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Short Communication

Electrocatalytic Oxidation of Urea on Nickel Electrodeposited Glassy Carbon Electrode

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Nickel electrodeposited glassy carbon electrode was prepared and the activity to the electrocatalytic oxidation of urea in an alkaline medium was investigated by cyclic voltammetry. The experiment was carried out in 1 mol/L KOH+0.1 mol/L urea under a three-electrode system. The effects of different scan rates, urea concentration, KOH concentration on the electrocatalytic oxidation of urea at nickel electrodeposited electrode were investigated. The results showed that the nickel electrodeposited electrode had a good electrocatalytic performance for urea oxidation.

Keywords: Nickel electrodeposition; Electrocatalytic oxidation; Urea

1. INTRODUCTION

Urea is an organic substance containing carbon, oxygen, nitrogen, and hydrogen. It has the advantages of stability, non-toxic, high energy density, and low price, and is convenient for energy storage and transportation [1]. With the development of modern technology, urea is also essential in production and life. From the industrial production to the use of farmland, many urea containing wastewater will be produced. If these urea containing wastewater was directly discharged into rivers, lakes, or soils, the soil and water are prone to eutrophication due to the increase of nitrogen, phosphorus, and other elements[2]. Urea containing wastewater will also sink into the soil and groundwater through rainwater due to the water circulation system, which will directly affect human health [3].

The main methods for urea degradation including chemical oxidation, artificial biodegradation, electro-oxidation, and hydrothermal hydrolysis[4]. Among these methods, the electro-oxidation has the advantages of simple operation, long operation period, and large treatment capacity. Electro-oxidation technology can destroy the urea molecules to harmless H_2O, N_2, and CO_2 by inputting electric energy into the sewage and waste water[5]. Thus, this method is excellent for the treatment of urea containing wastewater with different concentrations and volumes. Many reports showed that $Ni(OH)_2$, NiO, and Ni as non-noble-metal materials can provide excellent electrocatalytic performance, effective active site, low initial oxidation potential, high oxidation current density, and good catalytic stability in the electrocatalytic oxidation of urea [6-22].

In this work, the electrodeposition of nickel on a glassy carbon electrode was performed. Because the electrodeposition method is mainly used in the preparation of structure and function coating, the electric field under the electrode system will disperse the charged particles in the solution to the electrode surface. At the same time, the cost of electrodeposition is low, the operation is easy, and the thickness of the deposition film can be controlled. Cyclic voltammetry can reflect the change of current and potential in the process of urea electrocatalytic oxidation. Therefore, the electrocatalytic activity of nickel electrodeposited glassy carbon electrode was studied in an alkaline medium by cyclic voltammetry.

2. EXPERIMENTAL

2.1. Reagents and instrumentation

Urea (H_2NCONH_2), potassium hydroxide (KOH), and nickel sulfate hexahydrate ($NiSO_4$. $6H_2O$) were purchased from China Pharmaceutical Group Chemical Reagents Co., Ltd. The experimental solutions were prepared with double-distilled water.

The electrodeposition of nickel on glassy carbon electrode and cyclic voltammetry experiments were performed on a CHI660B electrochemical workstation (Chenhua Instrument Company of Shanghai, China) with a conventional three-electrode system. Nickel electrodeposited glassy carbon electrode (Ni/GCE) was used as the working electrode. The saturated calomel electrode was used as the reference electrode and platinum foil was used as the counter electrode.

2.2. Preparation of Ni/GCE

The GCE was used as the underlying substrate for nickel electrodeposition. Before use, it was mechanical polished with a leather containing 0.05 μm Al_2O_3 and then ordinal washed in ethanol and distilled water to obtain a clean surface. For the preparation of Ni/GCE, GCE was transferred into a solution containing 30 mmol/L $NiSO_4$ and 0.5 mol/L KCl for the electrodeposition of Ni. Electrodeposition potential is -1V and electrodeposition time is 180s with stirring.

