

Langmuir–Blodgett film of tetraoxocalix[2]arene[2]triazine modified electrode for voltammetric determination of copper ion

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Abstract In the present work, a new voltammetric sensor, Langmuir–Blodgett (LB) film of tetraoxocalix[2]arene[2]triazine (TOCT) modified glassy carbon electrode (LB_{TOCT}-GCE), for trace analysis of copper ion in water samples, was prepared. The morphology of LB_{TOCT}-GCE was characterized by cyclic voltammetric method, electrochemical impedance spectroscopy, and atomic force microscope. The recognizing mechanism of LB_{TOCT}-GCE for copper ion in aqueous solution was discussed. Under the optimum experimental conditions, using square wave stripping voltammetry and accumulation time of 300 s, the peak currents were linear relationship with Cu²⁺ concentrations in the range of 2×10^{-9} to 1×10^{-6} mol L⁻¹, with detection limit of 1×10^{-10} mol L⁻¹. By this method, real samples (lake water, drinking water, and city wastewater) were analyzed with satisfactory results. In addition, the fabricated electrode exhibited a distinct advantage of simple preparation, non-toxicity, good reproducibility, and stability.

Keywords Tetraoxocalix[2]arene[2]triazine · Voltammetric sensor · Langmuir–Blodgett film · Copper

Introduction

The recognition of toxic metal ion is one of the concerned areas of current research due to its wide application in chemical, biological, and environmental assays [1]. In case of copper ion, it is not only an environmental pollutant at high concentrations [2, 3] but also an essential trace

element for many biological processes and systems because it plays a key role as an integral component of many enzymes. Thus, in trace amounts, it is essential for normal metabolic processes [4]. Several analytical techniques for the determination of copper ion are available, such as photometric methods [5], atomic absorption spectroscopy [6], and inductively coupled plasma emission spectrometry [7]. For expensive apparatus or poor sensitivity, they are unsatisfactory for routine measurements of traces of metals in environmental samples. Electrochemical methods such as mercury (film and drop) electrodes are the most favorable techniques for the determination of metal ions because of its low cost, high sensitivity, easy operation, and the ability to carry out speciation analysis [8]. However, because mercury is highly toxic and poses health concerns, usages of mercury electrodes are limited. Chemically modified electrodes using various materials such as conductive polymers [9], self-assembled monolayer [10], and nano-sized materials [11] have been used to determine copper ion devoid of the drawbacks associated with the traditional electrodes. Typical techniques of chemical modifications include chemisorption, covalent binding, and polymer film coating. However, most of these procedures have difficulties in achieving the sensitivity required for the determination of low levels of copper in some real samples. Therefore, researchers have attempted to exert more direct control over the property of an electrode. Langmuir–Blodgett (LB) techniques have been devoted a great deal of keen interest recently, which is a useful method of fabricating a molecular assembly with a controlled thickness at molecular dimensions and a well-defined molecular orientation [12].

Calixarenes have been successfully used for molecular and ionic recognition because of their conformational and structural flexibility. They are a versatile class of macrocy-

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clic compounds and have attracted extensive interest due to their excellent ability of forming host–guest complexes. Calixarenes act as the receptors for ions when they are appropriately functionalized [13, 14]. Oxacalixarene is one of the important derivatives of calixarene synthesized from substitution of methylene group by oxapropylidene. The presence of oxygen atoms (which possess lone pairs and vacant 3D orbitals) in the place of methylene groups imparts many novel features and properties compared with conventional calixarene. The specific metal-binding property should be one of the most noticeable features of these oxacalixarene ligands [15]. But to the best of our knowledge, there are no paper about the study of using oxacalixarene in recognition and determination for transition metal ions.

In this report, an oxacalix[4]arene derivative, tetraoxacalix[2]arene[2]triazine, was firstly used to design LB film modified GCE (LB_{TOCT} -GCE). As a novel voltammetric sensor, the fabricated LB_{TOCT} -GCE was successfully used for recognition trace Cu^{2+} and applied for measuring Cu^{2+} in several natural water samples. A possible reaction mechanism of Cu^{2+} on the modified electrode was discussed.

