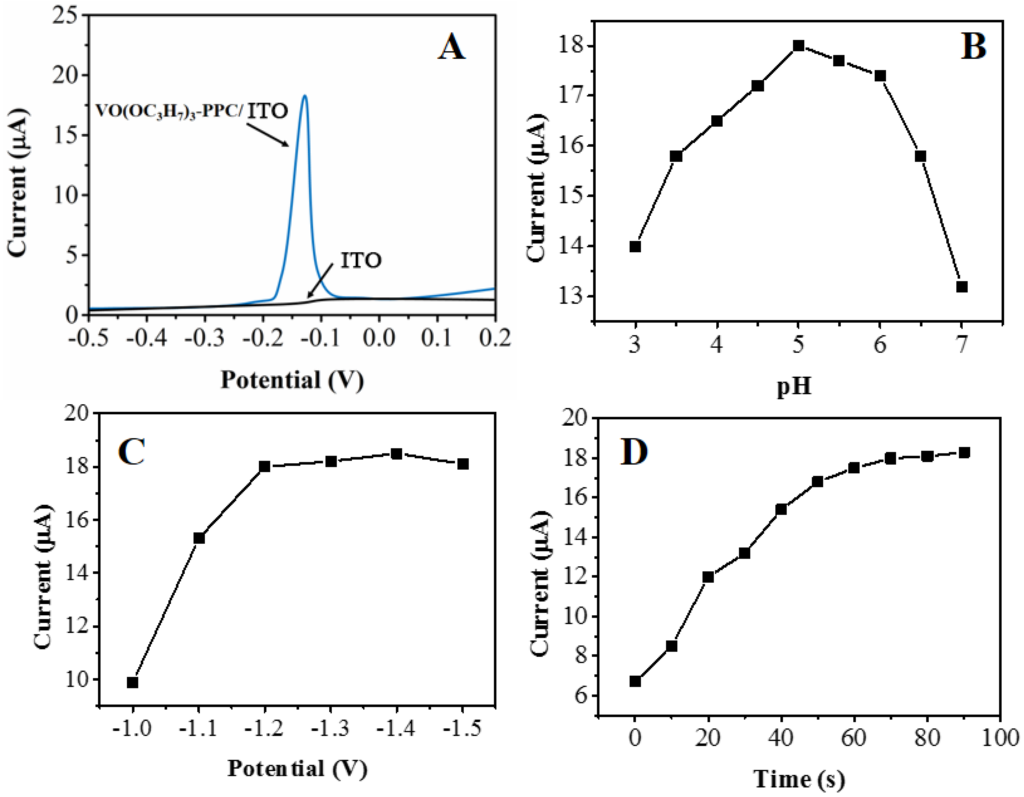

Figure 3. (A) SLV profiles of bare ITO and $VO(OC_3H_7)_3$-PPC/ITO in 0.1 M acetate buffer containing 0.5 μM Cu^{2+}. Effect of (B) pH value, (C) accumulation potential and (D) accumulation time on $VO(OC_3H_7)_3$-PPC/ITO towards 0.5 μM Cu^{2+} detection.

After optimization, the simultaneous detection of trace heavy metal ions was studied. Four heavy metal ion species including Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} were detected using $VO(OC_3H_7)_3$-PPC/ITO. As shown in Figure 4A, the SLV profile exhibited four individual peaks located at -0.59, -0.38, -0.12 and 0.19 for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} reduction, respectively. The separation of adjacent peaks were large enough for distingwish each reduction current. After determining the peak location for each heavy metal ions, amperometric responses of each ions at concentration range from 0.05 to 2.00 μM were investigated. Figure 4B-D shows the typical amperometric responses of $VO(OC_3H_7)_3$-PPC/ITO towards the successive addition of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, respectively. It can be seen that the response current increases rapidly after each addition of heavy metal ions. Three profiles all returned to the steady-state within 3 s, suggesting the high response speed of the $VO(OC_3H_7)_3$-PPC/ITO. The detection of the Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} all showed linear response in the concentration range from 0.05 to 2 μM. The detection limit of the Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} can be determined as 0.022, 0.018, 0.021 and 0.015 μM, respectively. Table 1 shows the comparison of analytical performances of the $VO(OC_3H_7)_3$-PPC/ITO with other heavy metal ions electrochemical sensors. The detection limit obtained is comparable with that reported so far with carbon based electrochemical sensor [23], and it is significantly lower than those of 30 nM at nanoporous gold nanoparticles [24], indicating that the proposed $VO(OC_3H_7)_3$-PPC/ITO is reliable for the determination of methyl parathion. As can be seen that the proposed electrochemical sensor showed a relative lower detection linear range of Cd^{2+} and Hg^{2+}compared with previous works. Therefore, the $VO(OC_3H_7)_3$-PPC/ITO can be used for trace amount of Cd^{2+} and Hg^{2+} detection. In contrast, the detection range using proposed method can be applied for high concentration level of Pb^{2+} and Cu^{2+}determination, which suitable for analysis of environmental water sample located at the area around manufacturing district.