2.3. Cyclic voltammetry experiments

Cyclic voltammetry was used to test the electrochemical performance of the prepared Ni/GCE. The scan potential range is 0 - 0.8 V. After each use, the Ni/GCE, reference electrode, and auxiliary electrode were cleaned with distilled water for reuse.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of Ni/GCE

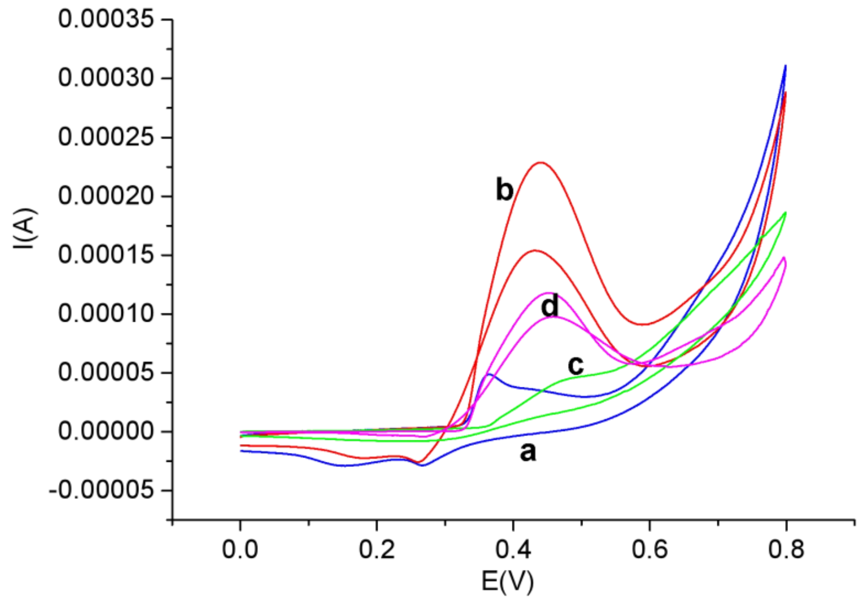


Figure 1. Cyclic voltammograms of Ni/GCE in 1M KOH solution (curve a), and Ni/GCE(curve b) bare GCE(curve c) and Ni electrode (curve d) in 1M KOH solution containing 0.1 mol/L urea. Scan rate is 50 mV/s.

As can be seen from curve a in figure 1, a pair of redox waves with a peak potential of 0.37 and 0.27 V was observed, which ascribed to the oxidation of $Ni(OH)_2$ to NiOOH and reduction of NiOOH to $Ni(OH)_2$. The electrochemical phenomena of Ni/GCE in KOH is similar to that of Ni anode [23, 24]. The broad cathodic peak can be ascribed to the phase transformation of β -NiOOH to γ -NiOOH due to slow, irreversible overcharging during cycling, and the corresponding reduction to α -$Ni(OH)_2$. This phenomenon had been reported by Bode et al. [25]. After the addition of 0.1 mol/L urea, it can be seen from curve b that the oxidation peak current enhanced greatly and enlarged the peak region because of the overlapped of nickel hydroxide and urea oxidation [26, 27]. The redox peak potentials are 0.44 and 0.27 V, respectively. The results suggested that excellent electrocatalytic oxidation of urea on the Ni/GCE. The electrocatalytic mechanism could be explained as:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad (1)$$