Experimental

Apparatus

LB films were deposited on GCE surface (3 mm in diameter) by using a JML-04 LB trough (Shanghai Zhongchen Company, China). All electrochemical measurements were performed with a RST3000 electrochemical system (Zhengzhou Shiruisi Instrument Technology Co., Ltd, China) and a CHI650 electrochemical analyzer (CH Instruments Company, USA). A traditional three-electrode system consisting of LB_{TOCT} -GCE working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode was used in the current studied; 5500 Atomic Force Microscopy (Agilent, USA) was employed.

Chemicals and reagents

All reagents were of analytical grade and used without further purification. The water used was double-distilled water. Tetraoxacalix[2]arene[2]triazine (TOCT; Fig. 1) was self-synthesized according to the reported method [16]. Standard Cu^{2+} stock solution (10^{-3} mol L^{-1}) was prepared from $Cu(NO_3)_2$ and diluted to needed concentration before use.

Fabrication of LB_{TOCT} -GCE

Before fabrication, the GCE was polished with 0.1 μm aluminum slurry, rinsed thoroughly with double-distilled

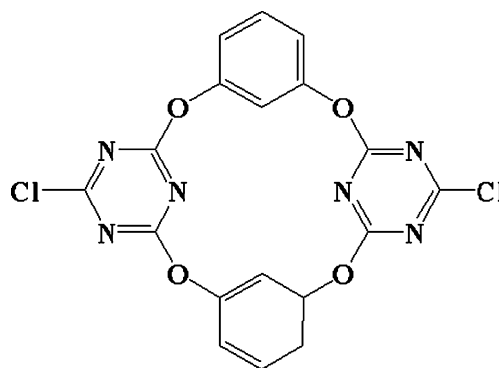


Fig. 1 Chemical structure of TOCT

water, and then sonicated successively in ethanol and double-distilled water, respectively, each for 3 min. A sample of TOCT in chloroform solution (5×10^{-4} mol L^{-1}) was spread on pure water subphase at about 25 °C. A Wilhelmy balance was used as the surface pressure sensor and situated in the middle of the trough. After the evaporation of the solvent, the monolayer was compressed with a rate of 10 mm min^{-1} and then transferred onto the GCE (vertical dipping) with rate of 2.5 mm min^{-1} under a surface pressure of 25 mN m^{-1} . This modified electrode was named LB_{TOCT} -GCE. The multilayer films were assembled by sequential monolayer transfer. For comparability, a direct modified GCE of TOCT was prepared by direct smearing of some TOCT solution on GCE surface, named as TOCT-GCE. After drying for 60 min, a direct modified TOCT-GCE was obtained.

For AFM experimental, LB_{TOCT} was transferred on wafer silicon surface. These wafer silicon substrates were ultrasonic cleaned with ethanol and double-distilled water respectively, each for 10 min. Then the substrates were dipped in Piranha solution (1:3 mixtures of H_2O_2 and H_2SO_4) for 20 min and ultrasonic cleaned in double-distilled water for 5 min again. The surfaces of samples were scanned in air using a 5500 Atomic Force Microscopy (Agilent, USA) by contact mode at a scan of about 0.500 Hz and 2×2 μm of size.

Analytical procedure

Analytical determination of Cu^{2+} was performed by square wave stripping voltammetry. The accumulation step was carried out under potential of -0.7 V for a certain period of time concurrently stirring solution. After resting solution for 30 s, the square wave voltammograms were recorded from -0.4 to $+0.5$ V. The square wave conditions of instrumental parameters were selected, and the optimal parameters were square wave amplitude of 25 mV, square wave frequency of 25 Hz, and sampling width of 5 ms. After each determination, the LB_{TOCT} -GCE was held at

0.6 V for at least 1 min and then dipped in a 0.02-mol L^{-1} EDTA solution for 5 min to renovate it. All measurements were carried out at room temperature ($25\pm 1\text{ }^{\circ}\text{C}$).

