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Ni@C Microspheres as Efficient catalyst for Urea Electro-oxidation

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Urea is able to be used as a useful fuel in the direct urea fuel cell. Novel structure and morphology is essential to improve the catalytic performance of catalysts for urea electro-oxidation. Preparation of Ni@C microspheres with Ni-btc (btc=benzene-1,3,5-tricarboxylate) microspheres as precursor was developed herein. These Ni@C microspheres are modified to the glassy carbon electrode and the electrocatalytic performance of Ni@C microspheres for urea electro-oxidation is investigated in an alkaline solution. Experimental results showed that Ni@C microspheres have excellent urea electro-oxidation performance which attributes to the electrocatalytic activity of Ni and high electrical conductivity of C in the Ni@C microspheres.

Keywords: Ni@C microspheres; Ni-btc microspheres; Electro-oxidation ; Urea

1. INTRODUCTION

Fuel cells are highly efficient and have been used in industrial production and daily life. Urea ($CO(NH_2)_2$) is able to be used as a useful fuel in the direct urea fuel cell (DUFC). As a hopeful sustainable fuel, it has many advantages such as inexpensive, attainable from urine and urea-rich wastewater, non-poisonous, can be simply stored and transported [1-8]. Urea wastewater can be purified by the electro-oxidation reaction [9], the reaction mechanism of urea electro-oxidation can be expressed by following equation:

Anode: $CO(NH_2)_2 + 6OH^- \rightarrow 5H_2O + N_2 + CO_2 + 6e^-$ (1)

Cathode: $6H_2O + 6e^- \rightarrow 3H_2 + 6OH^-$ (2)

Total reaction: $CO(NH_2)_2 + H_2O \rightarrow 3H_2 + N_2 + CO_2$ (3)

Generally, due to the slow intrinsic kinetics (6-electron process) and the complex gas precipitation process (N_2 and CO_2), urea electro-oxidation usually requires noble metal based catalysts such as platinum and ruthenium [10, 11]. However, the high cost of precious metal materials makes it difficult to actual production in large quantities. Thus, the key problem of urea electro-oxidation is to explore efficient and low-cost catalyst. So, the idea of a transition metal based catalyst was proposed. It has also been proved that the Ni based catalysts have good urea electro-oxidation performance in alkaline solutions[12-26]. There are many factors affecting the catalytic performance of the catalysts , including the composition of catalyst, structure and morphology. Botte et al reported that the microscopic morphology of Ni based catalysts has great effect on the electrocatalytic activity to the urea electro-oxidation [27, 28]. Thus, design and preparation of Ni based catalysts with novel structure and morphology is essential to improve the catalytic performance for urea oxidation.

In this work, we demonstrate the preparation of waxberry-like hierarchical Ni@C microspheres with Ni-btc (btc=benzene-1,3,5-tricarboxylate) microspheres as precursor. These Ni@C microspheres are modified to the glassy carbon electrode and the electrocatalytic activity of Ni@C microspheres for urea oxidation is investigated in alkaline solution. Experimental results showed that Ni@C microspheres have excellent urea electro-oxidation performance with higher catalytic current and lower onset potential than those of Ni-btc microspheres. It attributes to the electrocatalytic activity of Ni and high electrical conductivity of C in the Ni@C microspheres. It is expected that the Ni@C microspheres can be used as efficient electrode catalysts for direct urea fuel cells.

2. EXPERIMENTAL SECTION

2.1 Chemicals and instrumentation

Nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$), 1,3,5-benzenetricarboxylic acid, Sodium hydroxide (NaOH), urea (H_2NCONH_2), N,N-dimethylformamide (DMF) and ethanol were all analytical grade. Deionized water was used in all experiments.

