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Published on: 21 Apr 2018 - Mikrochimica Acta (Springer Vienna)

Topics: Glassy carbon, Copper, Cyclic voltammetry, Polarography and Differential pulse voltammetry

Microchimica Acta
https://doi.org/10.1007/s00604-018-2799-1

ORIGINAL PAPER

Voltammetric determination of copper in seawater at a glassy carbon disk electrode modified with Au@MnO$_2$ core-shell microspheres

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Received: 29 January 2018 / Accepted: 12 April 2018

Abstract

Anodic stripping voltammetric determination of copper ions was accomplished at a glassy carbon disk electrode modified with core-shell microspheres of the gold@manganese dioxide (Au@MnO$_2$) type. These were synthesized via electrochemical deposition. The gold nanoparticles (AuNPs) were electrochemically deposited and employed as an active support material for the growth of MnO$_2$ to yield Au@MnO$_2$ core-shell particles with unique and regular spherical morphology. The microspheres have a diameter of 200–250 nm and scrolled edges like a cactus. Due to the absorption capacity of MnO$_2$ and the electrocatalytic ability of the AuNPs, an excellent anodic signal is obtained for copper ions. Response is linear in the 20 nM to 1 μM copper ion concentration range, with a 4.9 ± 0.2 nM ($n = 3$) detection limit under optimized conditions. The electrode is stable and excellently reproducible. It was successfully applied to the analysis of copper ions in spiked seawater samples.

Keywords Core-shell microspheres · Manganese dioxide · Cyclic voltammetry · Differential pulse voltammetry · Electrochemical deposition · Adsorption · Scanning electron microscopy

Introduction

Copper, an indispensable trace element in human beings, plays a significant role in normal physiological conditions since it is not only an essential component of several enzymes but also involved in the transport of Fe [1, 2]. Copper, a great hazard of metal pollutants, has a severe toxicity as a result of its extensive use and complex distribution in the environment. Especially in the ocean environment, copper ions directly exposed to marine organisms can cause bio-accumulation and endanger people's health eventually. As we know, the aquo-complexed "free" cupric ion (Cu^{2+}) rather than the inorganic or organic complexes [3] cause greatly harm to the environment. Thus, it is important to have a reliable and sensitive analytical method for accurately detecting copper ions in the ocean environment. Many methods have been investigated to detect copper ions, such as UV–vis spectrometer or visual (bare-eye) determation [4], flame atomic absorption spectrometry (FAAS) [5], inductively coupled plasma spectroscopy (ICP-MS) [6, 7], and X-ray fluorescence spectrophotometry (XRFS) [8]. However, these methods are relatively time-consuming, fiddly and costly. Comparatively, the properties of short analysis time, low power consumption, and inexpensive equipment without any prior separation, inherent miniaturization and portability [9–11] make stripping voltammetry prominent in the field of electrochemical analytical chemistry.

Gold possesses unique properties, such as fast electron transfer rate, excellent bio-compatibility and high catalytic

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00604-018-2799-1) contains supplementary material, which is available to authorized users.

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activity [12–14]. In addition, some researchers had found that the performance of the electrode could be improved by the deposition of metal particles. For example, Ashis Das et al. [15] used the electrodeposition of tin nanorods on glassy carbon electrodes and selectively detected progesterone using voltammetric method. In Wang groups [16], a well-defined three-dimensional gold hierarchical dendrites was prepared by one-step electrodeposition on a glassy carbon electrode and had amplification detection of Pb^{2+} with high sensitivity. Lu et al. [13] used a screen-printed carbon electrode (SPCE) co-modified with an in-situ plated bismuth (Bi) particles for determination of the Zn(II), Pb(II) and Cu(II) ions. As we know, the adsorption can improve the selectivity and sensitivity of the modified electrode. For many years, metal oxide had attracted wide attention in the aspect of detection and removal of heavy metals [16–18], where manganese dioxide was particularly prominent in terms of excellent adsorption ability [18–20]. Moreover, manganese dioxide is considered to be an economical and easy accessible adsorbent in the environment. Some researchers were synthesized several times for Au-MnO_2 nanomaterials before. Veeramani et al. [21] did synthesize of an Au-MnO_2 nanocomposite dispersed on an electrophoretically prepared graphene surface. Qiu groups [22] synthetized Au@MnO_2 core-shell nanomesh structure on a flexible polymeric substrate through nanosphere lithography combined with electro-deposition processing.