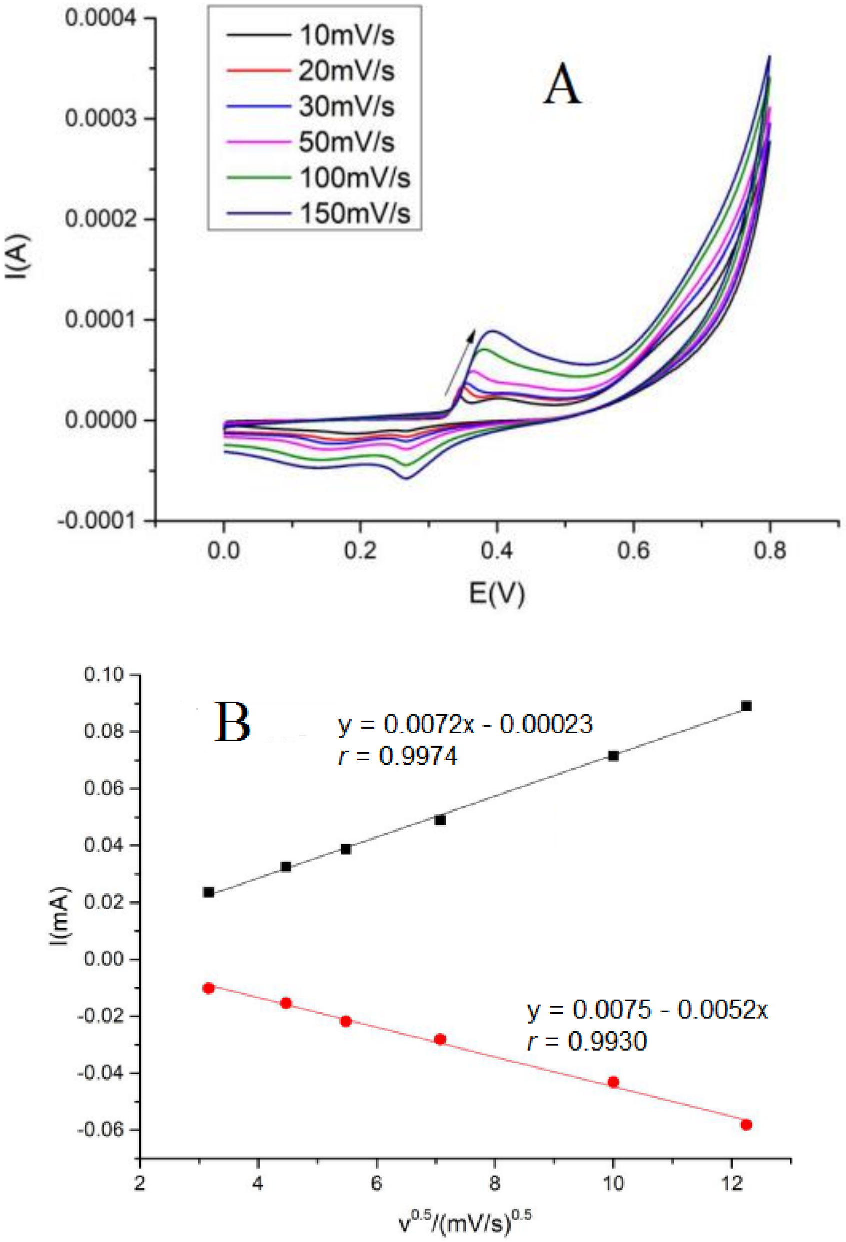
$$6NiOOH + CO(NH_2)_2 + H_2O \rightarrow 6Ni(OH)_2 + N_2 + CO_2 \qquad (2)$$

Firstly, $Ni(OH)_2$ is electro-oxidized to NiOOH and then NiOOH reacts with urea. At the same time, $Ni(OH)_2$ is regenerated. For the Ni/GCE, it shows higher current density than that of Ni electrode. It means that Ni/GCE has higher electroactivity toward urea oxidation.

For comparison, the cyclic voltammetric behavior of Ni electrode and bare GCE in 1M KOH solution containing 0.1 mol/L urea was investigated. As can be seen from the curve c, a small and broad oxidation peak at 0.49V was observed, suggesting a low catalytic activity of bare GCE towards urea oxidation. As can be seen from the curve d, Ni electrode showed high catalytic activity towards urea oxidation. However, the oxidation peak current is much smaller than that of Ni/GCE. The above results further identified the excellent electrocatalytic performance of Ni/GCE to urea oxidation.

3.2. Effect of scan rates on Ni/GCE

Cyclic voltammograms of Ni/GCE in 1M KOH solution at different scan rates (from 10 to 150 mV/s) were illustrated in Figure 2A.



