



Surface decoration of multi-walled carbon nanotubes modified carbon paste electrode with CuO nanoparticles for electrocatalytic oxidation of nitrite

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In this paper, CuO nanoparticles have been electrodeposited onto the film of multiwalled carbon nanotubes (MWCNTs) modified carbon paste electrode (MWCPE), which fabricated a sensitive nano-copper oxide coated multi-walled carbon nanotubes modified carbon paste electrode (CuO_{nano}/MWCPE) to detect nitrite. Scanning electron microscope (SEM) image have indicated that copper oxide nanoparticles desposited on MWCPE are homogeneous. The CuO_{nano}/MWCPE has been used to detect nitrite by square wave voltammetry and cyclic voltammetry techniques. The sensor has exhibited outstanding performance for the electrocatalysis of nitrite. Electrocatalytic oxidation of nitrite at the surface of CuO_{nano}/MWCPE has been remarkably improved compared to the unmodified CPE and the MWCPE. Under optimum conditions, the oxidation current is linear with the concentration of nitrite ion in the range of 5 μM – 1000 μM . The detection limit has evaluated to be 1.25 μM ($S/N = 3$). The sensor has been successfully used to determine nitrite in water samples with excellent recoveries.

Keywords: Nitrite, Nano-copper oxide, Carbon paste electrode, Square wave voltammetry

Nitrite (NO_2^-) has been diffusely used in food, agricultural and industrial production and also is found in drinking water, biology and environment¹⁻³. However, it is harmful to the human body because it can interact with amines to form nitrosamine carcinogenic compounds^{4,5}. When the concentration of nitrite in the blood is high, it can combine with hemoglobin². According to the World Health Organization, the maximum allowable content of nitrite in drinking water is 3 mg L⁻¹. Drinking water contaminated with nitrite can cause different diseases such as methemoglobinemia and stomach cancer⁶. Consequently, it is very important to create a simple, sensitive and rapid method to detect NO_2^- in drinking water, food, and environmental systems. So far, there are several analytical methods to detect NO_2^- , such as chemiluminescence⁷, capillary electrophoresis⁸, high-performance liquid chromatography⁹, spectrophotometry¹⁰. However, these analytical methods often suffer from expensive equipment, the toxicity of used reagents and time-consuming pretreatments¹¹. Compared to these methods, electrochemical methods are faster, cheaper and safer¹². In general, electrochemical oxidation and reduction can both be used to determine nitrite, whereas oxidation is generally preferred since the reduction of nitrite is readily interfered with by other

easily reducible compounds such as molecular oxygen¹³. The electrochemical oxidation of nitrite at the surface of bare electrodes is limited by several substances that can poison the electrode surface and reduce the sensitivity and accuracy¹⁴. Nonetheless, it has been reported that the development of various modified electrodes for nitrite detection overcomes the above limitations^{15,16}.

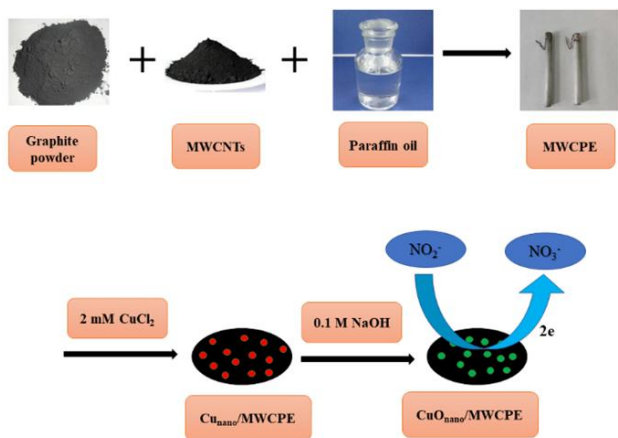
Since their invention in 1958, carbon paste electrodes (CPEs) have underwent a very impressive development, with progress in electrochemical, electroanalysis and instrumental analysis¹⁷. Chemically modified carbon paste electrodes (CMCPEs) can be prepared by adding a suitable modifier to carbon paste. The property of CMCPEs depends on the selectivity and sensitivity of the modifier towards the target species. Originally, non-conductive reagents, such as mineral oil or paraffin oil were used as binders¹⁸. Transition metallic nanoparticles, such as silver (Ag), gold (Au), palladium (Pd), nickel (Ni), copper (Cu), platinum (Pt), can be used to improve electrochemical activity. Because of their large surface-to-volume ratio, they can provide higher catalytic efficiency per gram than larger materials¹⁹. The metal nanoparticle modified electrodes exhibit good catalytic performance, mass transfer capability, high specific surface area and