The electrochemical experiments were tested in a conventional three-electrode system cell by CHI660 electrochemical working-station (Shanghai Chenhua Instrument, China). Ni@C microspheres modified glassy carbon electrode (Ni@C/GCE) or Ni-btc microspheres modified glassy carbon electrode (Ni-btc/GCE) was used as the working electrode. The saturated calomel electrode(Saturated KCl) was applied as the reference electrode and platinum foil was used as the counter electrode. The morphology of the Ni-btc microspheres and Ni@C microspheres were examined using a scanning electron microscope (SEM, FEI Inspect F50). The structure of the Ni-btc microspheres and Ni@C microspheres were tested by an X-ray diffractometer (XRD, X'Pert Powder) .

2.2 Synthesis of Ni-btc microspheres

Ni-btc microspheres were prepared through a simple solvothermal method similar to the previous report [29]. Typically, 1.0 mmol of 1,3,5-benzenetricarboxylic acid and 1.0 mmol of $Ni(NO_3)_2·6H_2O$ were added to a beaker containing 30 mL of DMF with continuous stirring for 30 min. The solution was then transferred into a Teflon-lined autoclave for solvothermal treatment at 150 °C for 12 h. The green solid (Ni-btc) was collected by centrifugation, and washed several times with ethanol. Then, dried at 60 °C for 24 h in a vacuum.

2.3 Synthesis of Ni@C microspheres

The preparation of Ni@C microspheres is similar to the previous report [30]. Namely, the as-prepared Ni-btc microspheres were pyrolyzed in a horizontally tubular furnace under Ar atmosphere at 750 °C for 3 h with a temperature ramp of 3 °C min^{-1}.

2.4 Fabrication of electrodes

The glassy carbon electrode (GCE, d = 3mm) was used for fabrication of Ni@C microspheres or Ni-btc microspheres. Prio to use, the GCE was mechanical polished with a leather containing 0.05μm alumina slurry and then washed in ethanol and deionized water by ultrasonication. The 4 mg/mL suspension of Ni@C microspheres or Ni-btc microspheres was prepared by adding 4 mg Ni@C microspheres or Ni-btc microspheres into a 1 mL 0.25 wt% nafion solution with ultrasonically treating for 30min. Finally, 5 uL of the suspension was dropped onto the clean surface of the GCE, then dried at room temperature.

3. RESULTS AND DISCUSSION

3.1. The morphology and crystal structure of Ni-btc and Ni@C microspheres

The morphology of the Ni-btc and Ni@C microspheres are observed by SEM. As can be seen from Figure 1A, the Ni-btc is composed of monodispersed microspheres with smooth surface. The average diameter is about 1μm. As can be seen from Figure 1B, after high-temperature(750 °C) pyrolysis, Ni@C microspheres were obtained from the spherical morphology of Ni-btc precursor, while their surface becomes rough apparently. As shown in Figure 1C, these microspheres are composed of numerous small uniform nanoparticles, which indicated that high-temperature pyrolysis induced a graphitic carbon layer on the surface of Ni nanoparticles.

The crystal structure of the Ni-btc and Ni@C microspheres are investigated by XRD. As can be seen from Figure 2, there is a diffraction peak at 2θ= 11.6° in XRD pattern of the Ni-btc, confirming the formation of Ni-btc crystals, which is similar to the previous reports [31, 32]. The Ni@C microspheres have three well-resolved diffraction peaks at 2θ= 44.5°, 51.9°, and 76.4° which are corresponding to the (111), (200) and (220) planes of Ni with fcc structure. The other three diffraction peaks at 2θ= 41.8°, 47.6°, and 62.5° in the XRD pattern can be indexed to crystalline carbon.