Results and discussion

$\pi \sim A$ isotherms and fabrication of $\text{LB}_{\text{TOCT}}\text{-GCE}$

The $\pi \sim A$ isotherm of TOCT on pure water subphase surface was shown in Fig. 2 (curve a). It exhibited a typical characteristic of condensed monolayer where a vertical condensed phase was observed. The limiting area and collapsing pressure of TOCT is 0.57 nm^2 per molecule and 34 mN m^{-1} , respectively. When Cu^{2+} ($1.0\times 10^{-4}\text{ mol L}^{-1}$) was introduced in the subphase, the $\pi \sim A$ isotherm changed prominently (Fig. 2, curve b). The values of collapse pressure decreased to 20 mN m^{-1} and the molecular area decreased to 0.37 nm^2 . These data indicated that some interaction occurred between TOCT and Cu^{2+} ions at the air–water interface. Moreover, the decrease of molecular area indicated that the conformation of TOCT changed from parallel to perpendicular orientation, when TOCT was coordinated with Cu^{2+} on the subphase surface [17]. This result implies that the $\text{LB}_{\text{TOCT}}\text{-GCE}$ may be a good voltammetric sensor for recognizing, separating, and detecting Cu^{2+} .

Cyclic voltammetry characterization and electrochemical impedance spectroscopy of the $\text{LB}_{\text{TOCT}}\text{-GCE}$

The cyclic voltammetric measurements were accomplished in 0.1 mol L^{-1} KCl containing $1.0\times 10^{-3}\text{ mol L}^{-1}$ $\text{Fe}(\text{CN})_6^{3-}$ solution at a scanning rate of 50 mV s^{-1} . As shown in Fig. 3, the $\text{Fe}(\text{CN})_6^{3-}$ showed a typical reversible reaction

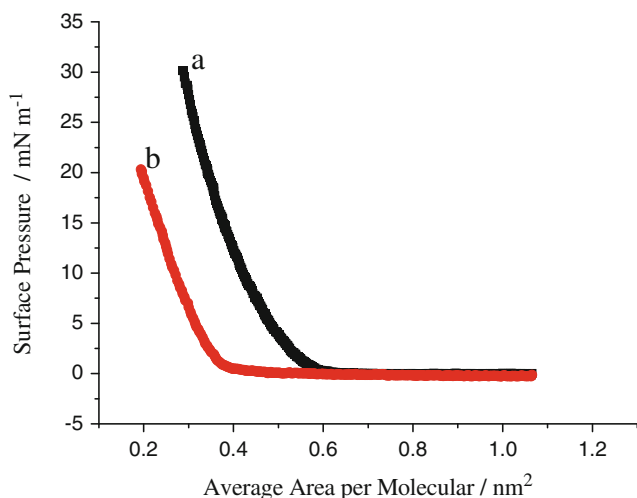


Fig. 2 $\pi \sim A$ isotherms of TOCT. Subphase conditions: pure water (a); $1.0\times 10^{-4}\text{ mol L}^{-1}$ Cu^{2+} (b)

