

## Preparation of a novel Cu-Sn-Bi cathode and performance on nitrate electroreduction

Weichun Gao, Lulu Gao, Jing Meng, Dan Li, Yinyan Guan, Li Cui, Xinjun Shen and Jiyan Liang

### ABSTRACT

Cu-Sn-Bi layer coated on Ti substrate was prepared using electrodeposition method and applied as cathode material for electrochemical reduction of nitrate in this research. Linear sweep voltammetry (LSV), chronoamperometry (CA), scanning electron microscope (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) were used to scrutinize the electrochemical performance and the cathode materials. LSV results illustrated that Cu-Sn-Bi cathode possessed the ability for nitrate reduction. Preparation conditions including deposition time, current density, temperature and the content of Bi were optimized based on  $\text{NO}_3^-$  removal and byproducts selectivity. Results showed that the cathode with Bi content of 3.18 at.%, and electrodepositing at current density of  $6 \text{ mA cm}^{-2}$ ,  $35^\circ\text{C}$  for 30 min achieved the best performance during the experiment. The increase of Bi content could improve the electrocatalytic activity and stability of the cathode. Compared with other common researched cathodes (Cu and Fe), Cu-Sn-Bi (3.18 at.%) exhibited better performance, i.e. the highest  $\text{NO}_3^-$  removal of 88.43% and the selectivity of harmless  $\text{N}_2$  was 77.80%. The kinetic studies showed that the reduction of nitrate on Cu-Sn-Bi followed pseudo-first-order kinetics.

**Key words** | electrochemical, reduction, nitrate, Cu-Sn-Bi cathode

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### INTRODUCTION

Nitrate is a worldwide contaminant of groundwater which poses potential human health risk (Sun & Nemati 2012). Although nitrate is a non-toxic ion, nitrite, a byproduct produced in the nitrate reduction process, is precursor to many carcinogens and binds to hemoglobin in the blood to hinder oxygen transport (Gupta *et al.* 2000; Majumdar & Gupta 2000; Shrimali & Singh 2001). The maximum limit  $\text{NO}_3^-$  in drinking water is 11.3 mg/L as recommended by World Health Organization (WHO 2011), and the value cannot exceed 10 mg/L in USA (USEPA 2004) and China (China 2006).

Traditional methods such as biological denitrification (Park & Yoo 2009; Mook *et al.* 2012), reverse osmosis (Schoeman & Steyn 2003), electrodialysis (Zhou *et al.* 2007; Kikhavani *et al.* 2014; Pirsahab *et al.* 2016), and ion exchange (Oscar *et al.* 2009) have the problems such as high cost, poor performance, and secondary pollution in the removal of nitrate from water (Dima *et al.* 2003; Duca & Koper 2012). Compared to traditional methods, the electrochemical can completely convert nitrate into nitrogen,

and has high reaction rate and high removal efficiency. Therefore, it is considered to be the most promising environment-friendly technology for nitrate removal (Liang *et al.* 2015).

So far, many cathode materials have been investigated for their activity towards nitrate reduction and selectivity for nitrogen formation, including Pd (Souza-Garcia *et al.* 2009), Pt (Estudillo-Wong *et al.* 2011; Yang *et al.* 2013), Rh (Tucker *et al.* 2004), Cu (Bouzek *et al.* 2001; Lima *et al.* 2012; Pérez-Gallent *et al.* 2017), Sn (Ambrosioni *et al.* 2013), Bi (Dortsiou & Kyriacou 2009; Katsounaros *et al.* 2009), Fe (Li *et al.* 2010), Pd-Cu (Reyter *et al.* 2009; Zhang *et al.* 2014; Mattarozzi *et al.* 2017), Cu-Zn (Fan *et al.* 2013), and Cu-Ni (Mattarozzi *et al.* 2013). Direct selective electroreduction of nitrogen oxyanions to  $\text{N}_2$  has been reported only seldom in the literature with serious drawbacks (Mattarozzi *et al.* 2013). Pb is not applied due to its high toxicity, electrodes based on expensive noble metals like Pt, Pd or Pd-Rh (Cheng *et al.* 2005) alloys showed great potential in nitrate reduction with many problems yet to be solved, such as

cathode cost, undesirable byproducts, which limits their application. Thus, research attention is focused on electrochemical reduction of nitrate to obtain higher activity and cheaper cathode materials. In the light of previous studies, as cathode materials for electrochemical reduction of nitrate, multi-metal electrodes have become a trend. Nitrate reduction on Cu-Sn cathode is expected to produce  $\text{NH}_3$ , not the desired harmless  $\text{N}_2$  (Polatides & Kyriacou 2005). Bismuth appears to be the most promising amongst the metals studied, since it exhibits high current efficiency (CE) as well as low corrosion rates (Dortsiou *et al.* 2013; Gao *et al.* 2018). Doping of metal Bi to Cu-Sn may improve the effectiveness.

To our knowledge, there is no detailed study about Cu-Sn-Bi cathode for nitrate reduction. In this research, Cu-Sn-Bi was coated on Ti substrate by electrodeposition method and worked as cathode material in electroreduction of nitrate. The electrocatalytic activity of Cu-Sn-Bi cathode was improved by optimizing cathode preparation conditions. The influences of electrodeposition times, temperature, current density and different Bi contents were studied. Their morphological, structural properties and stability were characterized by scanning electron microscope (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and chronoamperometry (CA). The linear sweep voltammetry (LSV) was used to measure electrochemical behavior. Nitrate reduction characterization of Cu-Sn-Bi cathode was researched by ultraviolet-visible spectroscopy (UV-Vis).