good biocompatibility²⁰. In addition, nanoparticle modified electrodes have also been used to improve the electrochemical response of nitrite²¹. Copper oxide nanoparticles have attracted particular interest due to their catalytic oxidation reactions of hydrocarbons and carbon monoxide in heterogeneous catalysis²². Krishnamoorthy *et al.*²³ used a simple precipitation method to prepare CuO nano-rice as a modified electrode for simultaneous determination of dopamine and uric acid. Gao *et al.*²⁴ prepared CuO nanostructures (heart/dumbbell-like and grass-like) via simple hydrothermal method without using any additives and their application in non-enzymatic hydrogen peroxide sensing.

In this work, we have prepared a nano-copper oxide/multi-walled carbon nanotubes (MWCNTs) modified carbon paste electrode ($\text{CuO}_{\text{nano}}/\text{MWCPE}$) by directly electrodepositing nano-copper oxide onto the MWCPE surface to obtain a nitrite electrochemical sensor. The prepared sensor showed outstanding catalytic activity and stability for catalytic oxidation of nitrite. The electrochemical behavior of nitrite on $\text{CuO}_{\text{nano}}/\text{MWCPE}$ was investigated. The nano-copper oxide could increase the rate of heterogeneous electron transport in the process of electrocatalytic oxidation of nitrite. The fabricated sensor can be used as an effective tool to detect nitrite. The fabrication method of the $\text{CuO}_{\text{nano}}/\text{MWCPE}$ is given in Scheme 1.

Materials and Method

Graphite (powder, $<20 \mu\text{m}$, 99.95%), liquid paraffin were purchased from Aladdin (Shanghai, China). Multi-walled carbon nanotubes (MWCNTs, purity, $>98\%$; o.d., 30-50 nm; length, $<10 \mu\text{m}$) were



Scheme 1 — Schematic illustration for the preparation of $\text{CuO}_{\text{nano}}/\text{MWCPE}$.

obtained from Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, NaNO_2 , NaOH and KCl were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals in this study are analytical and used as received. Unless otherwise stated, a 0.10 M , $\text{pH } 5.6$ phosphate buffer solution (PBS) served as the supporting electrolyte. All solutions were prepared using deionized water ($18.2 \text{ M}\Omega \text{ cm}$).

All electrochemical measurements were carried out using a CHI 660E Electrochemical Work Station (Chenhua Instruments, Shanghai, China). A three-electrode system was used to monitor electrochemical signal. A chemically modified carbon paste electrode (o.d., 3mm) was used as the working electrode. A saturated calomel electrode (SCE) was applied as the reference electrode, and a platinum wire served as the counter electrode. A Phs-3E pH meter (Leici, Shanghai, China) was used for measuring pH. All experiments were carried out at room temperature. Scanning electron microscopy (SEM) was obtained on VEGA3 field emission scanning electron microanalyser (TESCAN, Czech Republic) equipped with an energy-dispersive X-ray spectroscopy (EDX) analyzer.

Purification of MWCNTs

The MWCNTs were purified according to previous studies²⁵. MWCNTs were heated in air at $600 \text{ }^\circ\text{C}$ for 2 h and then soaked in hydrochloric acid for 24 h and centrifuged. The precipitate was rinsed with deionized water until the pH of the filtrate was 7.0 and dried at $80 \text{ }^\circ\text{C}$ for 5 h and stored at desiccator for later use.

Preparation of modified carbon paste electrode

The unmodified CPE was prepared by mixing 70% (w/w) graphite powder with 30% (w/w) paraffin in a mortar and pestle for at least 20 min to obtain a homogeneous carbon paste. The modified CPE was prepared as previous works²⁶ by mixing 75% (w/w) graphite powder and MWCNTs (graphite powder: MWCNT 90: 10 %) with 25% (w/w) liquid paraffin in a mortar and pestle for at least 20 min to obtain a homogeneous carbon paste. After that, the paste was packed into a Teflon tube (3 mm i.d., 6 mm o.d.) and compacted. The electric contact was established via a copper wire. Then the electrode was left unused for a certain time (12–24 h) to allow their final homogenization to proceed²⁷. The surface of the modified carbon paste electrode was polished on the weighing paper before use.