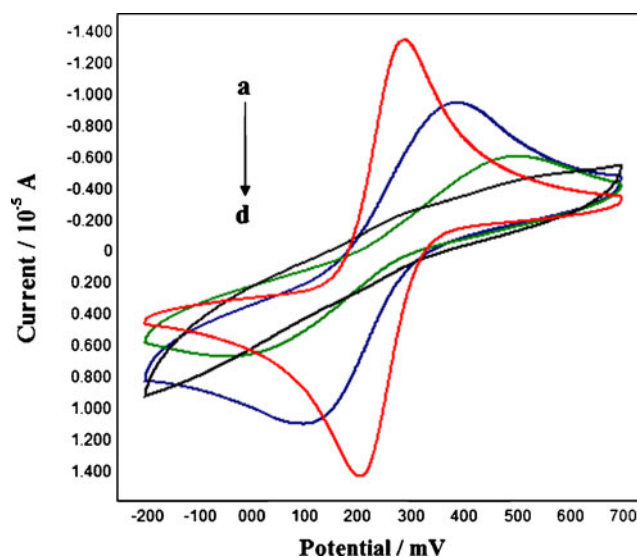


Fig. 3 Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ ($1\times 10^{-3}\text{ mol L}^{-1}$) with different electrodes. a Bare GCE; b one layer $\text{LB}_{\text{TOCT}}\text{-GCE}$; c two layers $\text{LB}_{\text{TOCT}}\text{-GCE}$; d three layers $\text{LB}_{\text{TOCT}}\text{-GCE}$. Scan rate 50 mV s^{-1}

at the bare GC electrode (Fig. 3, curve a). And the reversibility was decreased gradually by the layer number of LB_{TOCT} increased. (Fig. 3, curves b, c, and d for 1, 2, and 3 layers of LB_{TOCT} on GCE surface). Obviously, there was no redox peak apparent with three layers of LB_{TOCT} modified on GCE. It proved that LB_{TOCT} was act as a barrier for charge transfer and hindered the diffusion of ferricyanide toward to the electrode surface.

Electrochemical impedance spectroscopy (EIS) is also a powerful technique to study the interface properties of electrodes. The semicircle diameter at higher frequencies in the Nyquist plot of EIS equals the R_{ct} , controlling the charge transfer rate of the redox probe at electrode surface. Therefore, R_{ct} can be used to denote the impedance of electrode surface. In current study, the EIS was performed in 0.1 mol L^{-1} KCl containing $1.0\times 10^{-3}\text{ mol L}^{-1}$ $\text{Fe}(\text{CN})_6^{3-/4-}$ solution, with equilibrium potential of 0.246 V (vs. Ag/AgCl), perturbation amplitude of 5 mV , and frequency range from 100 KHz to 0.05 Hz . As shown in Fig 4, the Nyquist plot curves a, b, c, and d were recorded with bare GCE, one layer $\text{LB}_{\text{TOCT}}\text{-GCE}$, two layers $\text{LB}_{\text{TOCT}}\text{-GCE}$, and three layers $\text{LB}_{\text{TOCT}}\text{-GCE}$, respectively. The curve a was an almost straight line while b, c, and d were consisted of a semicircle portion and a linear part. After fitting suitable circuit and calculation, R_{ct} obtained were about 4.1 , 9.8 and $13.2\text{ k}\Omega$ for one layer, two layers, and three layers LB_{TOCT} film, respectively. These data explained the phenomenon of cyclic voltammetry and confirmed that the sensor was fabricated just as design.

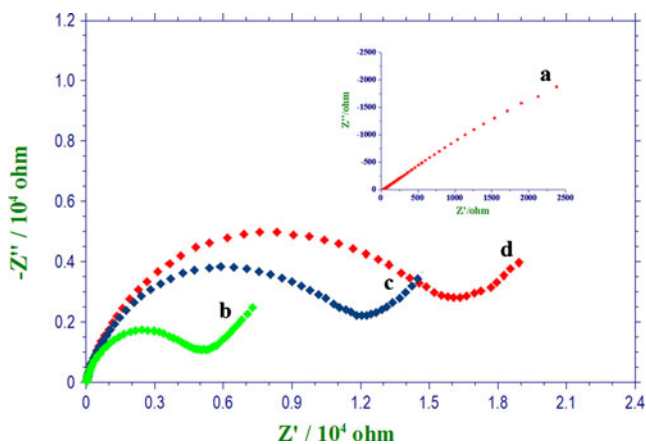


Fig. 4 The Nyquist plots of EIS with different electrodes **a** bare GCE, **b** one layer $\text{LB}_{\text{TOCT}}\text{-GCE}$, **c** two layers $\text{LB}_{\text{TOCT}}\text{-GCE}$, and **d** three layers $\text{LB}_{\text{TOCT}}\text{-GCE}$. Solution $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Fe}(\text{CN})_6^{4-/3-} + 0.1 \text{ mol L}^{-1} \text{ KCl}$. Frequency range $10^5 \sim 0.05 \text{ Hz}$; perturbation amplitude 5 mV