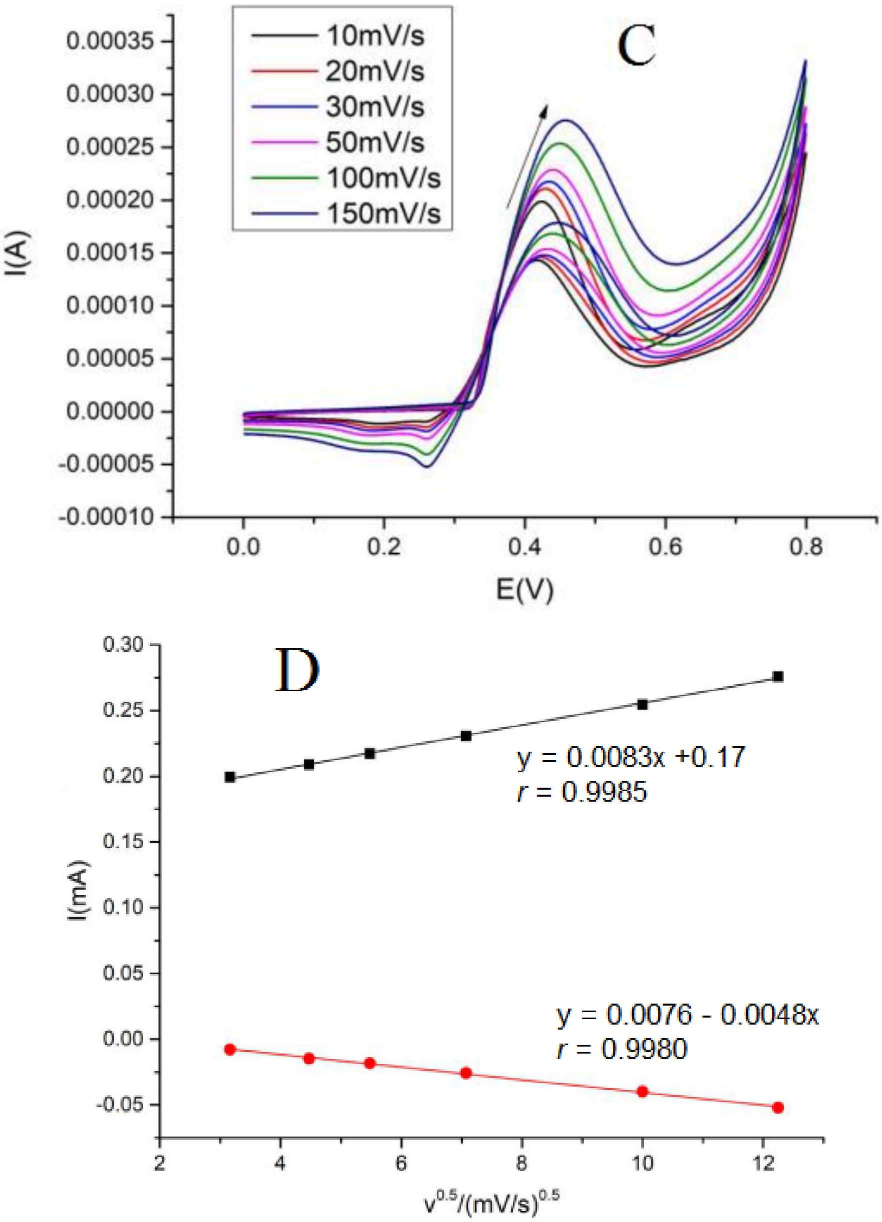


Figure 2. (A) The cyclic voltammograms of Ni/GCE in 1M KOH solution at different scan rates; (B) Linear fit of peak current vs the square root of scan rate; (C) The cyclic voltammograms of Ni/GCE in 1M KOH solution containing 0.1M urea at different scan rates; (D) Linear fit of peak current vs the square root of scan rate.

