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Efficient electrochemical nitrate reduction by bismuth nanosheets arrays *in-situ* grown on carbon cloth

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Excessive nitrate-containing in water pose great threat to the environment and public health. Tin as the nitrate promoter metal has been widely studied on the nitrate reduction reaction (NITRR), but it suffers unsatisfactory efficiency and unideal final-product selectivity at times. As the same main group metal as tin, bismuth have shown excellent performance in electrochemical reduction fields, but rarely focused on the NITRR performance. Here, the two-dimensional bismuth nanosheet *in-situ* grown on carbon cloth (Bi-CC) are designed and synthesized, which ensures the enlarged surface area and high electrical conductivity. The results showed that the nitrate removal efficiency reached to nearly 90% and the ammonia selectivity reached to 80% with none nitride generated as the final-product after 120 mins treatment of 10 mA cm^{-2}. Investigations on the effect of reaction parameters (PH, current density, chlorine concentration) for the nitrate reduction indicated that the nitrate reduction was improved with low nitrite selectivity at acid PH and the current density of 10 mA cm^{-2} presented the lowest energy consumption and satisfied NITRR efficiency, the presence of chlorine have no negative effect on the NITRR efficiency. The electrochemical analysis and scavenging experiments confirmed the mechanism of nitrate reduction are relying on the direct electron transfer and generated atomic H* during the process. Besides, the NITRR performance of Bi-CC was also verified by actual garbage fly ash wastewater, efficient nitrate reduction and harmful metal removal are achieved in the actual industrial wastewater. This study provides a new kind of materials for converting the harmful nitrate in industrial wastewater to the valuable feedstock chemical ammonia in high efficiency.

1. Introduction

Nitrate (QR_6^0) contained in the wastewater is a worldwide concerning problem, since the easy transformation from QR_6^0 to the harmful nitrite (QR_5^0) posed great theatre to human health, such as cancer, liver damage, and other health problems (Yao et al., 2019). Biological method, ion exchange, electrochemical reduction and other methods have been proposed to remove QR_6^0 in the wastewater (Jonoush et al., 2020). However, most of them have more or less drawbacks in time-consuming, low target product selectivity, complex post-treatment procedures (Duan et al., 2019). Among them, electrochemical technology attracts most attentions with the advantages of simple operation and no chemical addition.

In QR_6^0 reduction process, QR_5^0, nitrogen (N_2), and ammonium (QK_7^+) are the main reductive products. In past years, many efforts were devoted to converting QR_6^0 to N_2, which is seen as a clean resource (Tokazhanov et al., 2020). Recently, a new concept of electrochemical QR_6^0 reduction reaction (NITRR) to QK_7^+ was put forward (Chen et al., 2020). In terms of N recycling, QK_7^+ belongs to the active nitrogen, and it plays an important role in industry and agriculture generation(Chen et al., 2019). In addition, it can be easily recycled from wastewater as magnesium ammonium phosphate (Demeestere et al., 2015).

Main group metal Sn has been seen as the promoter metal for QR_6^0 reduction, but the high QR_2^0 selectivity affects its wide application(Park et al., 2019). However, the same main group metal bismuth has rarely been studied on the NITRR performance. Compared to the metal Sn, bismuth is safer with lower cost, the spatially

anisotropic and s-p orbital hybridization indicate that bismuth can be seen as active centres(Xu et al., 2019). Thus, it is assumed as a kind of ideal catalyst for NITRR process.
Bismuth is known for its high electrical resistance at room temperature, which affect its catalytic efficiency (Cornelius et al., 2008). In traditional working electrode preparation, polymers are used for the fixation of catalysts on the conductive supporting. However, not only the polymer would be played as the conductivity binder, but also the catalysts could be easily agglomerated in this way, which reduced the exposed active sites. To decrease the electron transfer energy, *in-situ* grown catalyst on conductive supporting was proposed. Carbon cloth was chosen as the conductive supporting, which has been proved to be favourable for the QR_6^0 adsorption for its high surface area (Afkhami et al., 2007).
In this work, bismuth nanosheets decorated on carbon cloth (Bi-CC) was designed and prepared by the *in-situ* topotactic transformation from the *in-situ* grown BiOCl nanosheets on carbon cloth (BiOCl-CC). And comparisons of the NITRR efficiency among different catalysts and comparative operation experiments (PH, current density, chlorine concentration) were carried out to study the catalytic activity of Bi-CC on the NITRR performance. More importantly, actual industrial wastewater was applied to verify the high NITRR efficiency of Bi-CC.