The morphology of LB_{TOCT}

Morphology of LB_{TOCT} film on GCE surface was also examined using atomic force microscope (AFM) imaging. As shown in Fig. 5, the AFM image of bare wafer silicon surface (a) was an even surface and no impurity on. The AFM image of one layer LB_{TOCT} (b) showed that the TOCT molecules were nearly well proportioned on the wafer silicon surface, but some flaws were existed. The second layer of LB_{TOCT} (c) retrieved these flaws and made the film more compact. These results can be used to explain the experimental phenomenon expressed in Figs. 3 and 4.

$\text{LB}_{\text{TOCT}}\text{-GCE}$ recognizing of Cu^{2+} and analytical application

The ability of $\text{LB}_{\text{TOCT}}\text{-GCE}$ for selective recognition of Cu^{2+} was studied using square wave stripping voltammetry

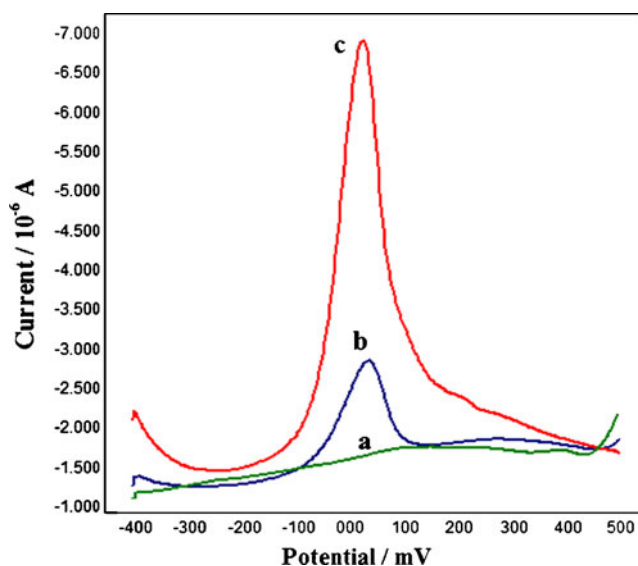


Fig. 6 Square wave stripping voltammograms of $4 \times 10^{-7} \text{ mol L}^{-1} \text{ Cu}^{2+}$ with different electrodes. **a** Bare electrode; **b** TOCT-GCE; **c** two layers $\text{LB}_{\text{TOCT}}\text{-GCE}$. Solution: HAC-NaAc (0.2 mol L^{-1} , $\text{pH}=3.6$); accumulation time 300 s ; accumulation potential -0.7 V

(SWSV) in the potential range of -0.4 to 0.5 V . Figure 6 shows the SWSV curves of Cu^{2+} ($4 \times 10^{-7} \text{ mol L}^{-1}$) in HAC-NaAc (0.2 mol L^{-1} , $\text{pH}=3.6$) solutions using different electrodes. The curve a was obtained using a GCE and a small bulging was observed at about 0.05 V . A sharp stripping peak was obtained using a TOCT-GCE (curve b). When a $\text{LB}_{\text{TOCT}}\text{-GCE}$ (two layers) was used, the peak current was enhanced greatly (curve c) under same experimental conditions. For reasons may be described that the surface of $\text{LB}_{\text{TOCT}}\text{-GCE}$ was more homogeneous and stable, which was favorable for selective recognition and accumulation of Cu^{2+} on it.

