

Metal Doped Copper Oxide Nanoparticles Modified Electrodes for Determination of Nitrite

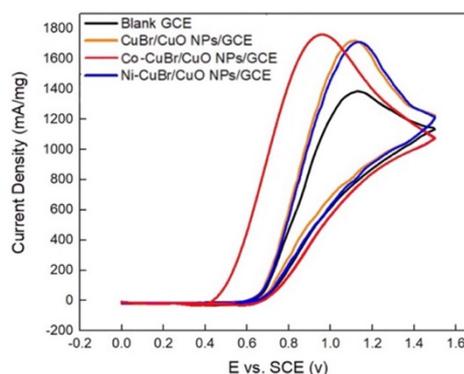
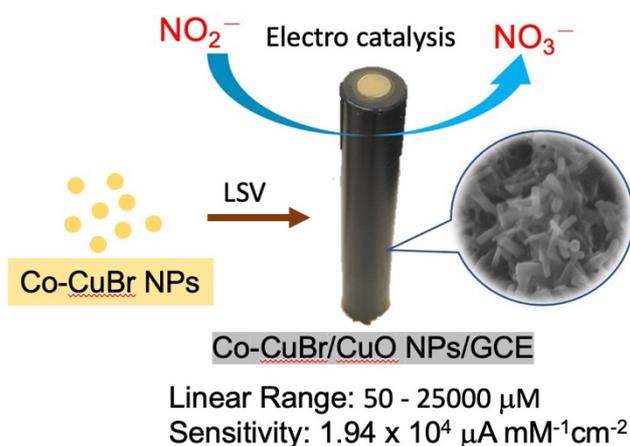
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Abstract

The occurrence of bacterial infection in the human urine will reduce the nitrate (NO_3^-) to nitrite (NO_2^-), so nitrite can be tested as a routine inspection item for urine. The most common methods for nitrite detection are spectrophotometric detection, chemiluminescence, the voltammetric techniques *etc.* In this study, CuBr/CuO NPs/GCE and metal doped copper oxide NPs electrode (M-CuBr/CuO NPs/GCE, M=Co, Ni) are prepared, and both are electrodes with a nanostructured surface. Co-CuBr/CuO NPs/GCE displays the lower oxidation potential of NO_2^- to NO_3^- and the better electrocatalytic efficiency in nitrite oxidation. A wide measurement range, 50 μM to 25 mM of $[\text{NO}_2^-]$, as well as a good sensitivity, $1.94 \times 10^4 \mu\text{A mM}^{-1}\text{cm}^{-2}$, were achieved by using Co-CuBr/CuO NPs/GCE for determination of nitrite. Co-CuBr/CuO NPs/GCE was applied to the nitrite test in an artificial urine, indicating that the sensitivity of NO_2^- concentration was $1 \mu\text{A mM}^{-1}\text{cm}^{-2}$.



1. Introduction

The occurrence of bacterial infection in the human urine will reduce the nitrate (NO_3^-) to nitrite (NO_2^-), so nitrite can be tested as a routine inspection item for urine. The voltammetric techniques are commonly reported for the determination of nitrite. However, the selectivity and the reproducibility are limited to the electrode material as well as structures. Recently the development of nanostructured CuO-based electrode as an efficient electrocatalyst applied on oxidation is very attractive. In this study, we prepare several electrodes with metal doped copper oxide nanoparticles (Ni or Co-CuBr/CuO NPs/GCE) by a simple method and Co-CuBr/CuO NPs/GCE exhibits a good sensitivity as well as reproducibility towards the oxidation of nitrite.