## EXPERIMENTAL

### Preparation and characterization of Cu-Sn-Bi electrodes

Electrodeposition method was used to prepare the Cu-Sn-Bi layers. Cu-Sn-Bi/Ti was prepared by the following procedure: Ti plates (purity > 99.9%) were used as substrate with dimensions of 40 mm × 50 mm × 1 mm. Firstly, the Ti plates was mechanically polished using sandpapers (120 mesh and 240 mesh) to remove oxides on surface, followed by immersing in a 40% sodium hydroxide at 80 °C for 1 h, then etched in a micro-boiling 10% oxalic acid solution for 1 h, and rinsed with ultra-pure water. Electrodepositions were performed in a single compartment cell with constant current. The electrodeposition solution consists of  $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_4\text{P}_2\text{O}_7$ ,  $\text{Cu}_2\text{P}_2\text{O}_7$ ,  $\text{Sn}_2\text{P}_2\text{O}_7$ , KCl, EDTA-2Na, and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , with the molar ratio of the Cu, Sn and Bi as 100:6:x (x = 1,3,5,7,9). The chemicals used are

analytical reagent and purchased in Tianjin, China. Using graphite as anode, electrodepositions were carried out while stirring the solution using a magnetic stirrer. After deposition, the electrodes were thoroughly rinsed in water, dried and examined.

The morphology of the cathodes was analyzed by SEM (Hitachi, Japan) equipped with an EDS analyzer for elemental analysis. The microstructure was examined by XRD measurements on a XRD-7000 X-ray diffractometer (Shimadzu, Japan) with  $\text{CuK}\alpha$  radiation and working at 40 kV/30 mA.

### Electrolysis experiments

A Teflon electrochemical undivided cell with a total volume of 400 mL was used in all experiments. Simulated nitrate wastewater reduction experiments were carried out by DC power supply (Shuangxu, China), and 0.125 mol/L  $\text{Na}_2\text{SO}_4$  as the supporting electrolyte. Both the immersed areas of Ti/Cu-Sn-Bi cathode and Ti/ $\text{IrO}_2$ - $\text{RuO}_2$  anode were 40 cm<sup>2</sup> (4 cm × 5 cm × 2). The distance between the two electrodes was maintained constantly at 2 cm. The initial concentration of  $\text{NO}_3^-$  was 100 mg/L. The experiments were carried out for a period of 5 h at initial pH of 7 and current intensity of 6 mA/cm<sup>2</sup>. The experimental conditions for electroreduction of nitrate on Cu and Fe cathodes were consistent with Cu-Sn-Bi. After electrolysis, all analyses were conducted following standard method, the concentrations of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ -N were determined by UV-vis spectroscopy (HACH, USA) (Wang *et al.* 2011; Zhu & Chen 2013; Liu *et al.* 2016).

The removal efficiency of nitrate (RE), the selectivity to nitrite, ammonium and nitrogen (S) for nitrate electrolysis and the CE were defined by the following equations:

$$\text{RE}(\%) = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

$$S(\%) = [S_t/(C_0 - C_t)] \times 100 \quad (2)$$

$$\text{CE}(\%) = [(C_0 - C_t) \times V / (M \times Q)] \times n \times 96485 \times 100 \quad (3)$$

where  $C_0$  and  $C_t$  are the  $\text{NO}_3^-$  concentration at the beginning and at the instant  $t$  of the electrolysis, respectively,  $S_t$  is the formed species ( $\text{NO}_2^-$ ,  $\text{NH}_4^+$ -N) in the electrolysis course, and the selectivity to  $\text{N}_2$ , defined  $S_t$  as  $C_0 - C_t - C_{(\text{NO}_2^-)_t} - C_{(\text{NH}_4^+)_t}$ ,  $M$  is the molar mass of nitrogen, 14 g mol<sup>-1</sup>,  $Q$  is the amount of electricity passed through the electrode,  $n$  is the total number of electrons that  $\text{NO}_3^-$  is reduced (calculated according to the conversion of nitrate nitrogen to nitrogen,  $n = 5$ ).

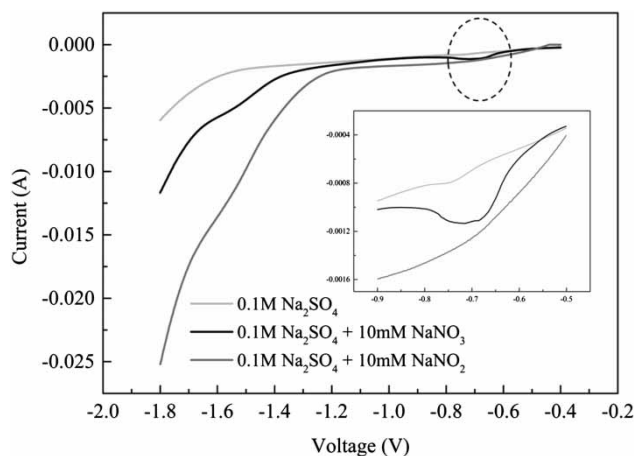
## Electrochemical measurements

Linear sweep voltammetry (LSV) and Chronoamperometry (CA) measurements were performed with an electrochemical workstation (WonATech, Korea). Cu-Sn-Bi electrode with area of  $1 \text{ cm}^2$  as working electrode, a Pt-plate ( $1.5 \times 1.5 \text{ cm}^2$ ) as counter electrode and saturated calomel electrode (SCE) as reference electrode were employed.