Preparation of the nano-copper oxide-modified electrode

The nano-copper oxide-modified electrode (Cu_{nano}/MWCPE) was prepared as follows: Cu nanoparticles were electrodeposited on the surface of the MWCPE by continuous cyclic voltammetry at 50 mV/s in 0.1 M KCl solution containing 2 mM CuCl₂¹⁹. After that, the electrode was put in 0.1 M NaOH solution and scanned continuous for 20 cycles under potential range -0.7 to 0.6V at 40mV/s²⁸. With this method, the nano-copper oxide particles were successfully loaded onto the MWCPE surface.

Results and Discussion

Characterization of the modified electrode

Fig. 1 showed the cyclic voltammograms of MWCPE in 0.1 M KCl solution containing 2.0 mM CuCl₂. The anodic peaks at -0.03 V and 0.15 V were ascribed to the conversion of Cu(0) to Cu(I) and Cu(I) to Cu(II), respectively. The cathodic peaks at 0.04 V and -0.35 V were attributed to the transition of Cu(II) to Cu(I) and Cu(I) to Cu(0), respectively.

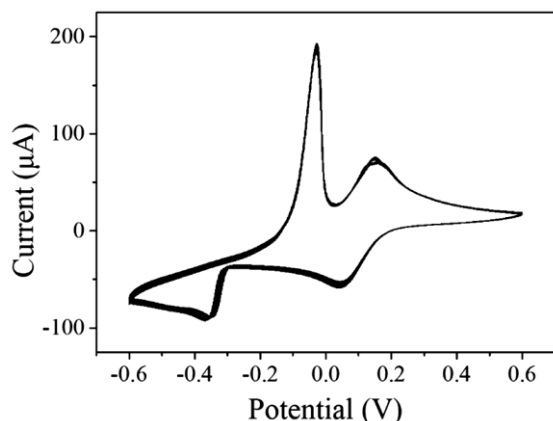


Fig. 1 — Cyclic voltammograms of CuO_{nano}/MWCPE in 0.1 M KCl solution containing 2 mM CuCl₂ at 50 mV/s.

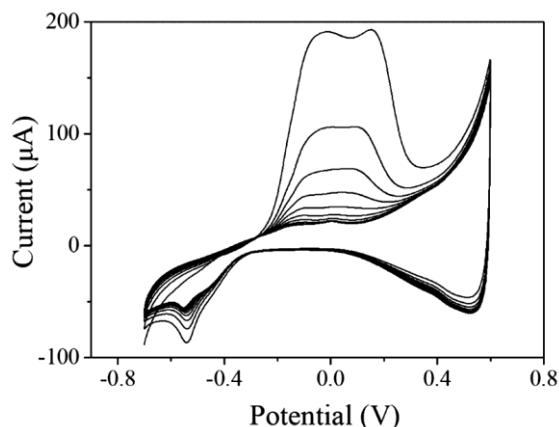
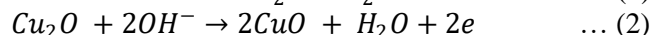
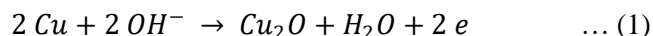


Fig. 2 — Continuous cyclic voltammograms of Cu_{nano}/MWCPE in 0.1 M NaOH solution at 40 mV/s.

Fig. 2 showed the continuous cyclic voltammograms of Cu_{nano}/MWCPE in 0.1 M NaOH solution. The mechanism involved in the electrochemical process can be described as follows²⁹:



The response of the electrochemical sensor to the analyte was related to its microtopography. Fig. 3 (a, b) showed the SEM images of an