2. Experimental Method

2.1 Preparation of electrodes with metal doped copper oxide nanoparticles (Co-CuBr/CuO NPs/GCE)

CuBr-NPs were synthesized by mixing 0.1 M $\text{KBr}_{(\text{aq})}$, 0.1 M $\text{CuSO}_{4(\text{aq})}$, 0.1 M PEG solution with 0.02 M ascorbic acid. After a vigorous stirring, a white suspension was observed. Add 0.1 M $\text{Co}(\text{CH}_3\text{COO})_{2(\text{aq})}$ into this suspension and let it stay for 10 min. The Co/CuBr-NPs was recovered by a set of repeated centrifugations, and washed several times with distilled water. Drop the Co/CuBr-NPs suspension on the glassy carbon electrode (GCE) and then linear sweep voltammetry (LSV) was used to oxidize the CuBr on the surface of the GCE electrode to CuO in 0.1 M $\text{NaOH}_{(\text{aq})}$.

2.2 Electrochemical measurements

All electrochemical syntheses and their characterization were performed on CHI 760d electrochemical workstation in a typical three-electrode-cell configuration, with a saturated calomel electrode (SCE) as a reference electrode. The current amperometry (CA) was carried out with a background solution of 0.1 M $\text{NaOH}_{(\text{aq})}$ and a constant potential of 0.94 V. The cyclic voltammetry (CV) with a potential range of 0~1.5 V and a scan rate of 0.05 V/s was used to compare the oxidation signals of each electrode material to detect $\text{NaNO}_{2(\text{aq})}$. The data obtained from the experiment were processed and compared with overlays.

3. Results and Discussion

3.1 The preparation of CuBr/CuO NPs/GCE and Co-CuBr/CuO NPs/GCE

CuBr NPs on the surface of GCE was converted to CuO by using LSV in 0.1 M NaOH_(aq). The SEM image (Fig. 1a) shows CuO NPs deposited on the surface of GCE.

The preparation of Co-CuBr/CuO NPs/GCE is from a cation exchange reaction of M²⁺ (M = Co or Ni) with CuBr NPs. After M-CuBr NPs/GCE was oxidized electrochemically by LSV, the nanostructure of M-CuBr/CuO NPs/GCE was observed as shown in Fig 1b. The nanostructured and modified electrode would provide advantages of low overpotential, improved reaction kinetics, and long-term stability toward the electrocatalysis of nitrite oxidation in basic media.

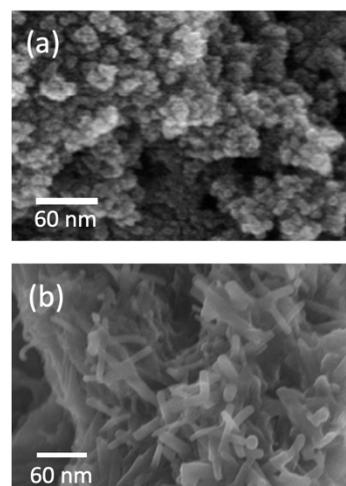


Fig 1. SEM images of (a) CuBr/CuO NPs/GCE (b) Co-CuBr/CuO NPs/GCE

3.2 The investigation of the electrocatalytic sensing of nitrite

The electrochemical behavior of bare GCE, CuBr/CuO NPs/GCE, Co-CuBr/CuO NPs/GCE, and Ni-CuBr/CuO NPs/GCE in the presence of 0.1 M NaNO_{2(aq)} was studied with a potential of 0.94 V as well as a scan rate of 0.05 V/s in 0.1 M NaOH shown as Fig. 2. The oxidation potentials of NO₂⁻ by using bare GCE, CuBr/CuO NPs/GCE, Co-CuBr/CuO NPs/GCE, and Ni-CuBr/CuO NPs/GCE in CV responses were approximately located at 1.13 V, 1.10 V, 0.94 V, and 0.94 V, respectively. (Fig 2) Co-CuBr/CuO NPs/GCE displays better electrocatalytical efficiency in nitrite oxidation.