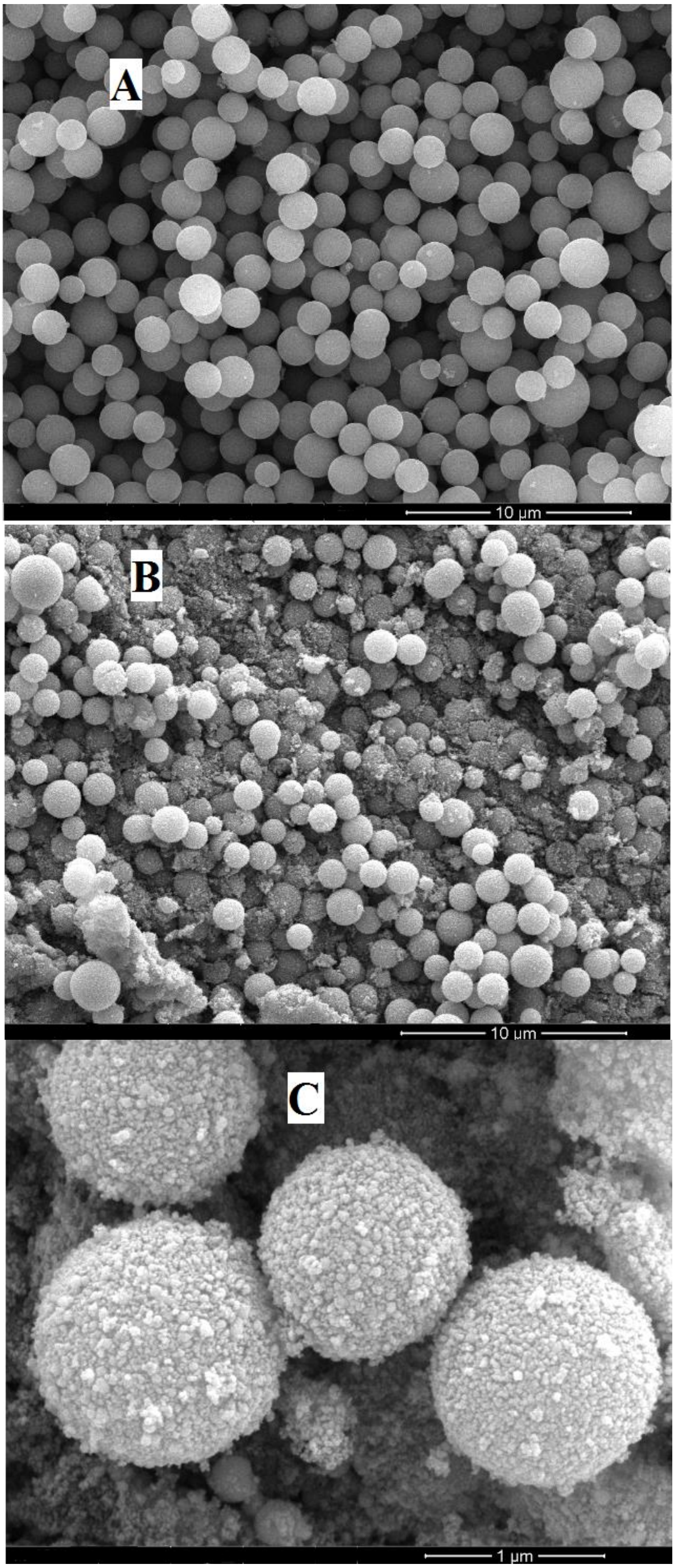


Figure 1. SEM images of Ni-btc (A) and Ni@C microspheres (B, C).

