Structure and electrochemical properties of copper wires with seamless 1D nanostructures

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Abstract

A seamless Cu nanowire array grown on Cu wire is prepared by combining thermal oxidation method and electrochemical reduction. The data set described in this paper includes the structure of the Cu nanowires electrode, electrocatalytic active surface area, linear sweep voltammetry and amperometry measurement for nitrate sensing. The electrochemical data show that Cu nanowire arrays exhibited a linear response to nitrate ions over a concentration range from 50 μM to 600 μM (R² = 0.9974) with a sensitivity of 0.357 μA μM⁻¹ cm⁻¹ and detection limit of 12.2 μM at a signal-to-noise ratio of 3, respectively.

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### Experimental factors

Cu wires were sonicated in 1 M HCl solution for 3 min and then put into deionized water for 3 min before further treatment.

### Experimental features

- Sample preparation:
  - Cu wires were annealed in air at 600 °C for 4 h with a heating rate of 10 °C/min.
  - Oxide CuOₓ electrode was reduced at −0.4 V (vs RHE) in N₂ purged electrolyte.

- Electrochemical analysis of data: electrocatalytic active surface areas and detection abilities were obtained from electrochemical workstation with three-electrode system in prepared electrolyte.

### Data source location

School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China.

### Data accessibility

Data is displayed within this article.

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#### Value of the data

- Growth of nanowire arrays on Cu wires by combining thermal oxidation and electrochemical reduction.
- Using high-density seamless nanowire array grown on Cu wire as nitrate electrochemical sensor.
- Nitrate sensing properties of 1D nanostructured Cu wires.

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#### 1. Data

The data set shows the crystal structure of Cu nanowires (Fig. 1), electrochemical active surface area (Fig. 2), Linear sweep voltammetry (LSV) responses of pristine Cu wire and Cu nanowires electrodes (Figs. 3 and 4), anti-interference properties of Cu nanowires electrode (Fig. 5), comparison of the performances of various nitrate sensors (Table 1) and stability performance of the Cu nanowires electrochemical sensor (Table 2).

The XRD patterns of the Cu wires in Fig. 1 show the crystal structural changes at each processing stage. After thermal oxidation, diffraction peaks assigned to CuO and Cu₂O can be observed and the majority of the peaks belong to Cu₂O crystal. After electrochemical (EC) reduction, the metallic Cu

![Fig. 1. XRD patterns of Cu wire, Cu oxides nanowires and prepared Cu nanowires electrode.](image-url)
peaks are well recovered with negligible oxides peaks. Compared to the pristine Cu wires, the diffraction peaks of Cu wires after electrochemical reduction are broader.

Fig. 2 shows the CV diagram of Cu electrodes with and without surface nanostructures in N2 purged NaOH (50 mM) electrolyte. The oxidation peak of nanostructured Cu wire improved enormously compared with the bare one in the voltage range from −0.4 V to −0.2 V. The charge of Cu2O formation in bare and nanostructured Cu wire electrodes, calculated by integrating the oxidation peak area, are 0.266 mC and 17.258 mC, respectively. By assuming the required charge quantity to form a monolayer Cu2O is 180 μC cm−2 [1], the ESA of pristine Cu wire and Cu-NWs is 1.478 cm2 and 95.88 cm2, respectively.

In Fig. 3(a), no obvious reduction peak is observed over pristine Cu wires electrode in the presence of nitrate. The well-defined reduction peaks of nitrate are found in the potential range of −0.4 to −0.5 V for wires after electrochemical reduction (Cu-NWs). What’s more, the peak current rose gradually with the increase of nitrate concentration.
Fig. 4 shows the dependence of cathodic peak current on scan rate \( (v) \). LSV curves were measured with scan rate in the range from 10.0 to 100.0 mV s\(^{-1}\) with step width 0.01 V s\(^{-1}\), respectively. The peak current due to reduction of nitrate displayed a linear relationship with the square root of scan rate.