2. Materials and methods

2.1 Reagents and materials

Ethylene glycol (EG, 99.5%), potassium chloride (KCl, 99%),Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, e98%), ethanol (C_2H_6O, 99.5%), sodium nitrate ($NaNO_3$, e99%), sodium sulphate (Na_2SO_4, 99.99%) sulfuric acid (H_2SO_4, 98%), tert-butyl alcohol (TBA, 99%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Carbon cloth (WOS1009) and nafion 117 membrane (Dupont) were purchased from Tianjin Allian Electronic Technology Co., Ltd. Ultrapure water was used throughout the experiments.

2.2 Synthesis of the catalyst

The synthesis of BiOCl-CC was through one-step hydrothermal. Firstly, carbon cloth (20*40 mm^2) was pre-treated by sonicating in HNO_3, acetone, ethanol for 60 mins respectively, dried at 60°C for 2 h. Then, 0.485 g Bi $(NO_3)_3{\cdot}5H_2O$ was dispersed in 6 mL EG and 12 mL ethanol stirring for 30 mins to form a transparent solution, 0.075 g KCl was added into the solution for anther 30mins stirring. Then, the pre-treated carbon cloth was immersed in the prepared solution for 4 h, and transferring the above solution to autoclave at 160°C for 5 h, in which carbon cloth kept vertical in the autoclave. Finally, washing the carbon cloth with ethanol and water respectively and vacuum freeze-dried for 6 h. The *in-situ* transformation of Bi-CC was achieved by the cyclic voltammetry (CV) scans (100 cycles) at the scan rate of 100 mV s^{-1} from –0.8 V to 0 V vs. RHE.
The synthesis of the dropped Bi/CC was based on the following procedures. Firstly, the BiOCl was prepared by the typical hydrothermal procedure in previous study (Li et al., 2019). Then, 10 mg of the prepared BiOCl was put into the mixed solution of 0.1 mL Nafion and 1.9 mL ethanol. And the mixed solution was sonicated for 120 mins to form the catalyst inks, which was dropped onto the carbon cloth (10*20 mm^2). Finally, the BiOCl-CC was electrochemical reduced to the Bi-CC according to the above *in-situ* transformation procedures.

2.3 Material Characterization

The catalysts were examined by X-ray diffraction (XRD, Rigaku, Tokyo, Japan) with Cu-K± radiation source ((» = 1.5418 Å) in the range of 10° to 70° at a scan rate of 8° min^{-1}. Field emission scanning electron microscopy (FESEM, FEI, Apreo S LoVac, Czech Republic) was used to record the morphology of catalyst. N_2 isotherms was tested by the Quantachrome Autosorb-IQ, and the specific surface areas was calculated by the Brunauer-Emmett-Teller (BET) method.

2.4 Electrochemical measurements

In this system, IrO_2-RuO_2/Ti and the prepared working electrode (10*20 mm^2) were used as the anode and cathode respectively. The H-type electrolytic cell dividing by the Nafion membrane was used for the electrochemical experiments with 30 mL of 0.5 M Na_2SO_4 into the anode and cathode cell respectively. And 25 ppm QR_6^0 was added into the cathode cell. A DC potentiostat (DH1718E-3, Beijing Dahua Radio Instrument Co., Ltd, China) was used to supply constant current. The current density kept at 10 mA cm^{-2} at room temperature during the experiments. All the experiments were carried out three times. The electrochemical workstation (CHI700E, Chenhua, Shanghai) was used for the CV tests. A saturated calomel electrode (SCE) was taken as the reference electrode, platinum electrode and the prepared electrode (10*10 mm^2) were taken as the counter electrode and working electrode respectively.

2.5 Analysis method

The concentrations of different ions (QR_5^0, QR_6^0, QK_7^-) were determined by the UV-vis spectrophotometry. To evaluate the catalysts performance, the QR_6^0 removal efficiency, the selectivity of QK_7^- ($V_{QK_7^-}$) and QR_5^0 ($V_{QR_5^0}$) were calculated using the following equations:

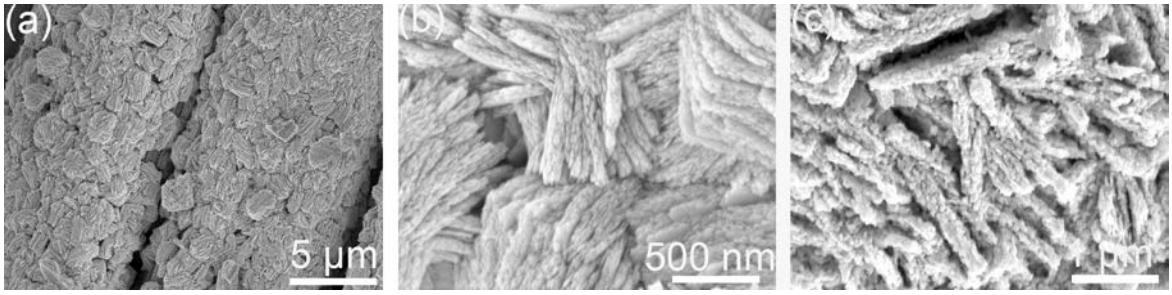

Figure 2. (a) FESEM images of the BiOCl-CC at low scales; (b) FESEM images of the BiOCl-CC at high scales. (c) FESEM images of the Bi-CC.