As reported, various modified electrodes had been employed to measure copper ions, such as rGO-AuNPs modified GCE [23], AuNP-SPCE electrode [24], NH_2-rGO/β-CD electrode [25], PPyNWs^g electrode [12], Bi-AuNPs/SPE electrode [13], etc. The above practical electroanalysis were performed in tap waters, lake waters or waster waters. When the real seawater samples were concerned, the salinity is a big problem. Although determination of copper ions in seawater was reported previously in our group [14], the direct analysis of free copper ions in seawater was still a challenge. Thus, the effect of different salinity of seawater on the application of our electrode was also be tested in this paper.

In this study, more effectively operations to synthesize Au@MnO_2 core-shell structure, just through electrodeposition processing, were taken. Au nanoparticles were employed as active support materials and which can speed up the rate of MnO_2 crystal production. Eventually, a novel type core-shell microspheres Au@MnO_2 was formed by electrochemical deposition. Core-shell microspheres Au@MnO_2 composites were used for copper ions determination in consideration of the electrocatalytic properties of gold and the excellent absorption capacity of MnO_2. The Au@MnO_2 modified electrode showed remarkable sensitivity and selectivity in voltammetric measurement of copper ions with a lower detection limit. In addition, this novel core-shell microsphere Au@MnO_2 modified electrode also applied for the determination of copper ions in seawater.

Experimental

Chemicals and solutions

Standard stock solution of copper was purchased from Acros Organics(USA. http://www.acros.com/). Chlorauric acid ($HAuCl_4$) was supplied by Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/). Manganese(II) acetate tetrahydrate ($MnAc_2·4H_2O$) was purchased from Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/). All other chemicals were analytical reagents that have not been further purified. Standard artificial seawater (salinity of 29.998 and 4.998) were purchased from Beijing Putian Tongchuang Biological Technology Co. (Beijing, China. Ltd. http://www.gbw114.com/). Deionized water (18.2 MΩ cm specific resistance), obtained from Pall Cascada laboratory water system (USA. http://www.pall.com/main/home.page), was used throughout the experience.

Apparatus

The morphology of Au, MnO_2, Au@MnO_2 modified electrodes were recorded on scanning electron microscopy and Back Scattered Electron (BSE) Imaging (SEM Hitachi S-4800 microscope, Japan. http://www.hitachi.com/), energy dispersive X-ray spectroscopy (EDX HORIBAEX-350 Japan. http://www.horiba.com/), X-ray diffraction spectroscopy (XRD ADVANCE-D8 Germany. https://www.bruker.com/cn.html) and X-ray photoelectron spectroscopy (XPS Escalab-250 USA. https://www.thermofisher.com). The comparative testing were used ICP-MS (ELAN DRC, Perkin Elmer Instruments, USA. http://www.perkinelmer.com/). All electrochemical experiments were performed with an Electrochemical Work Station (CHI 660E, CH Instruments, Inc. Shanghai, China. http://chi.instrument.com.cn/) carried out in a conventional three-electrode cell. A modified glassy carbon (GC) disk (3 mm in diameter, Chenhua Instruments, Shanghai, China. http://chi.instrument.com.cn/) was used as the working electrode, with Ag/AgCl and platinum foil serving as the reference and counter electrodes, respectively.

Preparation of Au@MnO_2 microsphere modified electrode

Prior to modification, the GC electrode was thoroughly polished with 0.3 μm and 0.05 μm aqueous slurries of alumina powder, and then sonicated for 3 min in ethanol and water respectively. Core-shell Au@MnO_2 microspheres were synthesized via two-step electrochemical deposition. Firstly, the GC electrode was immersed in 1.0 mM chlorauric acid containing 0.2 M sodium sulfate solution to electrochemically electrodeposit Au nanoparticles with constant potential at −0.2 V for

15 s. Then the gold modified electrode was rinsed with ultrapure water thoroughly. Then manganese oxide were deposited on Au modified electrode by cycling the deposition potential (scan rate of 0.2 $V{\cdot}s^{-1}$). The electrode was cycling from 0.0 V to 0.9 V in 1 mM manganese(II) acetate tetrahydrate and 1 mM sodium sulfate for 8 cycles. Then the obtained GC/Au@MnO_2 was washed carefully with deionized water and then dried at room temperature. Scheme 1 illustrated the stepwise assembly process of the Au@MnO_2 modified electrode. For comparison, Au or MnO_2 coated GCE was prepared with the same process, respectively.