## RESULTS AND DISCUSSION

### Electrochemical behavior analysis

The LSV curves of Cu-Sn-Bi cathode in the absence and presence of  $\text{NO}_3^-$  or  $\text{NO}_2^-$  were measured. As shown in Figure 1, in the base electrolyte, the current increased rapidly at about  $-1.6 \text{ V}$ , the main process was the initiation of hydrogen evolution by water electrolysis. When the nitrate or nitrite was added, the current was significantly higher than that in base electrolyte. This behavior indicated that nitrate and nitrite might undergo a reduction reaction on Cu-Sn-Bi cathode. The LSV curves of Cu-Sn-Bi cathode in the presence of  $10 \text{ mM}$  nitrate in  $0.1 \text{ M Na}_2\text{SO}_4$  showed two reduction waves at  $-0.6 \text{ V}$  to  $-0.8 \text{ V}$  and  $-1.5 \text{ V}$ , respectively. The LSV obtained in the presence of  $10 \text{ mM}$  nitrite in  $0.1 \text{ M Na}_2\text{SO}_4$  exhibited a similar shape except that the wave at about  $-0.6 \text{ V}$  to  $-0.8 \text{ V}$  did not appear. It might be assigned to the reduction of nitrate to nitrite at about  $-0.6 \text{ V}$  to  $-0.8 \text{ V}$ , while at about  $-1.5 \text{ V}$  might be attributed to the reduction of nitrite to ammonia (Reyter et al. 2008). This suggested that Cu-Sn-Bi cathode possess the ability for nitrate reduction.



**Figure 1** | Linear sweep voltammetry (LSV) curves of Cu-Sn-Bi cathode in the absence and presence  $\text{NO}_3^-$  or  $\text{NO}_2^-$ .

## Electrodeposition of Ti/Cu-Sn-Bi by galvanostatic method

### Effect of deposition time

Table 1 presents the effect of deposition time on  $\text{NO}_3^-$  removal and  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ -N selectivity. The initial  $\text{NO}_3^-$  concentration was  $100 \text{ mg L}^{-1}$  and the total treatment time was  $5 \text{ h}$ ,  $72.88\%$   $\text{NO}_3^-$  was removed and the selectivity of  $\text{NO}_2^-$  and  $\text{NH}_4^+$ -N was  $19.52\%$ ,  $43.14\%$  with the deposition time of  $30 \text{ min}$ . When deposition time was above  $30 \text{ min}$ , the nitrate removal gradually decreased, and more byproducts were generated. As the deposition time becomes longer, the concentrations of ions in solution decreases, some of the impurity ions are adsorbed on the surface of the plating layer, it may influence electroreduction of nitrate. Hence,  $30 \text{ min}$  is selected as the optimal electrodeposition time.

### Effect of current density

Table 2 shows the effect of current density on  $\text{NO}_3^-$  removal and  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ -N selectivity. The initial  $\text{NO}_3^-$  concentration was  $100 \text{ mg L}^{-1}$  and the treatment time was  $5 \text{ h}$ . The  $\text{NO}_3^-$  removal increased from  $59.01\%$  to  $76.54\%$  with current density rising from  $2 \text{ mA cm}^{-2}$  to  $4 \text{ mA cm}^{-2}$ , then decreased to  $55.74\%$  and  $48.81\%$  at  $6 \text{ mA cm}^{-2}$  and  $8 \text{ mA cm}^{-2}$ . The selectivity of  $\text{NO}_2^-$  and  $\text{NH}_4^+$ -N was lower at  $4 \text{ mA cm}^{-2}$ , indicating fewer byproducts generated, and the greater the possibility of the formation of  $\text{N}_2$ . When the current density is smaller, the grain growth rate is slower, and it is easy to form a flat morphology. Proper increase in the current density may refine the grain, thereby obtaining a fine crystal structure to form a larger surface area, and accelerating the deposition rate to shorten the electrodeposition time. However, an excessively large current density will lead to an increase in hydrogen evolution, which will cause the plating layer to generate cracks. Therefore,  $4 \text{ mA cm}^{-2}$  is chosen as the optimal current density.

**Table 1** | Effect of electrodeposition time on  $\text{NO}_3^-$  reduction ( $400 \text{ mL}$ ,  $100 \text{ mg/L NO}_3^-$ ,  $5 \text{ h}$ )

| Electrodeposition time (min) | $\text{RE}_{\text{NO}_3^-}$ (%) | $\text{S}_{\text{NO}_2^-}$ (%) | $\text{S}_{\text{NH}_4^+}$ -N (%) | $\text{S}_{\text{N}_2}$ (%) |
|------------------------------|---------------------------------|--------------------------------|-----------------------------------|-----------------------------|
| 15                           | 63.17                           | 15.49                          | 48.87                             | 35.65                       |
| 30                           | 76.54                           | 17.33                          | 37.11                             | 45.56                       |
| 45                           | 72.88                           | 22.23                          | 48.92                             | 28.85                       |
| 60                           | 47.13                           | 19.52                          | 43.14                             | 37.34                       |