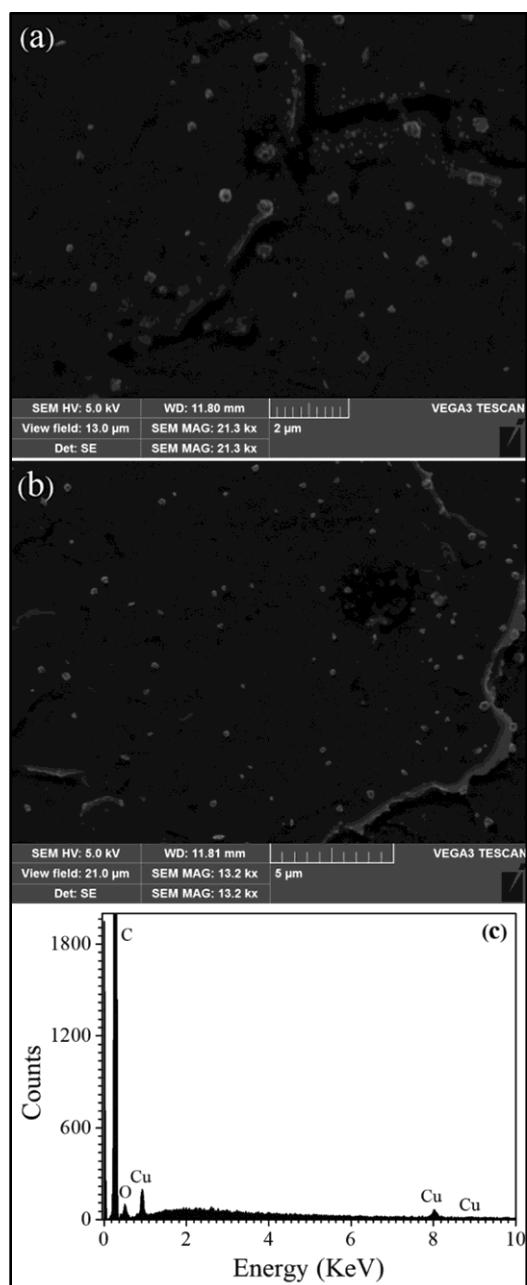


Fig. 3 — (a,b) SEM images of CuO_{nano}/MWCPE and (c) EDX pattern of CuO_{nano}/MWCPE.

electrodeposited nano-copper oxide film on MWCPE. It can be found from Fig. 3a that the nano-copper oxide were uniformly distributed on the surface of the MWCPE and the average particle diameter of the particles was about 300 nm. The nano-copper oxide can provide some unusual characteristics, such as large specific surface area, high surface reaction activity and efficient transmission channel for analyte molecules to reach the active site, which will help to improve the stability and sensitivity of nano-copper oxide/MWCPE²⁷. Fig. 3c showed the EDX of CuO_{nano}/MWCPE. The main elements on the surface of the electrode are Cu, C and O, demonstrating that the nano-copper oxide was successfully electrodeposited onto the electrode surface.

Surface area study

The microscopic areas of the electrodes were obtained by CV for 5.0 mM Fe(CN)₆^{3-/4-} in 0.1 M KNO₃ at different scan rates. For a reversible process, the following Randles-Sevcik formula can be used:

$$I_p = (2.69 \times 10^5) n^{3/2} D_R^{1/2} A C_o v^{1/2} \quad \dots(3)$$

Where, I_p refers to the anodic peak current, n is the number of electrons transferred, D_R is diffusion coefficient, A is the surface area of the electrode, C_o is the concentration of Fe(CN)₆^{3-/4-}, v is the scan rate. For 1 mM Fe(CN)₆^{3-/4-}, $n = 1$, $D_R = 7.6 \times 10^{-6}$ cm²/s. Thus, from the slope of the anodic peak current, the area of the CuO_{nano}/MWCPE was calculated to be 0.1519 cm², which was about 1.7 times greater than that for CPE (0.08548 cm²).

Electrochemical characterization

The electrocatalytic activity of the modified electrode for nitrite can be verified by electrochemical experiments in the presence of nitrite. Fig. 4a showed the cyclic voltammograms response of CPE (curve 1),