The synthesis of Bi-CC was through cyclic voltammetry electroreduction, the XRD pattern shows that BiOCl nanosheets grown on carbon cloth surface are fully transformed to bismuth. The characteristic peaks are perfectly corresponding to hexagonal bismuth standard card (ICDD PDF#44-1246) and carbon cloth peaks (Figure 1). The FESEM image of Bi-CC shows that the *in-situ* grown nanosheets attaches on carbon cloth firmly after the CV operation (Figure 2c). And the BET surface area increased to 5.78 m^2/g, which ensure the large surface area for supplying more reaction active sites.

3.2 NITRR performance of different catalysts

The NITRR performance of different catalysts were test. As shown in Figure 3a, owing to the adsorption ability of carbon cloth, the QR_6^0 removal efficiency reaches to 44.2%. When bismuth nanosheets are dropped on carbon cloth, the QR_6^0 removal efficiency increases to 66.6%. Furthermore, when bismuth nanosheets are evenly distributed on carbon cloth, the QR_6^0 removal efficiency reaches to nearly 90%. The above increased NITRR efficiency is due to that bismuth could donate electron for the QR_6^0 reduction process. The *in-situ* grown nanosheets owns high surface area (Table 1), which exposed more active site for the NITRR process.

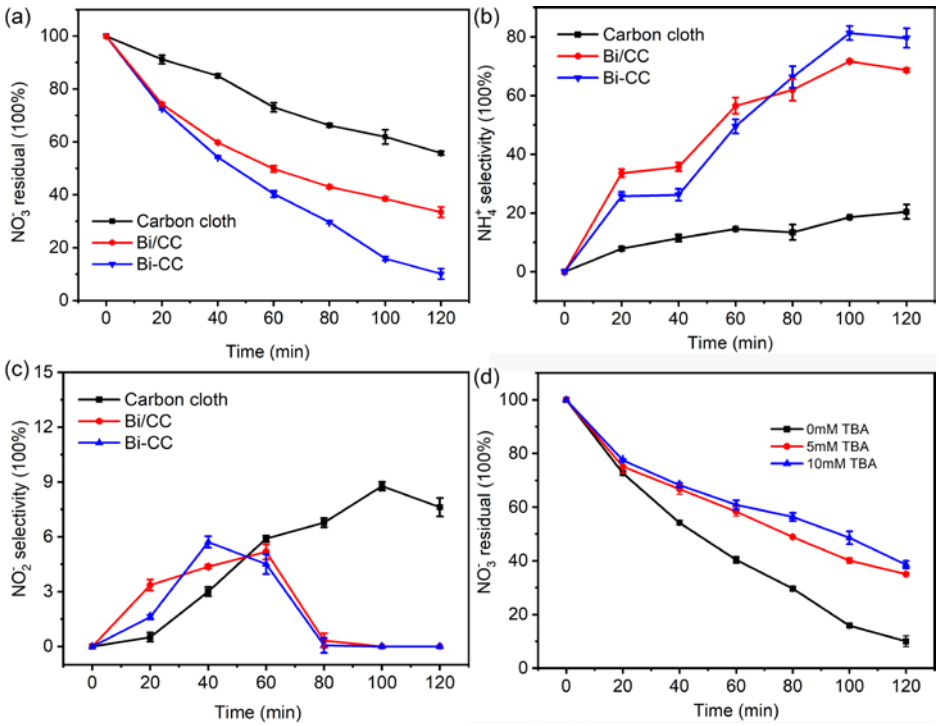

Figure 3. The NITRR efficiency of different catalysts: (a)residual QR_6^0 concentration, (b) QK_7^- selectivity, (c) QR_5^0 selectivity, (d) the QR_6^0 concentration decay of Bi-CC with different electrolyte (Reaction conditions: current density 10 mA $cm^{-2,}$ PH=3.5±0.2 and 25 ppm initial concentration of QR_6^0 for (a-d)).

The reductive products of NITRR process mainly focused on the QR_5^0 and QK_7^-. In Figure 3b, the QK_7^- selectivity of all the catalysts increased during the experiments. Bi-CC presents the highest QK_7^- selectivity of 80.2%. In addition, the QR_5^0 selectivity of carbon cloth is high, and the QR_5^0 selectivity in bismuths-based catalysts firstly

increased and finally disappeared (Figure 3c). The above phenomena are due to that bismuth could donate electrons for the QR_6^0 reduction. And the grown nanosheets present large surface area, and then exposed more active site for the NITRR process.
When different concentrations of TBA were added as H* capture, the QR_6^0 removal efficiency decreased a lot but still higher than the carbon cloth alone (Figure 3d). And there is no apparent difference in NITRR efficiency between the addition QR_6^0 of 5 mM and 10 mM, which indicates that the hinder effect of H* is completely. Therefore, direct electron transfer and generated atomic H* benefit the NITRR process.