Fig. 5 shows the anti-interference performance of the surface nanostructured Cu wire. With sequential addition of different interference anions of \( \text{Cl}^- \), \( \text{H}_2\text{PO}_4^- \), or \( \text{HCO}_3^- \), the response currents almost remain unchanged compared with the blank electrolyte. However, a current increase was found when 1 mM \( \text{NO}_2^- \) anion was present in the solution.

Table 2 displays the stability of nanowire Cu as electrochemical sensor for nitrate detection. The measurements were conducted in a solution containing 200 μM nitrate at – 0.46 V (vs. SCE), where \( I_m \) represents the average current for two tests (time interval 15 min) and RDS the relative standard deviation for the successive measurements. No obvious change was observed when repeating the test within 24 h, with RDS less than 5.58%. For long term stability, the \( I_m \) exhibits fluctuation shape with 6.08% (RDS) in 14 days.

**Fig. 4.** (a) LSV curves of Cu-NWs electrode of 0.1 M \( \text{NaNO}_3 \) in 0.1 M \( \text{Na}_2\text{SO}_4 \) solution (pH = 2) by sweeping at different scan rates (from a to e, 0.01–0.1 V s\(^{-1}\) with step width 0.01 V s\(^{-1}\), respectively); (b) The linear dependence of peak current on the square root of the scan rate.

**Fig. 5.** LSV curves of Cu-NWs electrode in 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte (pH = 2) with sequential addition of 1 mM \( \text{NaHCO}_3 \), 1 mM \( \text{NaCl} \), 1 mM \( \text{KH}_2\text{PO}_4 \), 1 mM \( \text{NaNO}_2 \), and 1 mM \( \text{NaNO}_3 \).

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**Table 2**

| Electrochemical Sensor | Nitrate Concentration (μM) | Applied Potential (V vs. SCE) | \( I_m \) (mA) | RDS (%) |
|------------------------|----------------------------|-------------------------------|----------------|---------|
| Cu-NWs                 | 200                        | –0.46                         | 4.56           | 5.58    |
|                        |                            |                               | 4.60           | 5.58    |
|                        |                            |                               | 4.62           | 5.58    |
|                        |                            |                               | 4.64           | 5.58    |
|                        |                            |                               | 4.66           | 5.58    |

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**Note:**

- \( I_m \) represents the average current for two tests (time interval 15 min).
- RDS is the relative standard deviation for the successive measurements.
2. Experimental design, materials and methods

2.1. Preparation of Cu nanowires electrode

Cu wires of 0.2 mm in diameter were prepared by wire-drawing under room temperature using pure copper. In a typical preparation, Cu wires were sonicated in 1 M HCl solution for 3 min and then put into deionized water for 3 min to remove surface oxide impurities. The Cu wires were annealed in air at 600 °C for 4 h with a heating rate of 10 °C/min. The metallic copper nanowire arrays were then obtained using electrochemical reduction method at −0.4 V (vs. RHE) in 0.1 M KOH solution purged with N2 gas. Copper oxide nanowires were completely reduced when the cathodic current reached a stable, near-zero horizontal.

2.2. Electrochemical measurement

Electrochemical measurements were conducted on a Zahner potentiostat in a three-electrode configuration, with platinum net as counter electrode and SCE as the reference electrode. The electrolyte was purged with N2 gas before measurement. The as-prepared Cu wires were cut into 5 cm for the measurement. Electrocatalytic active surface area (ESA) of the work electrode was measured through cyclic voltammetry (CV) in a 50 mM NaOH electrolyte at 5 mV s−1. Linear sweep voltammetry (LSV) was employed to characterize the ability of electrodes for nitrate reduction at 40 mV s−1. Amperometry (IT) measured at a constant −0.46 V (vs. SCE) was used to detect the concentration of nitrate in water. Both of the LSV and IT were carried out in a 0.1 M Na2SO4 electrolyte at pH = 2.