For testifying the interactive model between Cu^{2+} and TOCT, a $\text{LB}_{\text{TOCT}}\text{-GCE}$ was immersed in a solution

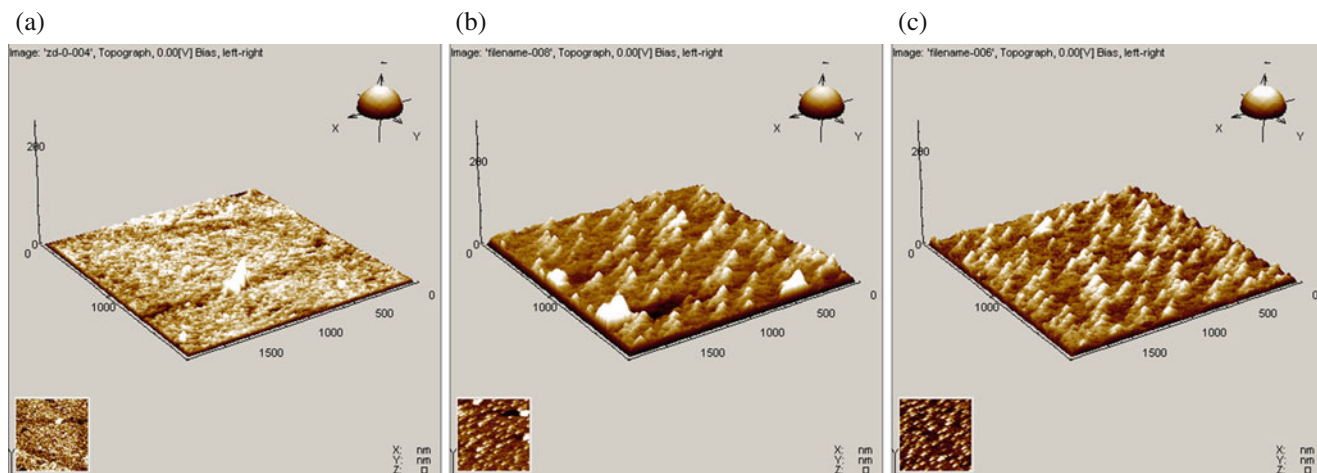


Fig. 5 AFM 3D topography images. **a** Bare wafer silicon surface; **b** one layer LB_{TOCT} ; **c** two layers LB_{TOCT} . Scan size $2 \times 2 \mu\text{m}$

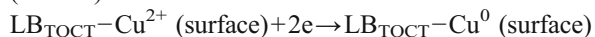
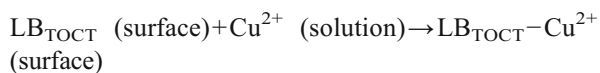
Table 1 Comparison of the current sensor with that of some other copper ion sensors

Different copper sensors	Linear range (mol L ⁻¹)	Detection limit (mol L ⁻¹)	Accumulation potential (V)	Ref.
Aminopropyl silica gel/carbon paste electrode	5.0 × 10 ⁻⁸ ~2.0 × 10 ⁻⁷	3 × 10 ⁻⁹	\	[18]
Crosslinked chitosan functionalized carbon nanotubes paste electrode	7.9 × 10 ⁻⁸ ~1.6 × 10 ⁻⁵	1.0 × 10 ⁻⁸	-0.3	[11]
N-Phenylcinnamohydroxamic acid/carbon paste electrode	1.0 × 10 ⁻⁹ ~1.0 × 10 ⁻⁸	5.0 × 10 ⁻¹⁰	\	[19]
Calix[4]arene/carbon paste electrode	5.0 × 10 ⁻⁸ ~1.6 × 10 ⁻⁶	1.7 × 10 ⁻⁸	\	[20]
Zincon/carbon paste electrode	3.1 × 10 ⁻⁸ ~3.4 × 10 ⁻⁶	1.7 × 10 ⁻⁸	-0.6	[21]
Bare glassy carbon electrode	7.8 × 10 ⁻⁷ ~7.8 × 10 ⁻⁶	6.2 × 10 ⁻⁷	\	[22]
LB _{TOCT} -GCE	2.0 × 10 ⁻⁹ ~1.0 × 10 ⁻⁶	1.0 × 10 ⁻¹⁰	-0.7	This work