Electrochemical analysis procedure

Unless stated otherwise, the experiments were carried out in the 0.1 M acetate buffer (pH 5.0). Differential pulse voltammetry (DPV) scans over the potential range from 0 V to 0.6 V were recorded by using the following parameters: amplitude of 0.05 V, pulse width of 0.2 s, pulse period of 0.5 s, and an equilibrium time of 2 s. Prior to the next cycle, the electrode was cleaned for 30 s at 0.6 V with stirring.

Preparation of real samples

Seawater sample was collected from the local (Yellow Sea, Shandong Province, China). The sample treatment was prepared as follows: all the seawater samples were filtered (0.45 μm membrane filters) in acid-cleaned polyethylene bottles and kept at 4 °C until determination. The sample seawater was acidified with a certain amount of HNO_3 and H_2O_2 was added to adjust the pH of water samples less than 2.0, finally digested samples in quartz tubes using a 500 W UV lamp (Metrohm MVA-UV 705, Switzerland). Standard artificial seawater did not need any treatment, and was directly applied to the detection of copper ions.

Results and discussion

Choice of materials

Various materials had been used to preparation of modified electrodes for improvement of the selectivity and sensitivity in copper determination, such as PPy [12], PANI [26], rGO [23], GQDs [27], AgNPs [28], ZnO [29], SiO_2 [30], etc. In contrast, AuNPs had unique excellent catalytic performance better than AgNPs, which had been widely studied for practical applications in many fields such as catalysis, nanodevices, and electroanalysis [12, 13]. Manganese dioxide was particularly prominent in terms of excellent adsorption ability [18–20]. It was also considered as an economical and accessible adsorbent in the environment instead of PPy and PANI. In particular, the excellent intrinsic conductivity of AuNPs could speed up the growth rate of MnO_2, resulting in the form of core-shell microspheres Au@MnO_2.

Morphology of Au@MnO_2 microsphere modified electrode

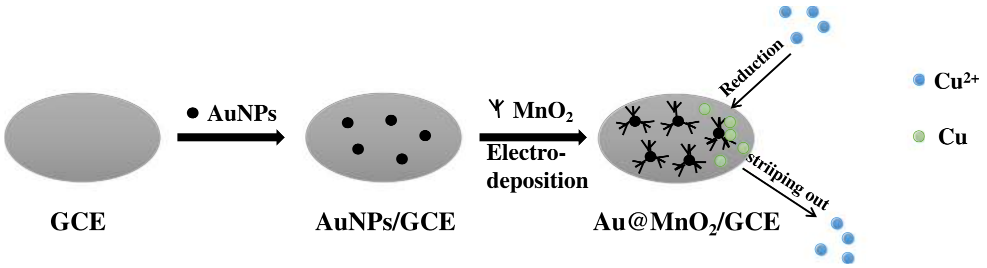
The SEM micrographs of Au nanoparticles, MnO_2 and Au@MnO_2 were shown in Fig. 1. BSE micrograph, EDX, XRD and XPS images were also used to characterize the composites. The respective data and explanations were given in the Electronic Supporting Material (ESM). In Fig. 1a, the spherical Au is compactly coated on the GCE surface with size distribution ranging from 50 nm to 100 nm. As shown in Fig. 1b, the morphology of flaky MnO_2 are rough, non-uniform and crowded together with scrolled edges form. Figure 1c, d show the surface morphology of the Au@MnO_2 modified electrode at different magnifications. The Au@MnO_2 surface morphology is spherical with largely scrolled edges form. The shape of Au@MnO_2 was uniform and the size distribution ranged from 200 nm to 250 nm. The core-shell structure morphology formation mechanism is described in detail in the following part. The Au@MnO_2 composite possesses a core-shell structure, in which Au nanoparticles are employed as active support material and the fate of the Mn^{3+} intermediate is a key feature of this electrodeposition mechanism. In Eq. 1, the MnO_2 are formed from Mn^{2+} via electrochemical oxidation, and this process can be explained as a three-step model (Eq. 2–4) suggested by Paul and Cartwright [31]:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \tag{1}$$

$$Mn^{2+} \rightarrow Mn^{3+} + e^- \tag{2}$$

$$Mn^{3+} + 2H_2O \rightarrow MnOOH + 3H^+ \tag{3}$$

$$MnOOH \rightarrow MnO_2 + H^+ + e^- \tag{4}$$



Scheme 1 The schematic illustration of the stepwise assembly procedure

The formation of MnO_2 depends on the substrate [32]. Gold nanoparticles were used in here. Since Au nanoparticles might promote the rapid growth of Mn^{3+}, the morphology of MnO_2 would be changed. Growth began as the thin film along gold grain boundaries, soluble Mn^{3+} are produced initially, followed by MnOOH. The initial morphology is determined by the stability of soluble Mn^{3+} species. The growth of MnO_2 occurs primarily through the precipitation of a 2D film of MnOOH, which rapidly covers the surface of gold nanoparticles in all directions. Eventually, the entire surface of the sample is covered with core-shell Au@MnO_2 microspheres.