Table 1
Comparison of the performances of various nitrate sensors. S: sensitivity, A: area, DL: detection limit (signal/noise = 3), R²: Correlation coefficient.

| Electrode materials                                      | Analytical method | Linear range (μM) | S/A⁰ (μA μM⁻¹ cm⁻²) | DL (μM) | R²   | Ref. |
|---------------------------------------------------------|-------------------|-------------------|----------------------|---------|------|------|
| Copper-plated copper wire                               | LSV               | 10–200            | 0.085                |         | 0.998| [2]  |
| Cu sheet                                                | Amperometry       | 100–250           | 0.0082               | 4.2     | 0.9991| [3]  |
| Cu-Ni alloy                                             | LSV               | 16–200            | 0.7                  | 11      | 0.998| [4]  |
| Porous copper nanoclusters                              | LSV               | 6.25–300          | 5.26                 | 5       | 0.9993| [5]  |
|                                                       |                   | 300–3500          | 3.53                 |         | 0.9918|      |
| Cu nanowire                                             | LSV               | 10–400            | 0.7143               | 3.0     | 0.998| [6]  |
| Cu on Pt                                                | Amperometry       | 100–4000          | 3.931                |         | 0.9951| [7]  |
| Cu nanoparticles on multi-wall carbon nanotubes         | SWV               | 0.1–75            | 0.2257               | 0.02    | 0.9992| [8]  |
| reduced graphene oxide                                  |                   |                   |                      |         |      |      |
| This work                                               | Amperometry       | 50–600            | 5.647                | 12.2    | 0.9974|      |

a The diameter and length of extruded Cu wire were used to calculate the surface of our nanostructured electrode for comparison.

Table 2
Stability performance of the Cu-NWs electrochemical sensor.

| Testing cycle | Iₘ RDS (%) |
|---------------|------------|
| Day 1         | −1.823 2.08|
| Day 3         | −1.741 0.56|
| Day 14        | −1.859 5.58|
| Overall       | −        6.08|

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Transparency document. Supplementary material

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References

[1] T. Heumann, I.-H. Moon, Oxygen adsorption on copper and determination of the roughness factor, Surf. Sci. 24 (1971) 370–390. http://dx.doi.org/10.1016/0039-6028(71)90269-X.
[2] J. Davis, M.J. Moorcroft, S.J. Wilkins, R.G. Compton, M.F. Cardosi, Electrochemical detection of nitrate and nitrite at a copper modified electrode, Analyst. 125 (2000) 737–742. http://dx.doi.org/10.1039/a909762g.
[3] J.C.M. Gamboa, R.C. Peña, T.R.L.C. Paixão, M. Bertotti, A renewable copper electrode as an amperometric flow detector for nitrate determination in mineral water and soft drink samples, Talanta 80 (2009) 581–585. http://dx.doi.org/10.1016/j.talanta.2009.07.028.
[4] M.J. Moorcroft, L. Nei, J. Davis, R.G. Compton, Enhanced electrochemical detection of nitrite and nitrite at a Cu-30Ni alloy electrode, Anal. Lett. 33 (2000) 3127–3136. http://dx.doi.org/10.1080/00032719.2000.10395490.
[5] Y. Li, J. Sun, C. Bian, J. Tong, S. Xia, Micro electrochemical sensor with copper nanoclusters for nitrate determination in freshwaters, Micro Nano Lett. 7 (2012) 1197–1201. http://dx.doi.org/10.1049/mnl.2012.0533.
[6] A.M. Stortini, L.M. Moretto, A. Mardegan, M. Ongaro, P. Ugo, Arrays of copper nanowire electrodes: preparation, characterization and application as nitrate sensor, Sens. Actuators B Chem. 207 (2015) 186–192. http://dx.doi.org/10.1016/j.snb.2014.09.109.
[7] Y. Li, J.Z. Sun, C. Bian, J.H. Tong, H.P. Dong, H. Zhang, S.H. Xia, Copper nano-clusters prepared by one-step electrodeposition and its application on nitrate sensing, AIP Adv. 5 (2015) 41312. http://dx.doi.org/10.1063/1.4905712.
[8] H. Bagheri, A. Hajian, M. Rezaei, A. Shirzadmehr, Composite of Cu metal nanoparticles-multiwall carbon nanotubes-reduced graphene oxide as a novel and high performance platform of the electrochemical sensor for simultaneous determination of nitrite and nitrate, J. Hazard. Mater. 324 (2017) 762–772. http://dx.doi.org/10.1016/j.jhazmat.2016.11.055.