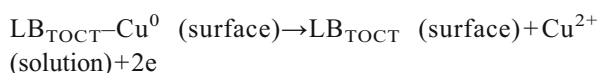
containing Cu²⁺ (1 × 10⁻⁶ mol L⁻¹) for a moment under open-circuit with stirring and then transferred it in HAC-NaAc (0.2 mol L⁻¹, pH=3.6) solution for cyclic scan. A pair of redox peaks of Cu²⁺ was obtained and the oxidizing peak (*i*_{pa}) was more sensitive than that of reducing peak (*i*_{pc}), while no obvious peaks appeared using a bare GCE (figure not shown). This indicated that TOCT played an important role in the accumulation process of Cu²⁺ on the electrode surface and significantly increased the sensitivity of determining Cu²⁺. These data testified that the interaction between Cu²⁺ and TOCT was complexation. As shown in Fig. 1, there are several oxygen atoms and nitrogen atoms existing in the structure of TOCT, which will provide hapto for Cu²⁺. On the other hand, the cavity and multi-dimensional structure of TOCT greatly increase the electrode surface area, which could make Cu²⁺ easier to be accumulated.

Because the *i*_{pa} was more sensitive than the *i*_{pc}, *i*_{pa} was considered as indicating signal in following study. For doing so, a reductive potential was applied on electrodes during the accumulation step to form the following electrode reaction process in determination of Cu²⁺:

Accumulation step (reductive simultaneously):



Stripping step:



Optimum operation conditions of determination

The influences of supporting electrolytes on stripping peak currents were investigated in KCl, NH₃-NH₄Cl, HNO₃, HAC-NaAc, phosphate buffer solution, and B-R buffer solution, respectively. The results showed that the best peak shape and largest stripping peak current were obtained in HAC-NaAc solution. For solution acidity investigated, pH 3.6 was the best choice. Therefore, HAC-NaAc (0.2 mol L⁻¹, pH=3.6) solution was employed as blank solution in following experiments.

Accumulation (reduction) potential (*E*_{acc}) and time (*t*_{acc}) are two important parameters in stripping techniques and have significant effect on the detection sensitivity. The effect of *E*_{acc} was investigated between potential of -0.3 and -0.9 V. The peak current of Cu²⁺ oxidation showed a maximum value at -0.7 V. Therefore, *E*_{acc} of -0.7 V was chosen in all subsequent work. In a solution containing 1 × 10⁻⁸ mol L⁻¹ Cu²⁺, the peak currents were enlarged with increasing *t*_{acc} up to 900 s. For further study, *t*_{acc} of 300 s was chosen to obtain a longer linear range. However, for the determination of a lower concentration of Cu²⁺, a longer *t*_{acc} is recommended.

The relationship between peak currents and the modified layers of LB_{TOCT} was also investigated, and the maximum stripping peak currents was obtained using two layers of LB_{TOCT}-GCE (data not shown). For reasons might be that there were some defects existing in one layer LB_{TOCT}, which would cause the lower accumulative efficiency for Cu²⁺ ion. The second layer of LB_{TOCT} remedied the defects and enhanced the accumulative efficiency. However, the

Table 2 Sample determination and recovery

Sample	Original found (1.0 × 10 ⁻⁷ mol L ⁻¹)	Added (1.0 × 10 ⁻⁷ mol L ⁻¹)	Total found (1.0 × 10 ⁻⁷ mol L ⁻¹)	SD (%)	Recovery (%)
Drinking water	ND	2.00	2.02	1.42	101.1
Lake water	ND	2.00	2.04	1.89	101.9
City wastewater	2.99	5.00	7.90	5.66	98.9

ND not detected

impedance may play an important action and block the electron transfer between GCE and TOCT when LB films are three layers and more. Therefore, a double layer film was chosen in all following experiments.