Electrochemical behavior of Au@MnO_2 microsphere modified electrode

The electrochemical behavior of the GC/Au@MnO_2 electrode at different buffers are investigated. As shown in Fig. S4, the redox peaks are significantly differentiated with the various buffer. The electrochemical oxidation and reduction of Au@MnO_2 disappeared when the pH value of the acetate buffer is larger than 5.0. In addition, taking into account the stable existence of copper ions, 0.1 M acetate buffer of pH 5.0 is chosen for the experiment.

The cycle voltammetry behavior of various electrodes were studied in 0.1 M acetate buffer (pH 5.0). The potential range was from −0.2 V to 1.3 V. As is shown in Fig. 2, the bare GCE (curve a) has no obvious redox peaks in the CV within the scan range. Besides, CV of the Au modified electrode (curve b) showed two obvious redox peaks in the potential ranges of 0.6–0.7 V, 1.0–1.1 V. In curve c, the CV of the MnO_2 modified electrode also shows two apparent redox peaks in the potential ranges of 0.5–0.6 V, 0.75–0.85 V. Moreover, the current of Au@MnO_2 composite modified electrode (curve d) has redox peaks of both the Au modified electrode and the MnO_2 modified electrode. These results showed that MnO_2 and Au is effectively stable on the electrode surface, and these electrochemical results further demonstrated that it is quite effective that the core-shell microspheres of Au@MnO_2 combined to the electrode surface.

Electrochemical impedance spectrum (EIS) was used to verify the capability of electron transfer of copper ions at different electrodes. The semicircle diameter of EIS, equal to the electron transfer resistance (R_{et}), was depended on the dielectric features at the electrode and electrolyte interface. As shown in Fig. 3, the Nyquist diagrams of bare GC (a), GC/MnO_2 (b), GC/Au (c) and GC/Au@MnO_2 (d) were measured in 5 mM $Fe(CN)_6^{3-/4-}$ solution containing 0.5 M KCl. A semicircle of about 37 Ω in diameter for bare (curve a), after modified by MnO_2 (curve b), the semicircle diameter was remarkably increased to about 110 Ω in diameter. It was clearly observed that R_{et} of MnO_2 modified electrode (curve b) was significantly larger than that of bare GC (curve a). A semicircle for Au@MnO_2 (curve d) modified electrode was about 20 Ω in diameter, while the semicircle for Au (curve c) modified electrode was about 13 Ω in diameter. The R_{et} of Au@MnO_2 modified electrode was significantly reduced compared with R_{et} of MnO_2 modified electrode. The phenomenon was due to the excellent electronic transfer ability of