As shown in the cyclic voltammograms, well-defined redox peaks in the potential range of 0.2–0.5V were observed, which is assigned for the redox transform of $Ni(OH)_2$/NiOOH. Both the oxidation peak current and reduction peak current increasing with the scan rate from 10 to 150 mV/s. The oxidation peak current is larger than the reduction peak current. Moreover, the oxidation peak potential had an obvious shift to high potential, and the reduction peak potential had little shift to low potential. Figure 2B shows the linear fit of redox peak current vs the square root of the scan rate. The fit lines and excellent correlation coefficient(r) suggests a diffusion-controlled process for the electrode reaction.

Figure 2C shows cyclic voltammograms of Ni/GCE in a 1M KOH solution containing 0.1M urea at different scan rates. As can be seen from the curves, the redox peak current increasing with the scan rate increases. The oxidation peak current is much larger than the reduction peak current because of the urea electro-oxidation, which suggests a completely irreversible process. The linear fit of redox peak current vs the square root of the scan rate was illustrated in figure 2D. The results also indicated a diffusion-controlled process for the urea electro-oxidation, which is in accordance with the Randles-Sevcik equation for a completely irreversible process [28].

3.3. Effect of urea concentration on Ni/GCE

As the main body of oxidation, the concentration of urea must play an important role in the oxidation process. Figure 3 shows the cyclic voltammograms of Ni/GCE at different urea concentrations in 1M KOH solution.

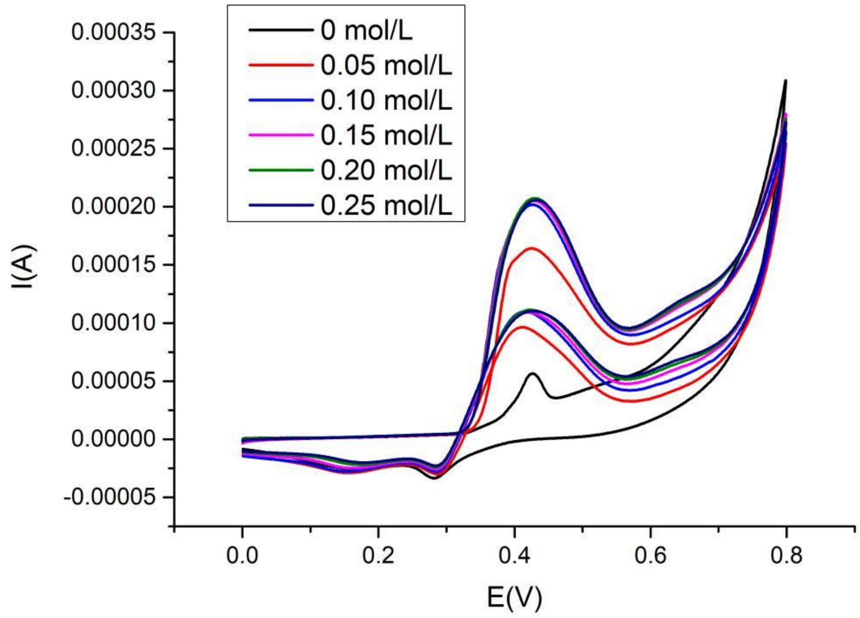


Figure 3. The cyclic voltammograms of Ni/GCE at different urea concentration in 1M KOH solution. Scan rate of 50 mV/s.

It can be seen from the figure that with an increase of urea concentration, the initial oxidation potential decreased from 0.39 V to 0.32 V, the oxidation peak current density increased from 5.81×10^{-5} to 2.08×10^{-4}A, but when the urea concentration exceeded 0.20 mol/L, the oxidation peak current density showed a downward trend. It can be inferred that 1 mol/L KOH is insufficient for the catalytic oxidation of 0.20 mol/L urea. As can be seen from equations (1) and (2), the best ratio of $[OH^-]/[CO(NH_2)_2]$ is 6. Thus, the suitable concentration of urea is 0.17M. When the urea concentration is higher than 0.2M, the ratio of $[OH^-]/[CO(NH_2)_2]$ is below 6, suggesting that the amount of NaOH is insufficient. At the same time, comparing the curves of the oxidation part and reduction part, it can be seen that the growth rate of oxidation current density is faster than that of the reduction reaction. Therefore, the electrocatalytic oxidation performance of urea is optimal when the concentration of urea in 1mol/L KOH solution is controlled between 0.10 mol/L and 0.20 mol/L.