The relationship between peak currents and Cu^{2+} concentrations

A series of determination were performed with different concentrations of Cu^{2+} under the optimized working conditions described above. The results showed that the peak currents were linear relationship with Cu^{2+} concentrations in the range of 2×10^{-9} to 1×10^{-6} mol L^{-1} under $t_{\text{acc}}=300$ s, which can be described by the following linear regression equation, with a correlation coefficient R of 0.998:

$$i_{\text{pa}}(\mu\text{A}) = 0.119 + 1.131 \times 10^7 C_{\text{Cu}} \quad (t_{\text{acc}} = 300 \text{ s})$$

The detection limit (defined as a concentration generating a signal that is three times greater than the noise) was 1×10^{-10} mol L^{-1} . For explaining the advantage of current approach, a comparison with other Cu^{2+} sensors was investigated and listed in Table 1. The lower detection limit and broader linear range suggested that the $\text{LB}_{\text{TOCT}}\text{-GCE}$ was a more sensitive sensor for copper ion.

The sensitive response of the $\text{LB}_{\text{TOCT}}\text{-GCE}$ is also highly reproducible. A series of ten successive measurements for Cu^{2+} (10^{-7} mol L^{-1}) solution was performed, and a value of 4.45% for the relative standard deviation was calculated. The stability of the electrode was examined by repetitive scanning in a 4×10^{-7} -mol L^{-1} Cu^{2+} solution. The anodic peak currents recorded on day 1 was 4.64 μA and 30 days was 4.34 μA , respectively, which indicated that $\text{LB}_{\text{TOCT}}\text{-GCE}$ had good stability.

Interferences

Interference effect of coexisting metal ions was investigated by adding various excess amounts of other species to a 2×10^{-7} -mol L^{-1} Cu^{2+} solution. The results showed that 10^3 -fold of alkali metal ions, earth metal ions, and equivalent of Fe^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Tl^+ , and Co^{2+} did not significantly influence the stripping peak currents of Cu^{2+} . However, equivalent of Pb^{2+} and Ag^+ decreased the response currents of Cu^{2+} because of the competitive complexation with TOCT. On the other hand, Hg^{2+} interfered the determination by increasing the Cu^{2+} signal. This could be explained as that the Hg^{2+} ions were reduced simultaneously to form a thin mercury film, which enhanced the accumulation efficiency of Cu^{2+} .

Analysis of real samples

To investigate the applicability of the proposed method described above, drinking water, lake water, and city

wastewater samples were employed for determining Cu^{2+} by standard addition technique. The standard Cu^{2+} solutions were added in sample solution before analysis, and the recovery was detected for proving the detection accuracy. The results were listed in Table 2.

Conclusions

A self-synthesized oxacalix[4]arene derivative, TOCT, was firstly employed as modifying material for fabricating LB film modified electrode, $\text{LB}_{\text{TOCT}}\text{-GCE}$. As a new kind of voltammetric sensor, the $\text{LB}_{\text{TOCT}}\text{-GCE}$ was successfully used for recognizing and determining Cu^{2+} using SWSV. The surface characterizations of the sensor were investigated using cyclic voltammetry, electrochemical impedance spectroscopy, and atomic force microscope. The recognizing mechanism of $\text{LB}_{\text{TOCT}}\text{-GCE}$ for copper ion in aqueous solution was discussed. Under the optimum experimental conditions, wide detect rang and low detect limit for copper ion were obtained. The proposed method was also applied to determine Cu^{2+} in water samples. Moreover, the $\text{LB}_{\text{TOCT}}\text{-GCE}$ exhibited a well-defined response to Cu^{2+} with good sensitivity, selectivity, reproducibility, and long stability.

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