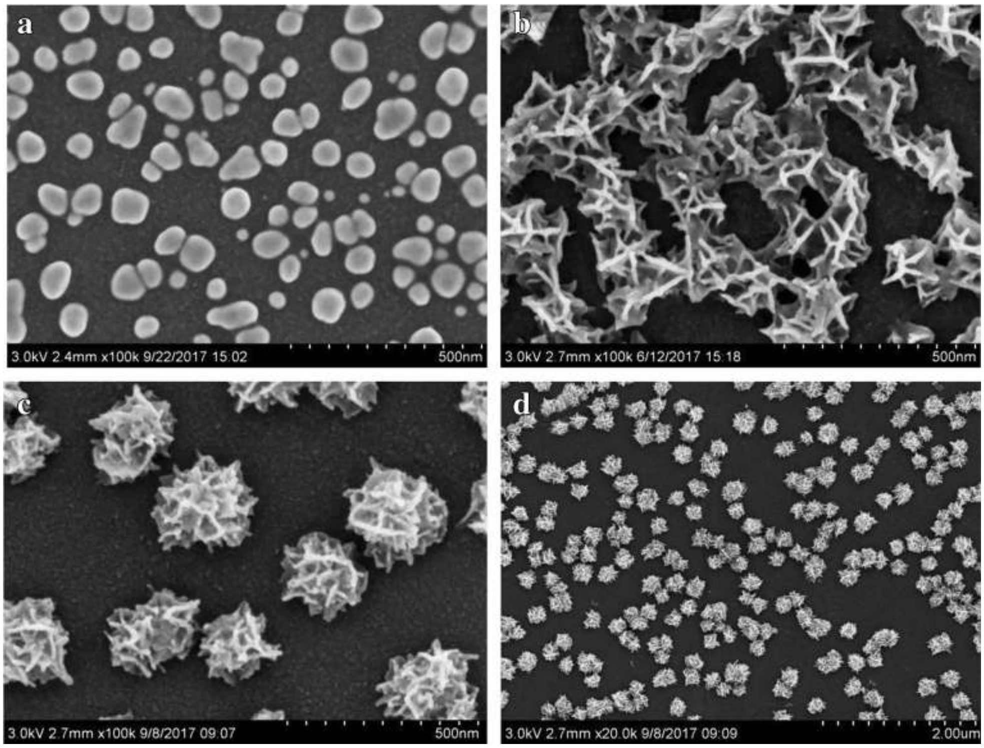
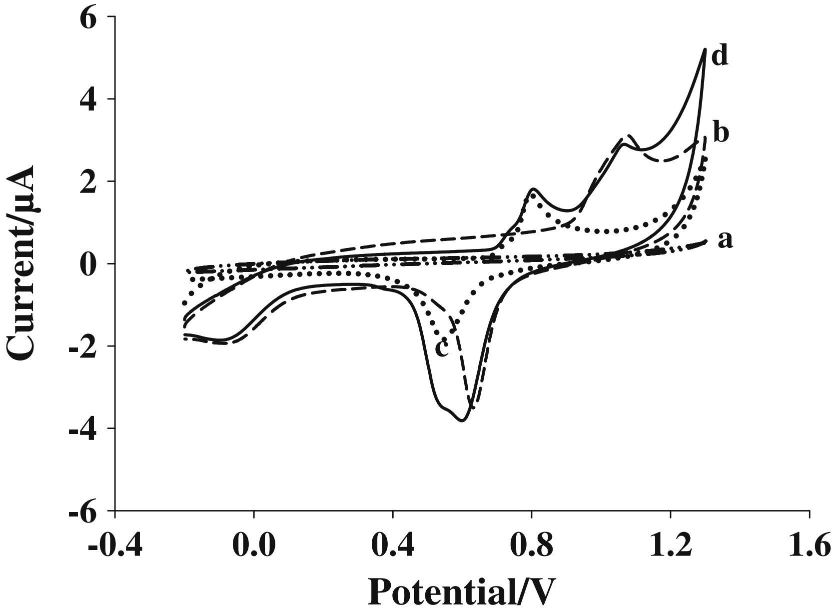


Fig. 1 SEM image of the GC/Au (**a**), GC/MnO_2 (**b**) and GC/Au@MnO_2 (**c** and **d**)

Fig. 2 CVs of bare GCE (**a**), GC/Au (**b**), GC/MnO_2 (**c**) and GC/Au@MnO_2 (**d**) in 0.1 M acetate buffer (pH 5.0) in the potential range of 0.2 to 1.3 V. Scan rate: 100 mV·s^{-1}



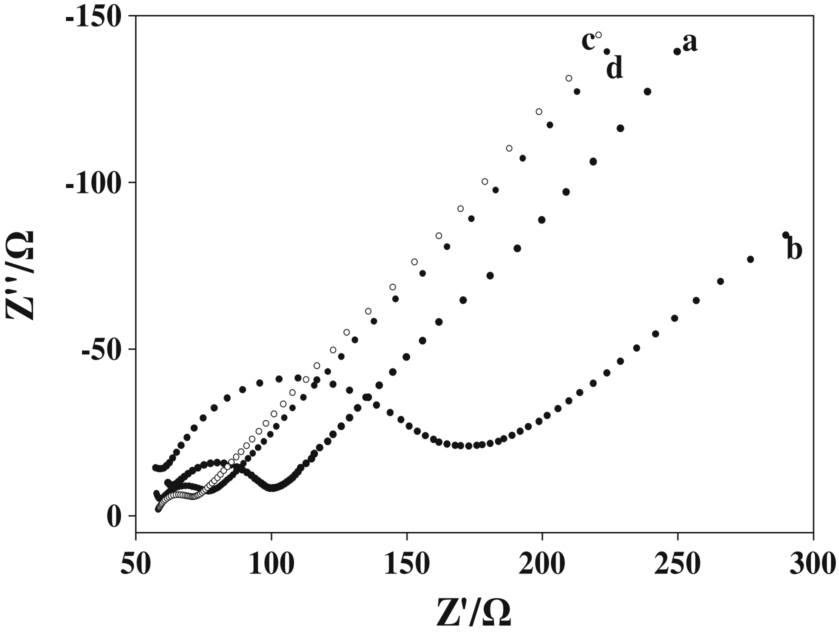
AuNPs which promotes the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox process. These results indicated that the electron transfer of copper ions at the Au@MnO_2 modified electrode was a typical electron transfer-limited process.