**Table 2** | Effect of current density on NO<sub>3</sub><sup>-</sup>N reduction (400 mL, 100 mg/L NO<sub>3</sub><sup>-</sup>N, 5 h)

| Current density (mA cm <sup>-2</sup> ) | RE <sub>NO<sub>3</sub><sup>-</sup>-N</sub> (%) | S <sub>NO<sub>2</sub><sup>-</sup>-N</sub> (%) | S <sub>NH<sub>4</sub><sup>+</sup>-N</sub> (%) | S <sub>N<sub>2</sub></sub> (%) |
|--|--|---|---|--------------------------------|
| 2                                      | 59.01  | 24.02   | 44.08   | 31.90                          |
| 4                                      | 76.54  | 17.33   | 37.11   | 45.56                          |
| 6                                      | 55.74  | 28.74   | 52.93   | 18.33                          |
| 8                                      | 48.81  | 12.29   | 84.63   | 3.08                           |

### Effect of deposition temperature

Table 3 shows the effect of deposition temperature on NO<sub>3</sub><sup>-</sup>N removal and NO<sub>2</sub><sup>-</sup>N, NH<sub>4</sub><sup>+</sup>-N selectivity. The initial NO<sub>3</sub><sup>-</sup>N concentration was 100 mg L<sup>-1</sup> and the treatment time was 5 h. It was found that with temperature increase, the NO<sub>3</sub><sup>-</sup>N removal increased first and then decreased. Nitrate removal achieved 84.86% using the cathode prepared at 35 °C, and byproducts generation was relatively small, and the selectivity of N<sub>2</sub> reached 54.04%. The selectivity of nitrite increased when the temperature was above 35 °C, increasing from 7.37% (35 °C) to 17.17% (55 °C), but nitrite was the undesirable byproduct. Using a cathode prepared at different temperatures for electroreduction nitrate, the selectivity of ammonia did not show significant differences. When the temperature is low, the diffusion rate of ions is slow, and the concentration polarization is large, resulting in poor adhesion of the plating layer. As the temperature increases, the diffusion and migration speed of the ions is high and the concentration polarization is small. But if the temperature is too high, the coating will crack. So, the optimum deposition temperature is 35 °C.

### Effect of Bi content

The content of Bi metal element of the Cu-Sn-Bi electrode was measured by EDS, the results showed that the actual values of Bi were 1.32 at.%, 2.11 at.%, 2.71 at.%,

**Table 3** | Effect of electrodeposition temperature on NO<sub>3</sub><sup>-</sup>N reduction (400 mL, 100 mg/L NO<sub>3</sub><sup>-</sup>N, 5 h)

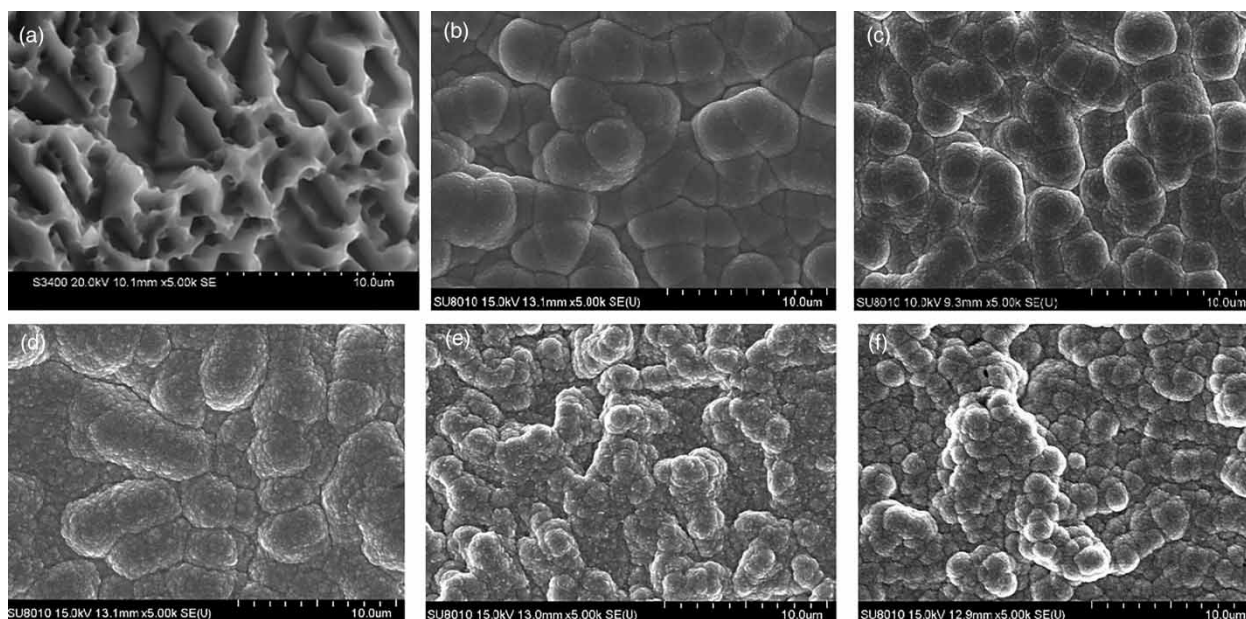
| Electrodeposition temperature (°C) | RE <sub>NO<sub>3</sub><sup>-</sup>-N</sub> (%) | S <sub>NO<sub>2</sub><sup>-</sup>-N</sub> (%) | S <sub>NH<sub>4</sub><sup>+</sup>-N</sub> (%) | S <sub>N<sub>2</sub></sub> (%) |
|------------------------------------|--|---|---|--------------------------------|
| 25                                 | 76.54  | 17.33   | 37.11   | 45.56                          |
| 35                                 | 84.86  | 7.37  | 38.60   | 54.04                          |
| 45                                 | 82.49  | 11.51   | 26.36   | 52.71                          |
| 55                                 | 63.96  | 17.17   | 33.99   | 48.85                          |