3.3 Effect of the reaction parameters

In NITRR process, the hydrogen evolution reaction is the main competition reaction, and the consequent decrease of H^+ leads to the rise of electrolyte PH. Since PH has an important impact on the reductive production selectivity (Garcia-Segura et al., 2018), experiments were carried out at the stable pH of 3.5, 6.5, and 9.5, in which 0.1 M H_2SO_4 was added into the electrolyte to stabilize the solution PH. As shown in Table 2, PH increase has little effect in NITRR efficiency, however the QK_7^- selectivity decreased a lot at high PH and QR_5^0 becomes the main reductive products.
The NITRR performance of the catalyst is significantly influenced by the current density. The QR_6^0 removal efficiency was enhanced as the current density increased (Table 2). And complete QR_6^0 removal was achieved at the current density of 20 mA cm^{-2}. However, the QK_7^- selectivity slightly decreased as the current density increased from 10 mA cm^{-2} to 20 mA cm^{-2}. The enhanced NITRR efficiency is due to the increased electrons makes more substance changes on the electrode surface. The reduced selectivity is because of the further conversion of QR_6^0 to N_2 (Yao et al., 2019). In addition, the lowest energy consumption is 28.32 kwh/kgNO_3-N at 10 mA cm^{-2}.

Table 2: The QR_6^0 removal efficiency and the QK_7^- selectivity of Bi-CC under different reaction conditions.

Reaction parameters		QR_6^0 removal efficiency	Selectivity of QK_7^-	Selectivity of QR_5^0
PH	3.5	90%	80.2%	0
	6.5	88.3%	62.1%	11.3%
	9.5	86.3%	20.8%	48.5%
Current density (mA cm^{-2})	5	66.8%	30.7%	12.5%
	10	90%	80.2%	0
	20	100%	70.6%	0
Concentration of Cl^- (g/L)	0.5	89.1%	76.1%	0
	1	92.5%	72.3%	0
	2	95.3%	68.2%	0

The effect of Cl^- concentration on NITRR performance was investigated. As shown in Table 2, When the addition of Cl^- increases from 0.5 g/L to 2 g/L, the QR_6^0 removal efficiency promotes a little with the QK_7^- selectivity decreases. The primary reason may be that the Cl^- will be oxidized to Cl_2 and the generated Cl_2 will be react with H_2O forming hypochlorite. The generation of hypochlorite will further react with QK_7^- to N_2. Therefore, the existence of Cl^- contributes to the NITRR process, and more QK_7^- will be converted to N_2.

3.4 Treatment of the actual industrial wastewater

The NITRR performance of Bi-CC was tested by the garbage fly ash washing wastewater. As shown in Table 3, the concentration of QR_6^0 decreases from 75.5 mg/L to 18.1 mg/L after the six hours treatment at the current density of 10 mA cm^{-2}. Compared to the previous study (Yang et al., 2020), Bi-CC presents satisfactory NITRR efficiency.

Table 3: Variation of the active nitrogen in the garbage flying wastewater before and after the treatment of the Bi-CC, using the current density of 10mA cm^{-2} over 6 h operation.

	PH	Concentration of QR_6^0 (mg/L)	Concentration of QK_7^+(mg/L)	QR_6^0 removal efficiency
Initial	6.3	75.5	19.4	/
End	3.5	18.1	25.3	76%

The concentration of QK_7^+ increases from 19.4 ppm to 25.3 ppm, the results indicates that most of the QR_6^0 are eventually reduced to QK_7^+. In conclusion, Bi-CC shows high potential for converting QR_6^0 in industrial wastewater treatment to valuable QK_7^+.

4. Conclusions

In this study, two-dimensional bismuth nanosheets decorated on carbon cloth was proposed for NITRR process, in which the QR_6^0 removal efficiency reaches to nearly 90% and the QK_7^+ selectivity reaches to nearly 80% after 120 mins treatment at the current density of 10 mA cm^{-2}. The effect of reaction parameters on the QR_6^0 reduction is carried out, the results shows that the change of PH has little effect on the NITRR efficiency, complete QR_6^0 removal was achieved at the current density of 20 mA cm^{-2}, and the presence of Cl^- is favourable for the NITRR process. More importantly, when applied to the garbage fly ash wastewater, the Bi-CC shows high potential in the effective QR_6^0 removal for industrial wastewater treatment.

Acknowledgments

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