As shown in Fig. 4, the redox behaviors of copper ions at the modified electrode are studied by DPASV. No anodic signal of copper ions is seen on the bare GCE (Fig. 4a). The DPASV response for Au@MnO_2 coated GCE (Fig. 4d) is greatly larger than the response for MnO_2 coated GCE (Fig. 4b) and Au coated GCE (Fig. 4c), which can be seen in Fig. 4. More importantly, the responses current at the core-shell Au@MnO_2 modified electrode is larger than the sum of the currents at the MnO_2 and Au nanoparticles single modified electrodes, indicating that MnO_2 combined with Au nanoparticles synergistically improves the anodic current response of copper ions. These results indicate that the response current of copper ions can be obviously increased by electrocatalytic synergistic and adsorption.

Mechanism of copper ions determination

In the anode stripping analysis, the target is very important for the effective adsorption of the surface on the modified electrode. It was clearly illustrated that the electrochemical

Fig. 3 Nyquist plots of bare GCE (**a**), GC/MnO_2 (**b**), GC/Au (**c**) and GC/Au@MnO_2 (**d**) in 5 mM $Fe(CN)_6^{3-/4-}$ and 0.5 M KCl solutions



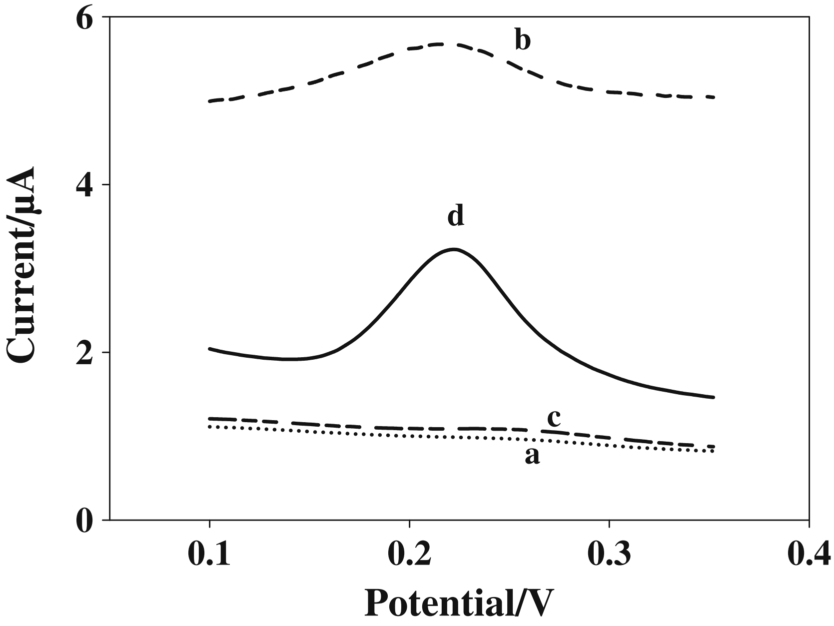


Fig. 4 DPASV of bare GCE (**a**), GC/Au (**b**), GC/MnO_2 (**c**), GC/Au@MnO_2 (**d**) in 0.1 M acetate buffer (pH 5.0) containing 200 nM copper ions. Scan rate: 50 mV·s^{-1}

detection interfaces were based on Au nanoparticles as a coupling medium, and the Au nanoparticles were used for the bridging of MnO_2 and the glassy carbon electrode to transfer electrons.

At this stage, the large amounts of copper ions were accumulated on the surfaces of the MnO_2 via adsorption. Then the electrons transfer to the surface of the Au or glassy carbon electrode. When the potential is kept in the scope of deposition region, copper ions can be reduced on the surface of the MnO_2, However, the copper ions in the lower part of the aqueous solution can not be reduced. In this way, copper ions were adsorbed on the surface of the flaky MnO_2 and then stripped out. And also, the more copper ions were adsorbed on the surface of core-shell composites, the more it would be reduced, accordingly, the stripping peak response was enhanced. This demonstrated that the modified electrode possessed good electrochemical response to copper ions.