2.98 at.%, and 3.18 at.%, which were lower than the theoretical value. The deposition potential and deposition order of the metal were different. As the electrodeposition progressed, the metal ions in the plating bath were not replenished or reduced, which might be the cause of the inconsistency between the composition of the layers and the bath. The SEM images of the deposited Cu-Sn-Bi coatings with different contents of Bi are shown in Figure 2. It could be seen that electrodes surface was covered completely. Compared with other micrographs, surface of electrode with Bi content 3.18 at.% possessed smaller particles size. The coating particles of Cu-Sn-Bi electrode were more compact than other electrodes, providing more reactive sites and increasing the electrochemical activity of electrodes.

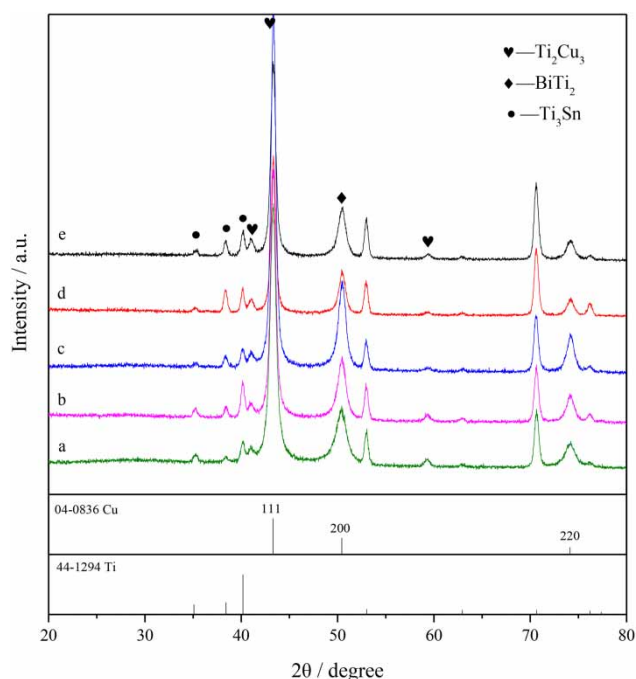
XRD analysis was used to research the crystal structure of Cu-Sn-Bi electrodes. The XRD patterns of Cu-Sn-Bi electrode with different contents of Bi could be seen in Figure 3. In the spectra, it could be confirmed that all the electrodes revealed the presence of square structure of Cu with peaks corresponding to (111), (200), and (220). No crystalline Sn and Bi peaks were detected. In addition, no peaks corresponding to Sn oxides and Bi oxides were detected, indicating that no oxide phase formed related with Sn and Bi. Due to the low content of Sn and Bi element, the BiTi<sub>2</sub> and Ti<sub>3</sub>Sn phases might be formed. However, since the crystallinity was not high, and based on the relationship between diffraction peak intensity and volume fraction of the phase, the volume fraction of the formed phase in the sample was low. As a result, there were no obvious characteristic peaks in XRD detection.

The electrochemical stability is an important factor for Cu-Sn-Bi cathode to be applied in an industrial scale. It was investigated by CA under -1.4 V as shown in Figure 4. As the Bi content increased, the current decay gradually decreased. The Cu-Sn-Bi (3.18 at.%) demonstrated excellent stability as no marked current decay was observed. For 1.32 at.% Bi content, a remarkable current decay was observed, implying its poor stability. The increase of Bi content not only improves the electrocatalytic activity of the cathode for nitrate reduction, but also enhances its stability. The cathode with 3.18 at.% Bi has excellent stability in this work.

Table 4 shows the effect of Bi content on NO<sub>3</sub><sup>-</sup>N removal and NO<sub>2</sub><sup>-</sup>N, NH<sub>4</sub><sup>+</sup>-N selectivity. The initial NO<sub>3</sub><sup>-</sup>N concentration was 100 mg L<sup>-1</sup> and the treatment time was 5 h. With the increase of the content of Bi, the NO<sub>3</sub><sup>-</sup>N removal increased from 69.02% to 88.43%. It was observed that when the Bi increased, the byproducts were less. Consequently, the selectivity to NH<sub>4</sub><sup>+</sup>-N and NO<sub>2</sub><sup>-</sup>N were the lowest using the Cu-Sn-Bi cathode with Bi content of

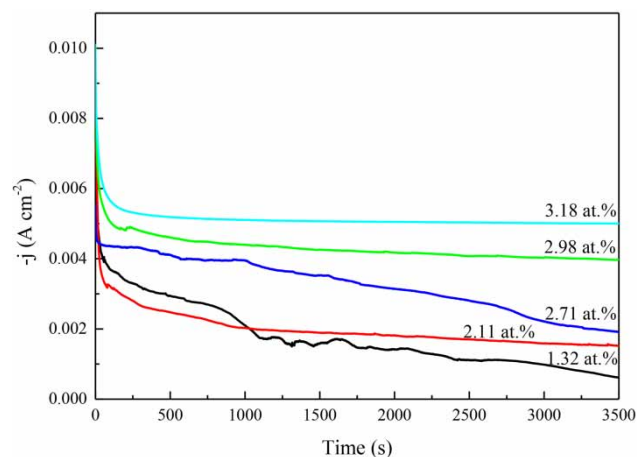


**Figure 2** | SEM images of Cu-Sn-Bi electrodes with different contents of Bi: (a) pre-treated Ti plate, (b) 1.32 at.%, (c) 2.11 at.%, (d) 2.71 at.%, (e) 2.98 at.%, (f) 3.18 at.%.