We applied our proposed $VO(OC_3H_7)_3$-PPC/ITO for real environmental water sample test. Water samples from Tai Lake were collected from four locations each month over 2015. Figure 5A-D show the detection average result of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} over 12 months. It can be seen that the small amount of heavy metal ions can be detected from the water sample in some months. The presence of Cu^{2+} content are relatively higher than other three species. Overall, the Tai Lake showed a mild heavy metal ions contamination status.

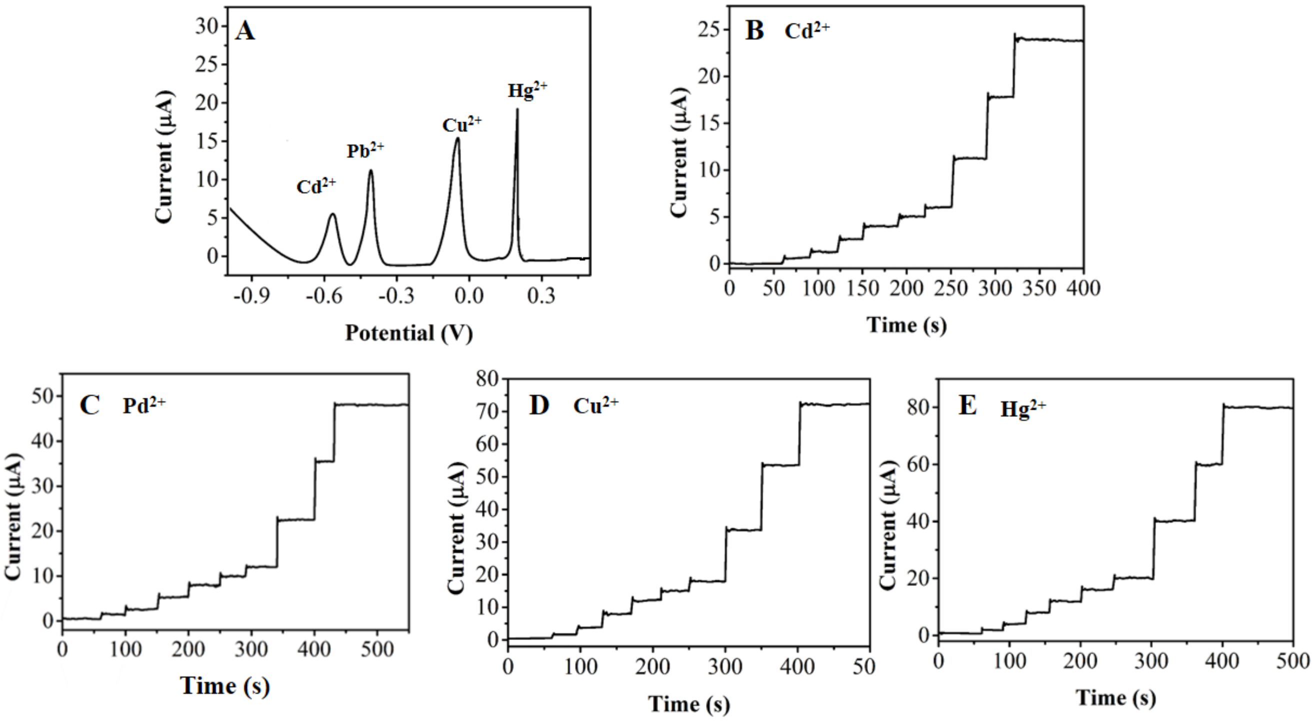

Figure 4. (A) SLV profile of $VO(OC_3H_7)_3$-PPC/ITO in 0.1 M acetate buffer containing 0.5 μM Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. Amperometric response of the $VO(OC_3H_7)_3$-PPC/ITO for the successive addition of (B) Cd^{2+}, (C) Pb^{2+}, (D) Cu^{2+} and (E) Hg^{2+}.

Table 1. Comparison of our proposed $VO(OC_3H_7)_3$-PPC/ITO with other heavy metal ions electrochemical sensors.

Electrode	Detection species	Linear detection range (μM)	Limit of detection (μM)	Reference
Graphene–polyaniline	Cd^{2+}	0.35-8	0.1	[23]
Fe_3O_4 NPs-Schiff base	Cd^{2+}	0.001-0.15	0.0005	[25]