MWCPE (curve 2), CuO_{nano}/CPE (curve 3), CuO_{nano}/MWCPE (curve 4) in 0.1 M pH 5.6 phosphate buffer solution containing 0.1mM nitrite at 50mV/s. As shown, no oxidation peak of nitrite was observed in the potential range of 0.4 to 1.2 V on the CPE electrode (curves 1). The CV for MWCPE shows a small oxidation peak in the positive-going scan (curves 2). The CuO_{nano}/CPE and CuO_{nano}/MWCPE electrodes have a significant oxidation current response to nitrite, which was ascribed to the transition of NO₂⁻ to NO₃⁻ through a two-electron reaction mechanism (curves 3 and 4). The use of carbon nanotubes plays an important role in the electro-synthesis of copper oxide nanoparticles and in the determination step. In the step of electro-synthesis, the addition of MWCNTs to the carbon paste can increase the surface of the electrode and the electrochemical performance of the electrode³⁰. Therefore, the addition of carbon nanotubes increases the electro-active surface of the electrode and improves the electrochemical performance of the electrode, so that more nanoparticles can be obtained. So, the carbon past modified by carbon nanotubes was selected as a substrate for electro-synthesis copper oxide nanoparticles and a nitrite electrochemical sensor was constructed.

Fig. 4b showed the electrochemical impedance spectroscopy (EIS) responses of the CPE (curve 1), MWCPE (curve 2), CuO_{nano}/CPE (curve 3), CuO_{nano}/MWCPE (curve 4) in 0.10 M KCl containing 5.0 mM [Fe(CN)₆]^{4-/3-}. The EIS consists of a semicircular portion and a linear portion, corresponding to the electron-transfer-limited process and the diffusion-limited process, respectively³¹. In general, the semicircle diameter of the Nyquist plot represents the interfacial electron transfer resistance (R_{et}) of the surface of the modified electrode³². The

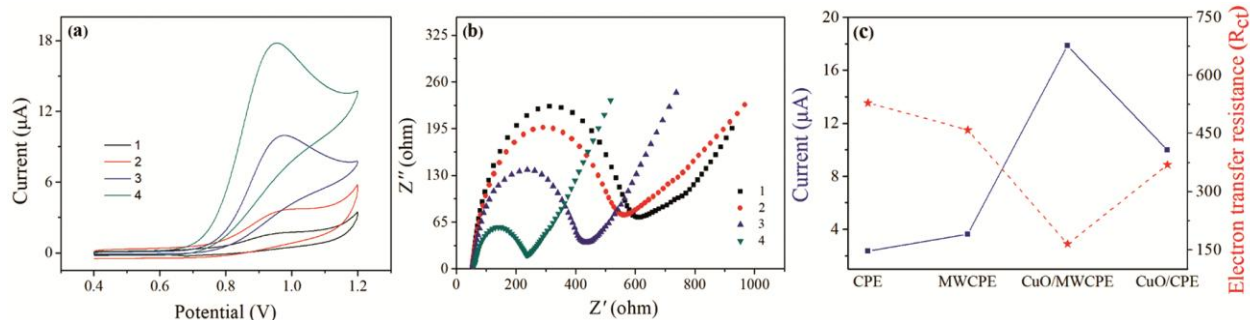


Fig. 4 — (a) Cyclic voltammograms response of CPE (1), MWCPE (2), CuO_{nano}/CPE (3), CuO_{nano}/MWCPE (4) in 0.1 M pH 5.6 Phosphate buffer solution containing 0.1 mM nitrite at 50 mV/s, (b) EIS responses of the CPE (1), MWCPE (2), CuO_{nano}/CPE (3), CuO_{nano}/MWCPE (4) in 0.10 M KCl containing 5.0 mM [Fe(CN)₆]^{4-/3-} for 0.1-10⁵ Hz at 0.27 V and (c) plot of peak current and electron transfer resistance against different modified electrodes.

EIS experiment was performed at a bias potential of 0.27 V with amplitude of 5 mV. The value of Ret for CPE, MWCPE, CuO_{nano}/CPE, CuO_{nano}/MWCPE were estimated to be 529, 459, 369 and 165 Ω , respectively. The Ret value of CuO_{nano}/MWCPE is lower than that of other electrodes. These results demonstrated that CuO nanoparticles can enhance the electron transport rate. These results are very consistent with the peak current values (I_p) obtained from CV measurements (Fig. 4c). Therefore, CuO_{nano}/MWCPE modified electrodes was used for further studies.