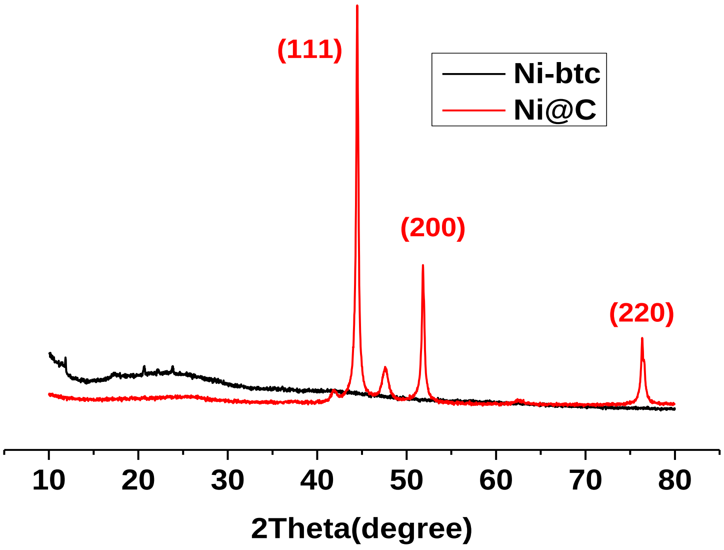
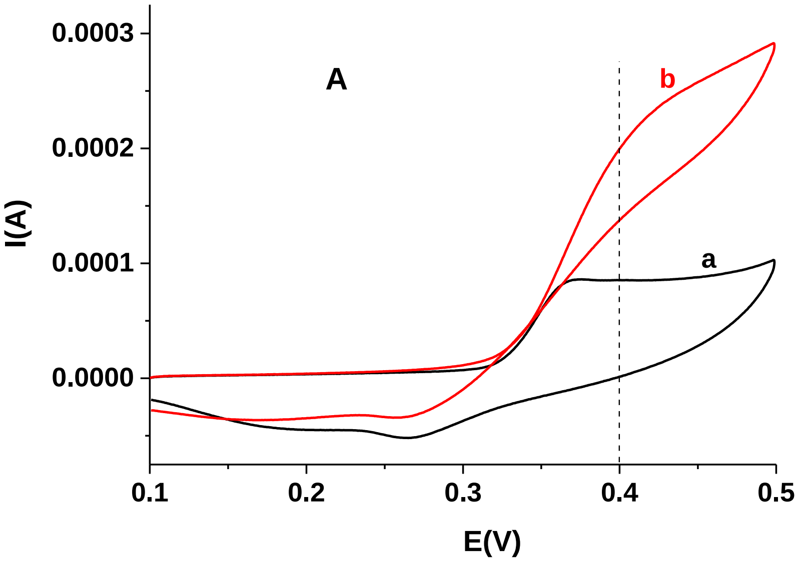


Figure 2. XRD patterns of Ni-btc (a) and Ni@C microspheres (b).

3.2. Electrochemical performance of modified electrode

The electrochemical performance of Ni@C microspheres or Ni-btc microspheres modified glassy carbon electrode were investigated by cyclic voltammetry technique.



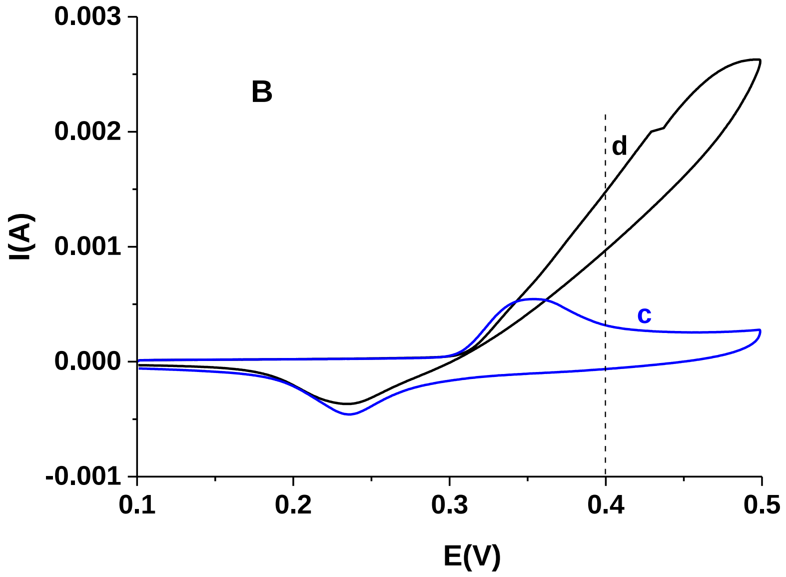


Figure 3. The CVs of Ni-btc/GCE (A) in 1M NaOH solution in the absence(a) and presence(b) of 0.1 M urea, and Ni@C/GCE (B) in 1M NaOH solution in the absence(c) and presence(d) of 0.1 M urea.