**Figure 3** | XRD patterns of Cu-Sn-Bi electrode with different contents of Bi: (a) 1.32 at.%, (b) 2.11 at.%, (c) 2.71 at.%, (d) 2.98 at.%, (e) 3.18 at.%.

3.18 at.%. Furthermore, the  $\text{NO}_2\text{N}$  selectivity decreased gradually with increasing Bi content, and  $\text{NO}_2\text{N}$  was recognized as an intermediate for the degradation of nitrates, it could be inferred that Bi offer active sites for intermediate N-species degradation.



**Figure 4** | Chronoamperometric curves of Cu-Sn-Bi electrode with different contents of Bi in 0.1 M  $\text{Na}_2\text{SO}_4$  + 10 mM  $\text{NaNO}_3$  at  $-1.4$  V.

### Comparison with other cathodes

The degradation performance of  $100 \text{ mg L}^{-1} \text{NO}_3\text{N}$  by Cu-Sn-Bi (3.18 at.%) cathode was compared with Cu and Fe cathode. The results are shown in Figure 5. Cu and Fe are commonly used cathode materials in electrochemical reduction of  $\text{NO}_3\text{N}$ . As shown in Figure 5(a), Cu-Sn-Bi cathode exhibited higher  $\text{NO}_3\text{N}$  removal efficiency than Cu and Fe. 88.43%  $\text{NO}_3\text{N}$  removal efficiency could be achieved on Cu-Sn-Bi cathode after 3 h treatment, whereas only 81.75% and 78.56% for Cu and Fe cathode, respectively.

**Table 4** | Effect of different contents of Bi on NO<sub>3</sub><sup>-</sup>N reduction (400 mL, 100 mg/L NO<sub>3</sub><sup>-</sup>N, 5 h)

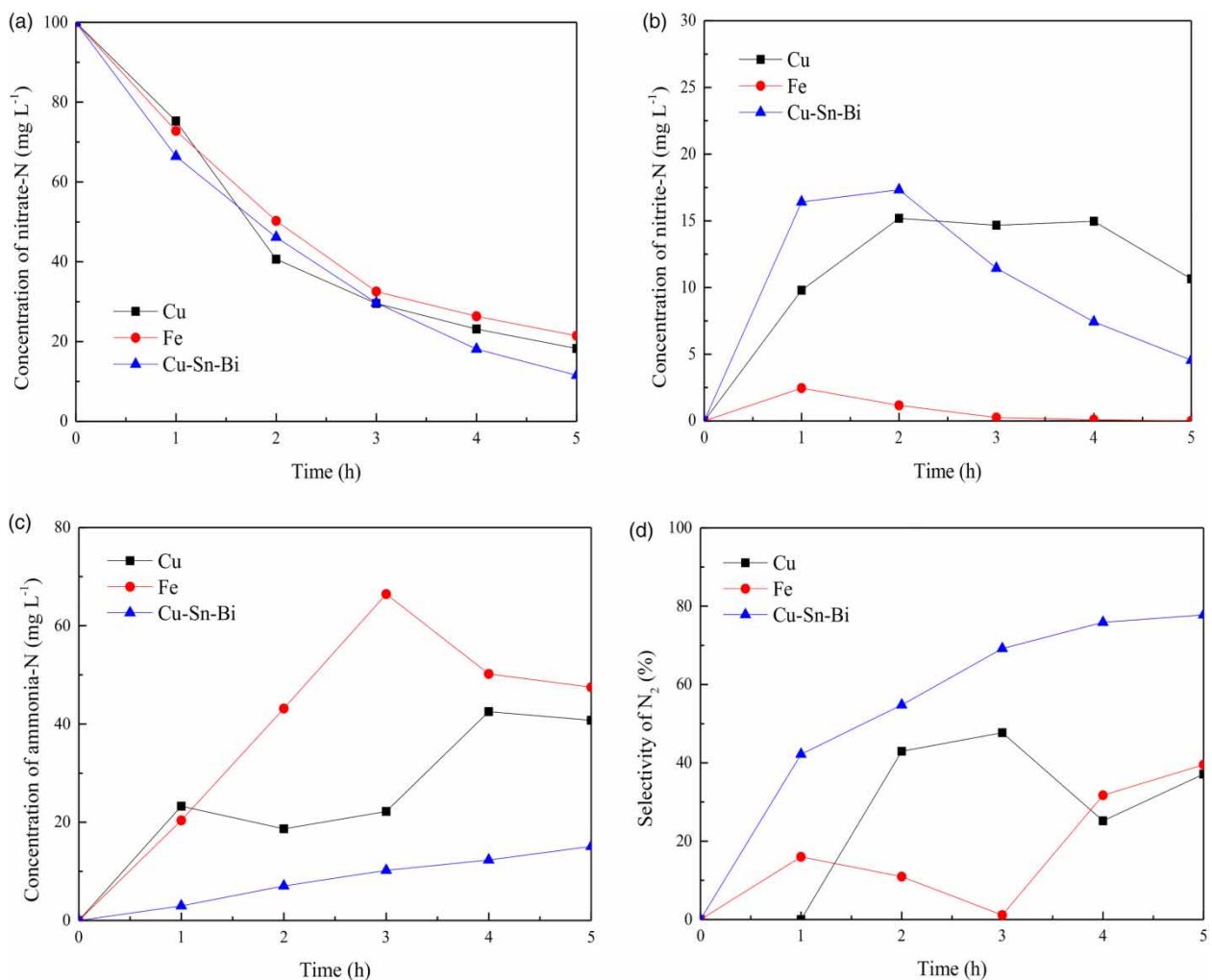
| Bi content (at.%) | RE <sub>NO<sub>3</sub><sup>-</sup>-N</sub> (%) | S <sub>NO<sub>2</sub><sup>-</sup>-N</sub> (%) | S <sub>NH<sub>4</sub><sup>+</sup>-N</sub> (%) | S <sub>N<sub>2</sub></sub> (%) |
|-------------------|--|---|---|--------------------------------|
| 1.32              | 69.02  | 10.97   | 41.79   | 47.24                          |
| 2.11              | 84.86  | 7.37  | 38.60   | 54.04                          |
| 2.71              | 71.79  | 7.85  | 52.79   | 39.36                          |
| 2.98              | 77.34  | 6.82  | 21.18   | 72.01                          |
| 3.18              | 88.43  | 5.27  | 17.04   | 77.68                          |