Effect of pH

The influence of the supporting electrolyte pH possesses significant impact on the peak current values. The effect of pH values of the PBS (0.1 M) was investigated in the range of 5.6 to 8.0 for 0.5 mM nitrite concentration at CuO_{nano}/MWCPE. As shown in Fig. 5, the oxidation peak current decreases from 5.6 to 8.0. Furthermore, this study indicated that the peak potential for nitrite oxidation is not affected by

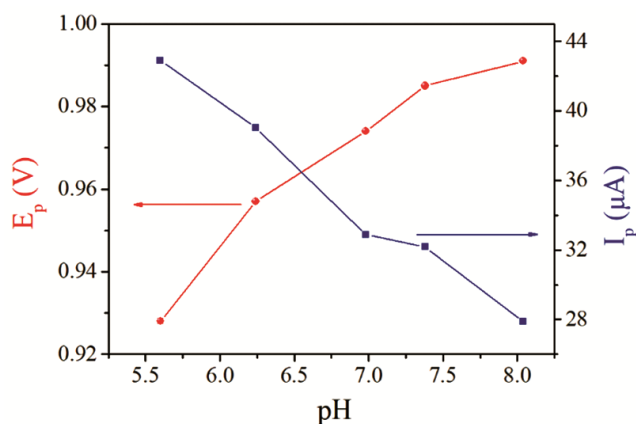


Fig. 5 — Cyclic voltammograms of CuO_{nano}/MWCPE in different pH solutions containing 0.5 mM nitrite at 50 mV/s.

the pH of the solution. It is therefore believed that oxidation process is controlled by kinetics rather than thermodynamics, that is a proton independent catalytic step²⁶. Since the pK_a of HNO₂ is 3.30, most nitrite ions were protonated in an acidic solution, or the conversion of NO₂⁻ to NO at very low pH³³. However, the oxidation of nitrite is a proton independent catalytic step. This means that the decrease of the peak current of nitrite at higher pH has a kinetic reason³⁴. In addition, basic solution can promote the formation of oxide layer on the surface of the electrode to inhibit the oxidation of nitrite. Consequently, the optimal value of 5.6 was chosen for subsequent studies.

Effect of scan rate

Scan rate has an effect on the current response of nitrite and the corresponding electrochemical parameters can be derived from the relationship between the scan rate of potential sweep and current responses of nitrite oxidation. Fig. 6 shows the cyclic voltammograms of the CuO_{nano}/MWCPE in 0.1 M PBS (pH 5.6) containing 0.5 mM nitrite with different scan rates (10–200 mV/s). The results obtained show that the catalytic effect of the mediator occurs within the range of the testing scan rate. From Fig. 6a, the peak potential shifts to more positive potential with increasing scan rate. However, the oxidation peak current was linear with the square root of the scan rate (Fig. 6b), and the equation can be expressed as follows: $I_p = 2.9353 v^{1/2} + 8.5512$ ($R^2 = 0.9968$). The obtained results indicated that the oxidation of NO₂⁻ on the CuO_{nano}/MWCPE was a diffusion-controlled process³⁵. In addition, the oxidation peak potential (E_p) of nitrite has changed positively with increasing the scan rates. The linear relation between peak potential and logarithm of scan rate obeys the