Figure 3 shows the cyclic voltammograms(CVs) of Ni-btc/GCE and Ni@C/GCE in 1M NaOH solution in the absence and presence of 0.1 M urea. It can be seen from Figure 3A, a pair of redox peaks was observed in curve a, the positions of the peaks are 0.37V and 0.26V, and the peak potential width is 0.11V. It is attributed to the oxidation of $Ni(OH)_2$ to NiOOH and reduction of NiOOH to $Ni(OH)_2$ of Ni-btc/GCE in 1M NaOH solution, which is similar to that of Ni anode [33, 34]. As shown in curve b, when 0.1 M urea was added into the NaOH solution, the oxidation current increased significantly and the reduction current decreased, which indicated that Ni-btc/GCE had a certain catalytic effect on the urea electro-oxidation. The electrode reaction process could be expressed as:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad (4)$$

$$6NiOOH + CO(NH_2)_2 + H_2O \rightarrow 6Ni(OH)_2 + N_2 + CO_2 \qquad (5)$$

For the Ni@C/GCE in 1M NaOH solution, a pair of well defined redox peaks was observed in curve c of Figure B, the positions of the peaks are 0.35V and 0.24V, and the peak potential width is 0.11V. It is also attributed to the oxidation of $Ni(OH)_2$ to NiOOH and reduction of NiOOH to $Ni(OH)_2$. When 0.1M urea was added into NaOH solution, as shown in curve d, the oxidation current increased sharply and the reduction current decreased, which indicated that Ni@C/GCE had obvious catalytic effect on urea oxidation. From the comparison of oxidation current at 0.4V in curve b and curve d, it can be seen that the oxidation current of Ni-btc/GCE is only 0.2mA, while that of Ni@C/GCE is 1.5mA. The oxidation current of Ni@C/GCE is much higher than that of Ni-btc/GCE, which indicated that Ni@C/GCE had stronger electrocatalytic performance for urea oxidation. It attributes to the electrocatalytic performance of Ni and high electrical conductivity of C in the Ni@C microspheres.