Shown in Figure 5(b), Fe cathode exhibited much lower NO<sub>2</sub><sup>-</sup>N generation performance than other cathodes, Fe owed the selectivity of nitrate reduction to ammonia (Figure 5(c)), which was consistent with previous studies (Li *et al.* 2009). For Cu and Cu-Sn-Bi cathodes, a large amount of NO<sub>2</sub><sup>-</sup>N was generated at the beginning of the reaction (in first 2 h). It gradually decreased with reaction time

increase, which indicated that NO<sub>2</sub><sup>-</sup>N could be an intermediate product.

It can be seen from Figure 5(c) that NH<sub>4</sub><sup>+</sup>-N is the main product for Fe and Cu cathodes. For Fe cathode, the concentration of NH<sub>4</sub><sup>+</sup>-N increased to 66.45 mg L<sup>-1</sup> in the first 3 h, and then dropped to 47.48 mg L<sup>-1</sup> after 5 h treatment. This could be due to the production of NH<sub>4</sub><sup>+</sup>-N on cathode which was further oxidized to N<sub>2</sub> on anode. For Cu and Cu-Sn-Bi cathodes, NH<sub>4</sub><sup>+</sup>-N generation increased with treatment time, after 5 h, the NH<sub>4</sub><sup>+</sup>-N concentration obtained by Cu-Sn-Bi was minimal, indicating Cu-Sn-Bi attributed its higher NO<sub>3</sub><sup>-</sup>N reduction activity to N<sub>2</sub> compared to other cathodes.

As shown in Figure 5(d), Cu cathode removed a larger amount of NO<sub>3</sub><sup>-</sup>N than Fe, the selectivity of N<sub>2</sub> was as low as that obtained by Fe cathode. Most of the NO<sub>3</sub><sup>-</sup>N transferred to NO<sub>2</sub><sup>-</sup>N and NH<sub>4</sub><sup>+</sup>-N. For Cu-Sn-Bi, due to the high NO<sub>3</sub><sup>-</sup>N

**Figure 5** | (a) NO<sub>3</sub><sup>-</sup>N concentration, (b) NO<sub>2</sub><sup>-</sup>N concentration, (c) NH<sub>4</sub><sup>+</sup>-N concentration and (d) N<sub>2</sub> selectivity obtained by different cathode materials (400 mL, 100 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>N, 5 h).

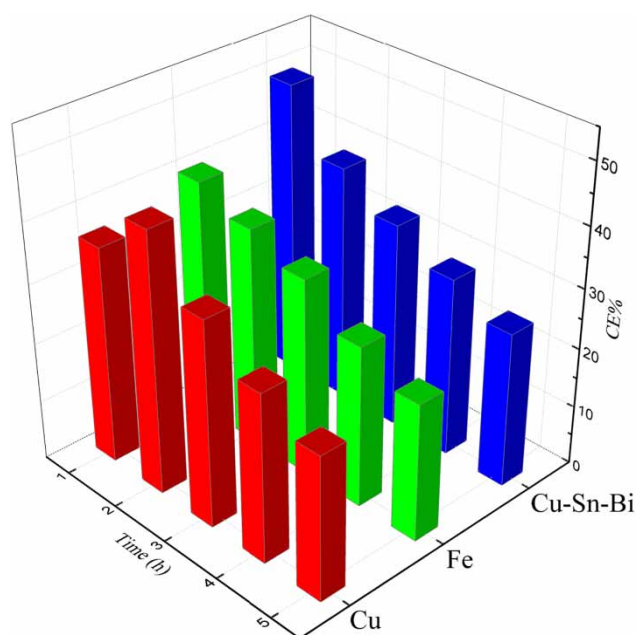


Figure 6 | Current efficiency with time on different cathodes.