MnO_2 nanocrystals	Cd^{2+}	0.1-20	0.03	[26]
$VO(OC_3H_7)_3$-PPC/ITO	Cd^{2+}	0.05-2	0.022	This work
MWCNTs/Au NPs	Pb^{2+}	0.000015-0.001	0.0000045	[27]
Amino-modified reduced graphene oxide	Pb^{2+}	0.0001-0.1	0.000087	[28]
Cetyltrimethylammonium-thiourea-organoclay	Pb^{2+}	0.001-0.07	0.00029	[29]
$VO(OC_3H_7)_3$-PPC/ITO	Pb^{2+}	0.05-2	0.018	This work
5,17-bis(4′-nitrophenylazo)-25,26,27,28-tetrahydroxycalix[4]arene	Cu^{2+}	0.005-0.2	0.0004	[30]
Rhodamine B hydrazide-immobilized graphene oxide	Cu^{2+}	0.0001-0.05	—	[31]
Polystyrene sulfonate–carbon nanopowders	Cu^{2+}	0.005-0.5	0.00173	[32]
Cysteine monolayer	Cu^{2+}	0.05-5	0.03	[33]
$VO(OC_3H_7)_3$-PPC/ITO	Cu^{2+}	0.05-2	0.021	This work
Activated graphite	Hg^{2+}	0.05-14.77	0.0046	[34]
Bis(indolyl)methane/mesoporous carbon nanofiber/nafion	Hg^{2+}	0.005-0.5	0.0003	[35]
Nanoporous gold nanoparticles	Hg^{2+}	0.1-10	0.03	[24]
$VO(OC_3H_7)_3$-PPC/ITO	Hg^{2+}	0.05-2	0.015	This work

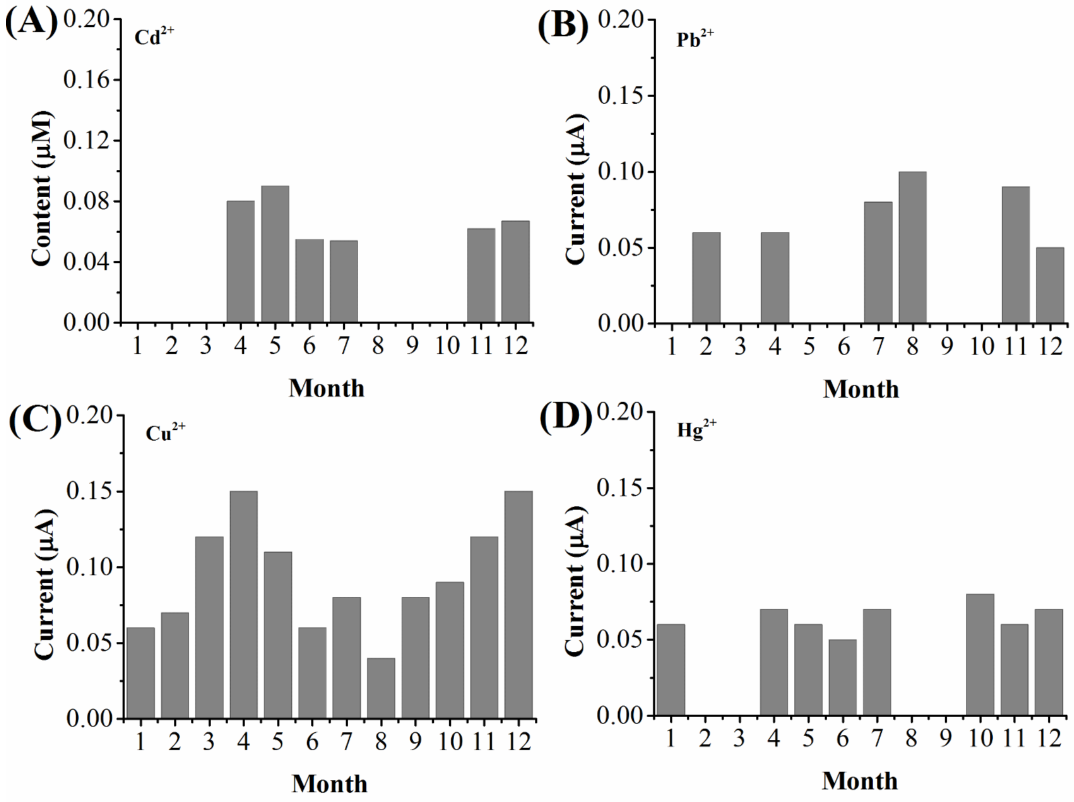

Figure 5. (A) Cd^{2+}, (B) Pb^{2+}, (C) Cu^{2+} and (D) Hg^{2+} value detected from Tai Lake water samples over 2015.

4. CONCLUSIONS

In summary, we proposed a $VO(OC_3H_7)_3$-PPC composite for simple and effective electrode surface modification. The morphology of the $VO(OC_3H_7)_3$-PPC composite showed a rough surface. The $VO(OC_3H_7)_3$-PPC composite modified ITO showed an excellent performance towards detection of heavy metal ions. After the optimizations, the $VO(OC_3H_7)_3$-PPC composite modified ITO exhibited linear detection ranges toward Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} from 0.05 to 2 μM. In addition, the $VO(OC_3H_7)_3$-PPC composite modified ITO has been successfully applied for analyzing the heavy metal ions content analysis in Tai Lake water samples. Over one year detection, a mild heavy metal ions contamination was confirmed for Tai Lake.

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