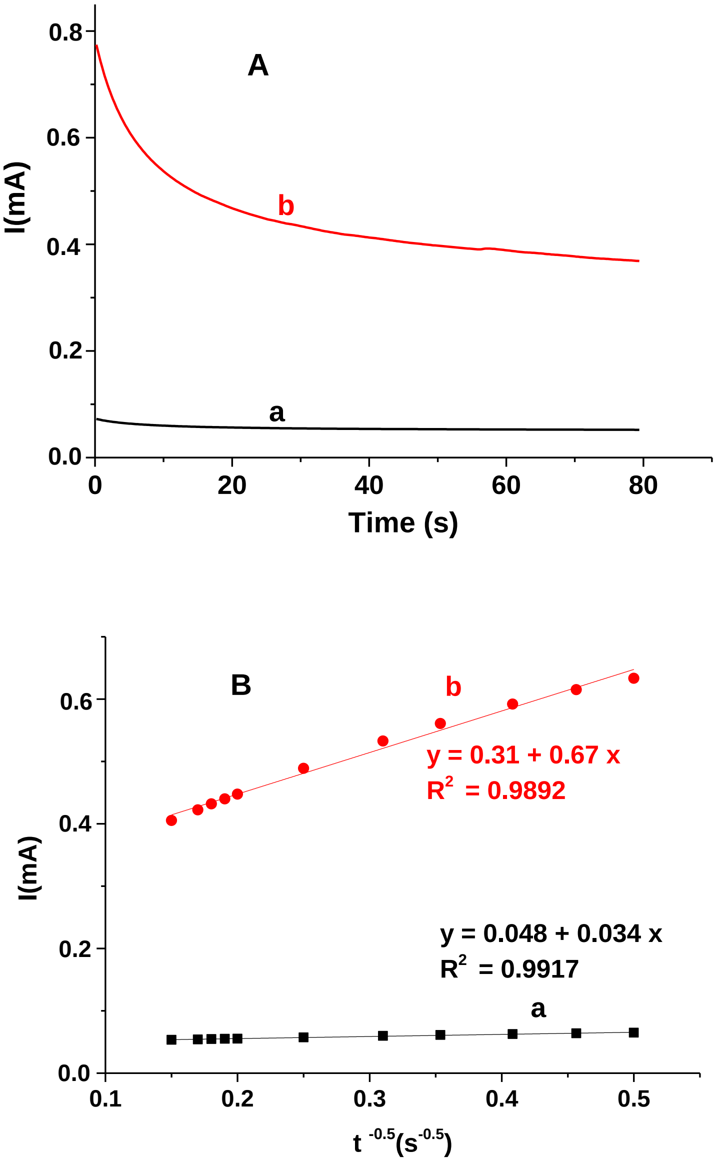


Figure 4. (A) Chronoamperometric curves of Ni-btc/GCE(a) and Ni@C/GCE(b) in 1M NaOH solution containing 0.1M urea, and (B) the corresponding I-$t^{-0.5}$ plots.

Further investigation of the Ni-btc/GCE and Ni@C/GCE on the electrocatalytic oxidation of urea was preformed by chronoamperometry measurements. Figure 4A shows the chronoamperometric curves of Ni-btc/GCE and Ni@C/GCE in 1M NaOH solution containing 0.1M urea. It can be seen that the catalytic oxidation current of Ni@C/GCE is much higher than that of Ni-btc/GCE, which is consistent with the results of cyclic voltammetric study. Figure 4B shows the corresponding I-$t^{-0.5}$ plots. According to the Cottrell equation:

$$I = n\,FA\,D^{0.5}C\pi^{-0.5}\,t^{-0.5} \qquad (6)$$

where n is the number of electrons for the urea conversion, F is the Faraday constant, A is the surface area of the working electrode, t is the time, D is the diffusion coefficient of urea, and C is the urea concentration. The surface area ratio of the Ni@C/GCE and Ni-btc/GCE is calculated to be 19.7

by using the slopes ratio of the straight lines. It can be explained that the large surface area of the Ni@C/GCE is favor of urea electrocatalytic oxidation. Thus, the following experiments were performed to further investigate the electrocatalytic performance of Ni@C/GCE for urea oxidation.