Optimization for copper ions measurement on Au@MnO_2 microsphere modified electrode

The following parameters were optimized: (a) deposition potential; (b) deposition time; (c) pH value of the buffer; Respective data and Figures were given in the ESM. The

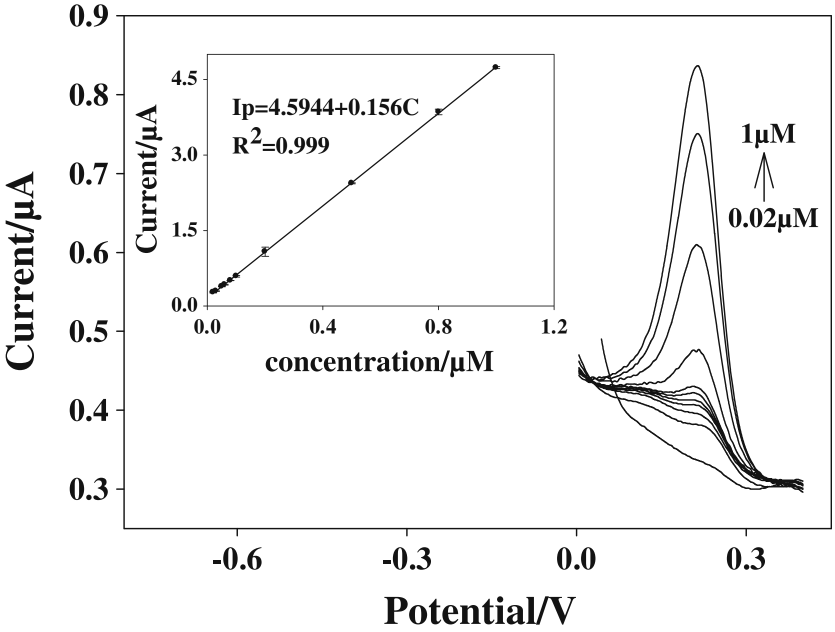


Fig. 5 The calibration plot for copper ions ($n = 3$). Left: DPASV of the GC/Au@MnO_2 at different copper ions concentrations (from 0.02 µM to 1 µM) in 0.1 M acetate buffer (pH 5.0). Scan rate: 50 mV·s^{-1}

Table 1 Comparison of the analytical performance and other analytical methods for copper ions determination

Methods	Electrode/agents	Linear range (μM)	Detecting limit (μM)	Applicable waters	References
Colorimetric	Br-PEI-AuNPs[a]	0.1–10	0.03	Lake waters	[4]
FAAS	Alumina-SDS[b]	No	0.04	Tap waters	[5]
ICP-MS	Ascorbic acid	0.008–0.8	0.01	Seawaters	[7]
XRFS	No	0.8–23	0.2	Ascorbic acid	[8]
ECL[c]	Lucigenin	0.03–1	0.002	Tap waters	[11]
SWASV	rGO-AuNPs[d]	1–12	0.03	Tap waters	[23]
SWASV	AuNP-SPCE	0.02–2	0.00002	Tap waters	[24]
SWASV	NH_2-rGO/β-CD[e]	0.03–100	0.003	Lake waters	[25]
DNPV[f]	PPyNWs[g]	0.05–1	0.05	Waste waters	[12]
DPV	Bi-AuNPs/SPE	0.02–2	0.0005	Lake waters	[13]
DPV	Au@MnO_2	0.02–1	0.005	Seawaters	Present work

[a] Branched polyethylenimine functionalized gold nanoparticles

[b] Nanometer-sized γ-alumina nanoparticles modified with sodium dodecyl sulfate (SDS)

[c] Electrochemiluminescence

[d] Reduced grapheme oxide-gold nanoparticles

[e] Amino-reduced graphene oxide and β-cyclodextrin

[f] Differential normal pulse voltammetry

[g] Polypyrrole nanowires

following experimental conditions were found to give best results: (a) deposition potential of −0.3 V; (b) 60s deposition time; (c) the buffer (pH 5.0).