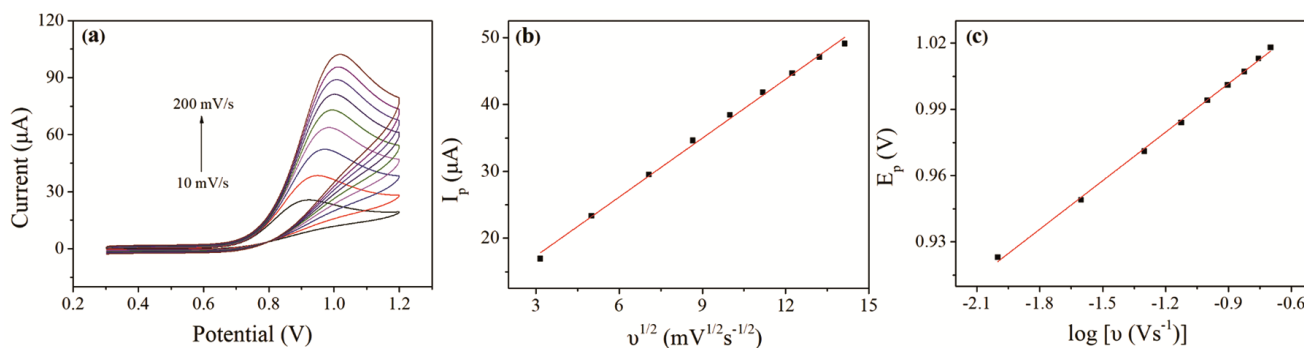


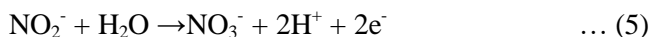
Fig. 6 — (a) Cyclic voltammograms of the CuO_{nano}/MWCPE in 0.1 mol/L PBS (pH 5.6) containing 0.5 mM NaNO₂ with different scan rates (10–200 mV/s) and corresponding linear calibration curves of (b) peak current vs. square root of scan rate and (c) peak potential vs. logarithm of scan rate.

following equation: $E_p = 0.07321 \log v + 1.0675$ ($R^2 = 0.9983$), (Fig. 6c) indicating a kinetic limitation in the reaction between the redox sites of $\text{CuO}_{\text{nano}}/\text{MWCPE}$ and nitrite.

For irreversible electrode process, according to Laviron's theory³⁶, E_p is defined by the following equation:

$$E_p = E^0 + (2.303RT/(\alpha nF)) \log(RTk_0/(\alpha nF)) + (2.303RT/(\alpha nF)) \log v \quad \dots (4)$$

Where, α is the transfer coefficient, k_0 is the standard heterogeneous rate constant of the reaction, n is the number of electrons transferred, v is the scan rate and E^0 is the formal redox potential. Other symbols have their common meanings. Thus, the value of αn can be easily calculated from the slope of E_p versus $\log v$. In this system, the slope was found to be 0.07321, taking $T = 298$ K and substituting the values of R and F , αn was calculated as 0.8078. According to Bard and Faulkner³⁷, α can be given as $\alpha = 47.7/(E_p - E_{p/2})$ where $E_{p/2}$ is the potential where the current is at half the peak value. From this, we obtained the value of α to be 0.402 for modified electrode. So the number of electron (n) transferred was calculated as $2.01 \approx 2$, thus suggesting that two electrons were involved in the oxidation mechanism of nitrite, with nitrate as the most likely product of the reaction. The value of k_0 can be determined from the intercept of the above plot if the value of E^0 is known. The value of E^0 in Eq. (4) can be obtained from the intercept of E_p versus v curve by extrapolating to the vertical axis at $v = 0$.³⁷ In our system the intercept for E_p versus $\log v$ plot was 1.0675 and E^0 was obtained to be 0.9706, the k_0 was calculated to be 650.3 s^{-1} . In addition, according to the report by Guidelli *et al.*³⁸, the catalytic oxidation mechanism can be explained with the following process:



Determination of nitrite

Under optimal conditions, SWV was used to determine nitrite in static solutions. SWV is a pulse technology which is more sensitive than traditional scanning techniques. As shown in Fig. 7, the peak current was linear with the concentration of NO_2^- in the ranges of $5.0 \mu\text{M}$ to $1000 \mu\text{M}$. The linear regression equation was $I_{pa} = 0.03347C - 0.1459$ ($R^2 = 0.9985$). The detection limit was found to be $1.25 \mu\text{M}$ ($S/N=3$).

The linear range, detection limit for nitrite at $\text{CuO}_{\text{nano}}/\text{MWCPE}$ compared with the recently reported chemically modified electrodes (Table 1). As mentioned above, the maximum amount of nitrite in drinking water is 3 mg/L . Therefore, the prepared electrode is more suitable for the determination of nitrite in real water samples.