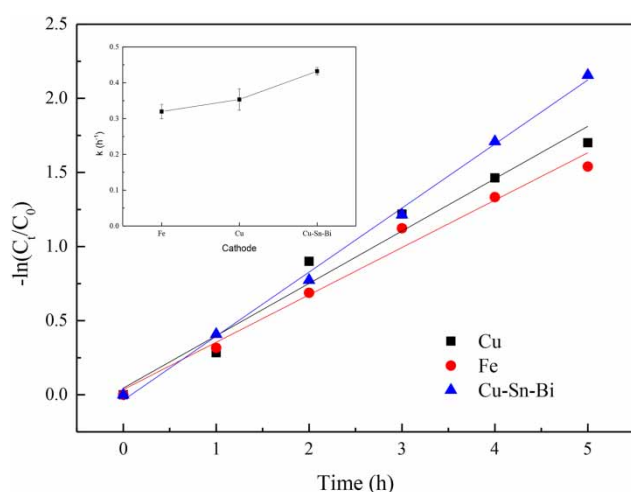


Figure 7 | Kinetics curve of  $\text{NO}_3^-$  degradation.

Table 5 | Comparison of electroreduction of nitrate on different cathodes

| Cathode                         | Anode                       | Initial $\text{NO}_3^-$ | Condition           | $\text{NO}_3^-$ removal | $\text{N}_2$ selectivity | Reference                  |
|---------------------------------|-----------------------------|-------------------------|---------------------|-------------------------|--------------------------|----------------------------|
| Cu-Sn-Bi                        | $\text{IrO}_2\text{-RuO}_2$ | $100 \text{ mg L}^{-1}$ | $6 \text{ mA/cm}^2$ | 5 h, 88.4%              | 5 h, 77.8%               | This Study                 |
| Bi                              | Pt                          | 0.05 M                  | -1.8 V              | 5 h, 70%                | 5 h, 58%                 | Dortsiou & Kyriacou (2009) |
| BDD                             | BDD                         | 6.9 mM                  | $400 \text{ A/m}^2$ | 5 h, 49%                | 5 h, 49%                 | Perez et al. (2012)        |
| Ti/ $\text{Cu}_5\text{-Pd}_5$   | Pt                          | $25 \text{ mg L}^{-1}$  | -0.9 V              | 24 h, 9.4%              | 24 h, 29.3%              | Zhang et al. (2014)        |
| $\text{Pd}_{80}\text{-Cu}_{20}$ | Pt                          | 0.1 M                   | -0.93 V             | 7d, 79%                 | 7d, 6%                   | Reyter et al. (2009)       |

reduction activity, the selectivity of  $\text{N}_2$  achieved 77.80% after 5 h treatment, which was much better than 37.10% and 39.55% that was obtained by Cu and Fe cathodes.

The CE on different cathodes is shown in Figure 6. The figure suggested that the CE decreased gradually with time on different cathodes. The CE values on the different cathodes were 36.41% (Cu), 40.02% (Fe), 49.42% (Cu-Sn-Bi) at 1 h. At 5 h, the values of CE on the cathode were 24.08% (Cu), 23.14% (Fe), and 26.04% (Cu-Sn-Bi). The Cu-Sn-Bi cathode had a highest CE in electroreduction nitrate.

Figure 7 shows the kinetics of nitrate removal on different cathodes. The decrease in the concentration of nitrate over time followed pseudo-first-order kinetics. The first-order rate constants decreased in the order of Cu-Sn-Bi ( $0.43 \text{ h}^{-1}$ ) > Cu ( $0.35 \text{ h}^{-1}$ ) > Fe ( $0.32 \text{ h}^{-1}$ ) as shown in Figure 7. Evidently, the reaction rate of electrochemical reduction nitrate was faster on the Cu-Sn-Bi cathode.

For comparison, the nitrate electroreduction on different cathodes, was summarized in Table 5.

## CONCLUSION

Cu-Sn-Bi layer coated on Ti substrate was prepared using electrodeposition method and applied as cathode material for electrochemical reduction of nitrate. LSV results illustrated that Cu-Sn-Bi cathode possessed the ability for nitrate reduction.  $\text{NO}_3^-$  might first be adsorbed on Cu-Sn-Bi cathode surface at about -0.6 V to -0.8 V, and then reduced from nitrate to nitrite. Then it was further reduced to ammonia at about -1.5 V. The cathode with Bi amount of 3.18 at.%, and electrodepositing at current density of  $6 \text{ mA cm}^{-2}$ ,  $35^\circ\text{C}$  for 30 min achieved the best performance. The increase of Bi content could improve the electrocatalytic activity and enhance stability of the cathode. Comparatively, the performance obtained by Cu-Sn-Bi (3.18 at.%) was much better than those obtained by Cu and Fe cathodes. For  $100 \text{ mg L}^{-1}$   $\text{NO}_3^-$ , 88.43%  $\text{NO}_3^-$

removal could be achieved for 5 h treatment at current density of  $6 \text{ mA cm}^{-2}$ , and the selectivity of  $\text{N}_2$  up to 77.80%. Comparably, Fe was more beneficial for ammonia generation. The electrochemical reduction of nitrate on Cu-Sn-Bi (3.18 at.%) followed the pseudo-first-order reaction model, with a  $k$  value of  $0.43 \text{ h}^{-1}$ . In this study, it was concluded that the Cu-Sn-Bi (3.18 at.%) cathode was effective for nitrate reduction.

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