Calibration plot

To further evaluate the stripping performance of the paper method with DPASV, it was performed at the GC/Au@MnO_2 in 0.1 M acetate buffer (pH 5.0) under the optimal conditions. As is revealed in Fig. 5, the stripping voltammograms are corresponding with different concentrations of copper ions. The peak current increased linearly in the copper ions concentration ranging from 0.02 to 1 μM. The linear regression equation was expressed as follows:

$$Ip = 0.156C + 4.5944 \quad \left(0.02\text{–}1\ \mu\text{M}, \text{R}^2 = 0.999\right)$$

The detection limit (3σ/m) with standard deviation for copper ions determination at the GC/Au@MnO_2 was 4.9±0.2 nM ($n = 3$). Furthermore, comparison about copper ions determination by electrochemical and other analytical methods is shown in Table 1. Compared with other electrodes, the Au@MnO_2 modified electrode revealed higher efficiency, higher sensitivity, lower detection limit and wider linear range. The results indicates that the modified electrode may be a good choice for determination of copper ions.

Reproducibility, repeatability and interference

The reproducibility of Au@MnO_2 modified GCE, in the solution with 100 nM copper ions, was evaluated by six independently modified electrodes with the same method and the relative standard deviation (RSD) was 5.3%, respectively,

Table 2 Results of real seawater samples detected by Au@MnO_2 microsphere modified electrode and inductively coupled plasma mass spectrometry (ICP-MS) methods

Real samples	Copper ions added (nM)	Mean (nM) ± SD		Recovery(%)
		Proposed method[a]	ICP-MS	
Seawater samples 1	0	105 ± 2	107	–
Seawater samples 2	0	110 ± 2	108	–
Standard artificial seawater samples 1[b]	50	51 ± 1	–	102
Standard artificial seawater samples 2[c]	50	51 ± 1	–	102

[a] Each value is calculated from three experiments

[b] The salinity of the standard artificial seawater sample 1 was 4.998

[c] The salinity of the standard artificial seawater sample 2 was 29.998

which indicated that the GC/Au@MnO_2 lacked significant difference in the respect of current of stripping peak among the prepared electrodes. To check the repeatability, one modified electrode was repeatedly used for 24 times in 0.1 M acetate buffer (pH 5.0) containing 200 nM copper ions. In Fig. S7, the stripping peak current almost did not change and the RSD was 5.9%. In addition, the stability for one modified electrode was performed once a day for 15 days in 0.1 M acetate buffer (pH 5.0) containing 200 nM copper ions. The current had no obvious changes with only decreased 3.7% after 15 days. Hence, the modified electrode had good reproducibility and repeatability.

It is a challenging task to detect copper ions accurately in the real sample without interference. Thus, the interference study was evaluated by adding some probably interfering metals under the optimized working conditions in the solution with 100 nM copper ions. The 100-fold Ca^{2+}, Zn^{2+}, Mn^{2+}, K^{+}, Mg^{2+}, Co^{2+} and anion NO_3^{-}, SO_4^{2-}, 50-fold Fe^{3+}, Cd^{2+},10-fold Bi^{3+}, Pb^{2+}, have no obvious interference in the determination of copper ions (<5% of response current change). These results strongly shows that the Au@MnO_2 modified electrode possess a great potential for online monitoring of copper ions in real seawater environment.

Analytical applications

To examine the practical application of the Au@MnO_2 electrode, the real seawater samples analysis had been performed. Furthermore, standard artificial seawater were also applied for the detection of copper ions. The salinity of the standard artificial seawater sample 1 was 4.998, and that of sample 2 was 29.998. Standard addition method was used for quantitative analysis. Recovery (%) was used to verity the accuracy of our method. A comparison of results in seawater between the paper method and ICP-MS were displayed in Table 2. The results indicates that the paper method is reliable and suitable for analysis of copper in seawater.

Conclusions

In summary, a novel and effective core-shell microsphere Au@MnO_2 modified electrode was successfully fabricated for sensitive determination of copper ions in real seawater sample and standard artificial seawater. The synthesis method was relatively uncomplicated and accessible compared to other reported methods. The tolerance of the Au@MnO_2 modified electrode to the pH value was poor, and the detection of the LOD was not particularly low. But this new modified electrode shows good repeatability and reproducibility. The Au@MnO_2 modified GCE facilitates to accurately detect copper ions in seawater. Accordingly, the fabricated electrode will be of great benefit to investigate the effects of copper ions in seawater.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (21575080), the Youth Innovation Promotion Association (2011170), and the Equipment Development Project (YZ201558) of Chinese Academy of Sciences.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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