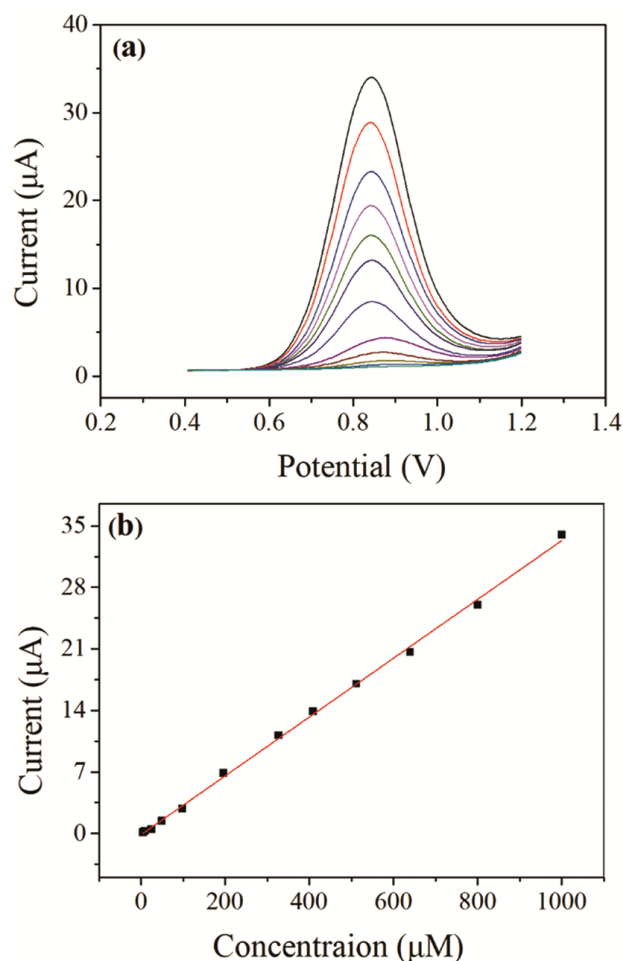


Fig. 7 — (a) SWV of the $\text{CuO}_{\text{nano}}/\text{MWCPE}$ in PBS (pH 5.6) with different concentrations of nitrite ($5 \mu\text{M}$ - $1000 \mu\text{M}$), step potential 6 mV , amplitude 25 mV and frequency 25 Hz and (b) corresponding linear calibration curve.

Table 1 — Comparison of $\text{CuO}_{\text{nano}}/\text{MWCPE}$ with other chemically modified electrodes for nitrite sensors

Modified electrode	Linear range (μM)	Detection limit (μM)	Ref.
Ag/HNTs/MoS ₂ -CPE	2-425	0.7	41
ZPOA/IL-CPE	2-50	1.05	42
Co ₃ O ₄ /RGO-GCE	1-380	0.14	43
IL-CPE	1-200	0.1	44
CuN _{ps} -GCE	50-3000	20	45
CuO-GCE	1-91.5	0.36	46
$\text{CuO}_{\text{nano}}/\text{MWCPE}$	5-1000	1.25	This work

Table 2 — Determination of nitrite at various concentrations in tap water

Sample	Added (μM)	Found (μM)	Recovery (%)	R.S.D. (%)
1	20	20.85	104.25	1.90
2	50	48.91	97.82	2.38
3	100	102.19	102.19	4.3

Interference study

The potential interference of various common ions on the detection of NO₂⁻ was tested using square wave voltammetry. The results showed that no change was observed for 0.1 mM nitrite in the presence of 100 fold higher concentration of foreign ions such as Mg²⁺, Cu²⁺, K⁺, Zn²⁺, Ca²⁺, Na⁺, NH₄⁺, SO₄²⁻, NO₃⁻, CO₃²⁻, H₂PO₄⁻, HPO₄²⁻, F⁻ and Cl⁻. It was observed that ethanol (200 folds), HOAc (100 folds), glucose (100 folds), H₂O₂ (100 folds), uric acid (100 folds), Na₂SO₃ (50 folds) did not interfere with the voltammetric signal of nitrite. Thus, this study shows that the prepared modified electrode has high selectivity for the determination of nitrite at low level concentrations.

Real sample analysis

The modified sensor has been successfully applied to the determination of nitrite in tap water samples. The results obtained are listed in Table 2. The tap water sample was processed according to the previous reports³⁹. As can be seen from calculation results, the recovery range was from 97.82% to 104.25%, the RSD ranged from 1.90% to 4.32%, which is within the acceptable range of ±5%. Thus the sensor has excellent applicability for the determination of nitrite in water samples.

Conclusions

In this work, CuO_{nan}/MWCPE was successfully fabricated and used for detection of NO₂⁻ with high selectivity. The results show that the proposed electrode has excellent electroanalytical for the detection of nitrite. The low detection limit and wide linear range of nitrite were 1.25 μM, 5–1000 μM, respectively. The prepared sensor was successfully applied to detect the concentration of nitrite in the tap water sample. Therefore, the proposed sensor has potential applications in the fields of electrochemistry, biotechnology and environmental chemistry.

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