3.4. Effect of KOH concentration on Ni/GCE

The effect of KOH concentration on Ni/GCE towards the electro-oxidation of urea was also investigated.

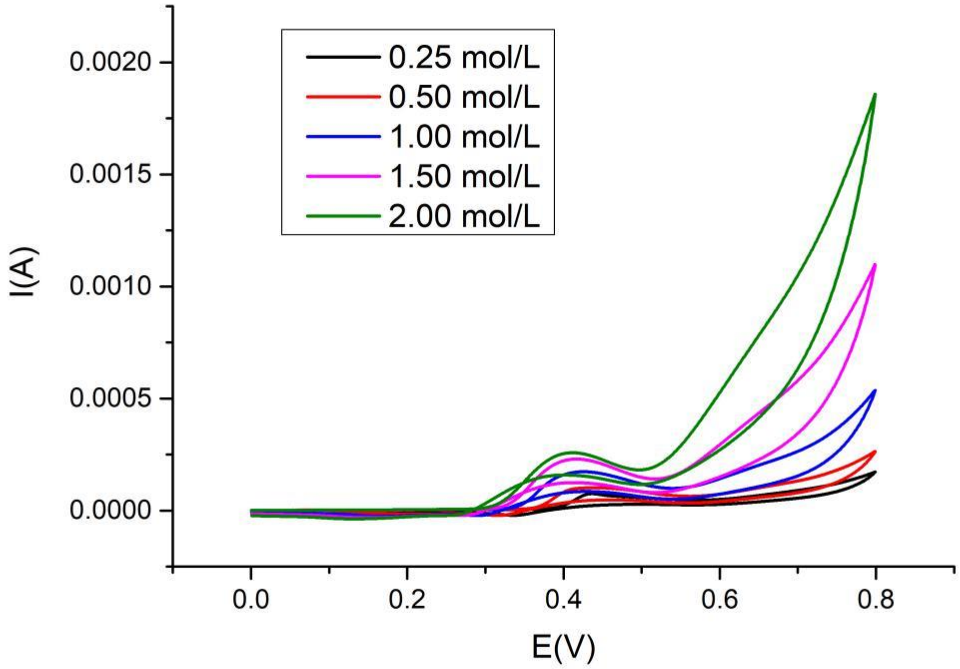


Figure 4. The cyclic voltammograms of Ni/GCE at different KOH concentration containing 0.1M urea. Scan rate of 50 mV/s.

Figure 4 shows the cyclic voltammograms of Ni/GCE at different KOH concentration with 0.1M urea. It can be seen that with the increase of KOH concentration from 0.25 mol/L-2.0 mol/L, the initial potential of oxidation negatively shifted from 0.38 V to 0.3 V, and the peak current density increased from 7.86×10^{-5} to 2.61×10^{-4}A. At the same time, the reduction peak potential also moved from 0.36 V to 0.27 V, and the peak current increased. Because the oxidation current density is much higher than that of reduction, the reduction peak current seems to be not obvious. When the KOH concentration reached 2.0 mol/L, the oxidation peak current has little increase. It shows that excessive KOH could not effectively enhance urea oxidation.

4. CONCLUSION

In this work, a simple electrodeposition method was used for the preparation of Ni/GCE. The electrochemical properties of Ni/GCE towards the electro-oxidation of urea was studied by cyclic voltammetry. The experimental results showed high catalytic current and low initial potential in the catalytic oxidation process. The effects of different scan rates, urea concentration, KOH concentration on the electrocatalytic oxidation of urea were also investigated.

ACKNOWLEDGMENT

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