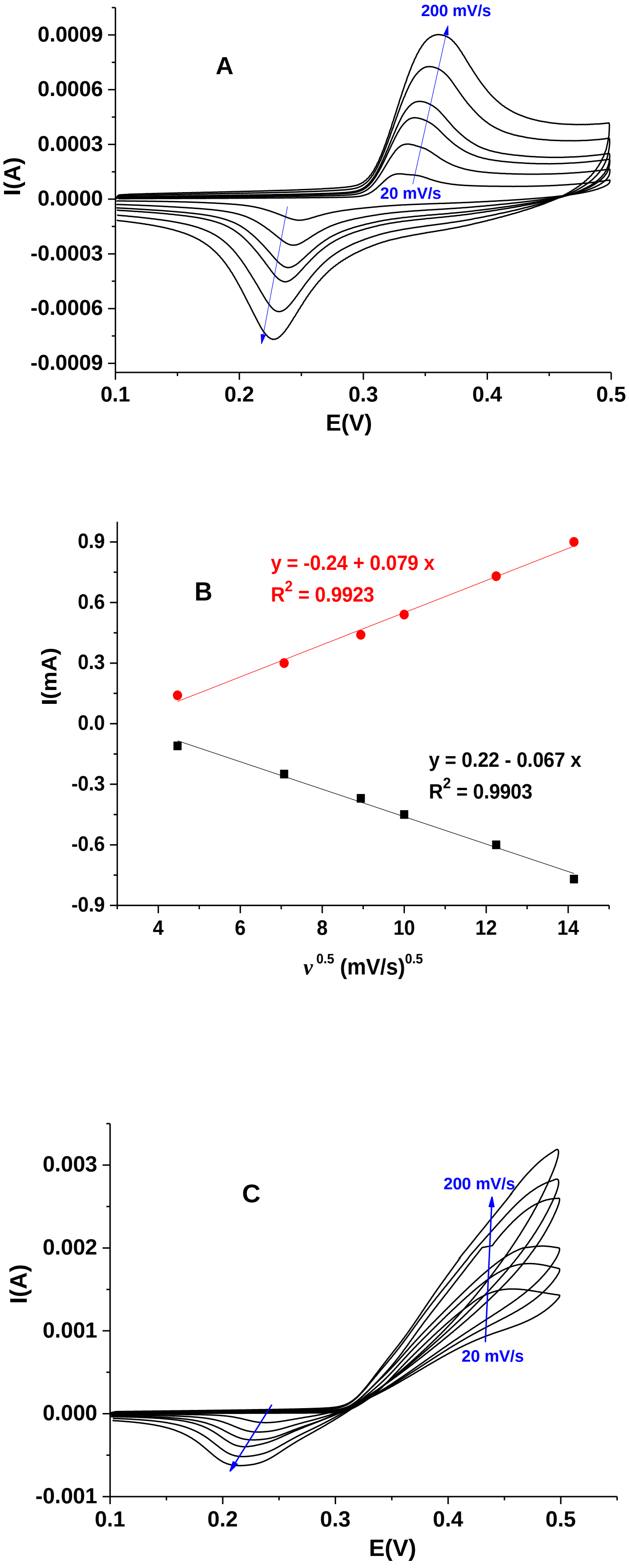
The obtained electro-catalytic activity of the Ni@C/GCE towards urea oxidation may be compared with other Ni-based catalysts. Table 1 shows the oxidation peak potential (*E*pa) and oxidation onset potential(OOP) of the Ni@C/GCE and other Ni-based catalysts modified electrodes in alkaline solutions. As shown in Table 1, Ni@C/GCE has lower *E*pa and OOP than many Ni-based electrodes. It may be attributed to the excellent electrocatalytic activity of Ni and high electrical conductivity of C in the Ni@C microspheres, which is favor of urea electro-oxidation.

Table 1. Comparison of electro-catalytic performance with other Ni-based catalysts.

Catalysts	*E*pa (V *vs.* Hg/HgO)	OOP	Refs.
Ni nanowires	0.65	0.50	[35]
Ru－Ni	0.70	0.45	[36]
Ni－Co nanowires/Ti	0.60	0.39	[37]
$Ni(OH)_2$ nanotube	0.60	0.29	[38]
$NiCo_2O_4$	0.70	0.35	[39]
Ni nanoparticle/graphene	0.60	0.32	[40]
Ni@C microspheres	0.59	0.42	this work

3.3. Scan rates study of Ni@C/GCE

Cyclic voltammetric behavior of Ni@C/GCE in 1M NaOH solution in the absence and presence of 0.1 M urea at different scan rates was studied. Figure 5A shows the CVs of Ni@C/GCE in 0.1M NaOH solution at different scan rates (from 20 to 200 mV/s). As shown in the curves, obvious redox peaks were observed, which is attributed to the redox transform of $Ni(OH)_2$/NiOOH. With increasing the scan rate, the anodic peak current and cathodic peak current increase, and the redox peak potential difference (ΔEp) enlarged.