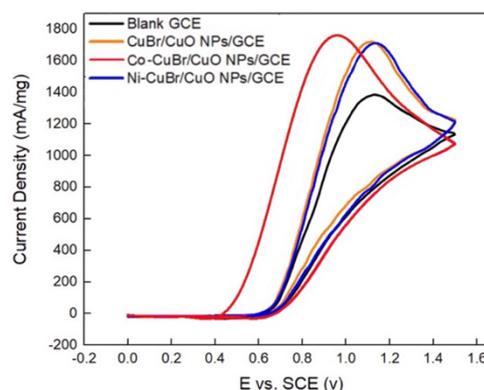


Fig 2. CV graph of modified CuBr/CuO NPs/GCE electrodes in 0.1 M NaNO_{2(aq)}

Table 1 Comparison of electrochemical simultaneous response of nitrite at different modified electrodes.

Electrode	Linear Range (μ M)	Sensitivity (μ A mM ⁻¹ cm ⁻²)
CuO-GCE	1 - 91.5	-
CuO-NS / GCE	100 - 1400	6.17
CuBr/CuO-NPs / GCE	-	-
Co-CuBr/CuO NPs/GCE	50 - 25000	19434

The current amperometry (CA) was used to study the sensitivity of the Co-CuBr/CuO NPs/GCE used in nitrite oxidation, the 10 μL 0.1 M $\text{NaNO}_{2(\text{aq})}$ was added every 30 sec to increase the NO_2^- concentration. A linear relationship exhibited over the 50 - 25000 μM of $[\text{NO}_2^-]$ suggested a wide measurement range as well as a good sensitivity, $1.94 \times 10^4 \mu\text{A mM}^{-1}\text{cm}^{-2}$. (Table 1) The presence of interferences, such as NaCl, uric acid, ascorbic acid, and Na_2SO_3 , do not influence the detection of nitrite. (Fig. 3)

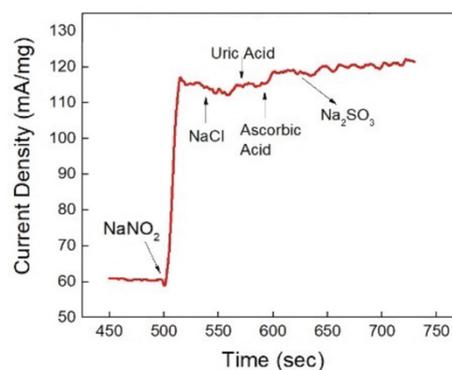


Fig 3. The interference test of the different adducts for nitrite determination. (Electrode: Co-CuBr/CuO NPs/GCE, 1.0 M 10 μL $\text{NaNO}_{2(\text{aq})}$ in 0.1 M NaOH, Adduct : 0.1 M 10 μL)

Because urinary tract infections are the most common cause of nitrites in urine, Co-CuBr/CuO NPs/GCE was applied to the nitrite test in an artificial urine containing CaCl_2 , NH_4Cl , MgSO_4 , NaCl, KCl, uric acid, ascorbic acid, sodium citrate, urine, or Na_2SO_4 . The sensitivity of NO_2^- concentration was 1 μM in the nitrite test in the artificial urine.

4. Conclusion and Future View

In summary, CuBr/CuO NPs/GCE and Co-CuBr/CuO NPs/GCE are prepared by using linear voltammetry (LSV) in 0.1 M $\text{NaOH}_{(\text{aq})}$ of CuBr NPs/GCE and Co-CuBr NPs/GCE, and both are electrodes with a nanostructured surface. Co-CuBr/CuO NPs/GCE displays the lower oxidation potential of NO_2^- to NO_3^- and the better electrocatalytical efficiency in nitrite oxidation. A wide measurement range, 50 μM to 25000 μM of $[\text{NO}_2^-]$, as well as a good sensitivity, $1.94 \times 10^4 \mu\text{A mM}^{-1}\text{cm}^{-2}$, were achieved by using Co-CuBr/CuO NPs/GCE for determination of nitrite. Co-CuBr/CuO NPs/GCE was applied to the nitrite test in an artificial urine, showing that the sensitivity of NO_2^- concentration was 1 $\mu\text{A mM}^{-1}\text{cm}^{-2}$.

In the future, the performance of Co-CuBr/CuO NPs/GCE would be investigated in detection of other harmful ions and food additives.

6. References

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