A
200 mV/s
20 mV/s
I(A)
0.0009
0.0006
0.0003
0.0000
-0.0003
-0.0006
-0.0009
0.1
0.2
0.3
0.4
0.5
E(V)
B
y = -0.24 + 0.079 x
R^2 = 0.9923
y = 0.22 - 0.067 x
R^2 = 0.9903
I(mA)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
4
6
8
10
12
14
$v^{0.5}$ (mV/s)$^{0.5}$
C
200 mV/s
20 mV/s
I(A)
0.003
0.002
0.001
0.000
-0.001
0.1
0.2
0.3
0.4
0.5
E(V)

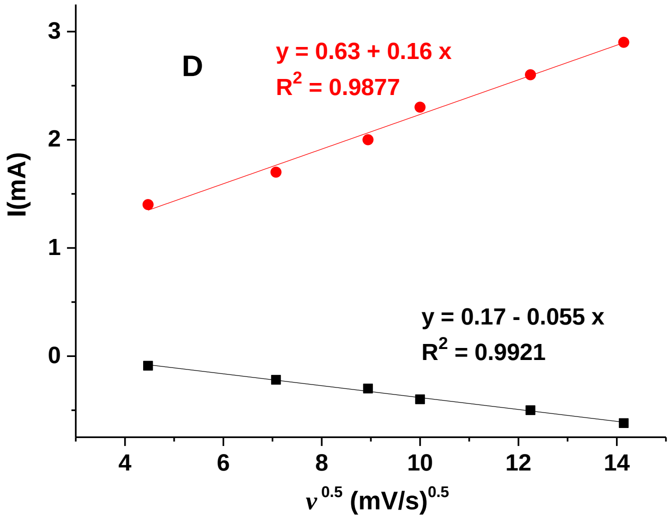


Figure 5. The CVs and the corresponding linear fit of Ip *vs* $v^{0.5}$ for Ni@C/GCE in 1M NaOH in the absence(A and B) and presence(C and D) of 0.1 M urea at different scan rates.

Figure 5B shows the linear fit plot of Ip *vs* $v^{0.5}$. As can be seen, the good correlation coefficient(R^2) in the plot indicates that the reaction process of Ni@C/GCE in 1M NaOH solution is a diffusion-controlled process.

Figure 5C shows Ni@C/GCE in 0.1M NaOH solution containing 0.1M urea at different scan rates (from 20 to 200 mV/s). As shown in the curves, with increasing the scan rate, the anodic peak current and cathodic peak current increase, and the redox peak potential difference (ΔEp) enlarged. The anodic peak current is much larger than the cathodic peak current because of the electrocatalytic oxidation of urea, which indicates a completely irreversible reaction process. The linear fit plot of Ip *vs* $v^{0.5}$ was showed in Figure 5D. The results also suggest a diffusion-controlled process for the electrode reaction of Ni@C/GCE in 1M NaOH solution containing 0.1M urea, which is in accordance with the Randles-Sevcik equation[41]. The electrode reaction of Ni@C/GCE in NaOH solution in the absence and presence of urea are both diffusion-controlled process. The results suggest that OH^- and $CO(NH_2)_2$ diffuse to the electrode surface at the same time in the process of urea oxidation.

3.4. Voltammetric properties of Ni@C/GCE at different concentrations of urea and NaOH

The effect of different urea concentration on the electro-oxidation of urea at Ni@C/GCE was investigated. Figure 6A shows the CVs of Ni@C/GCE in 1M NaOH solution at different urea concentration from 0.05 to 0.4M. As shown in the curves, the anodic current of urea increases gradually with the increase of urea concentration. But the increase of anodic current was very small when the urea concentration is higher than 0.2M. The results suggested that the amount of NaOH is insufficient for excessive urea oxidation. Therefore, the urea electro-oxidation needs an appropriate $[OH^-]/[CO(NH_2)_2]$ ratio [42].

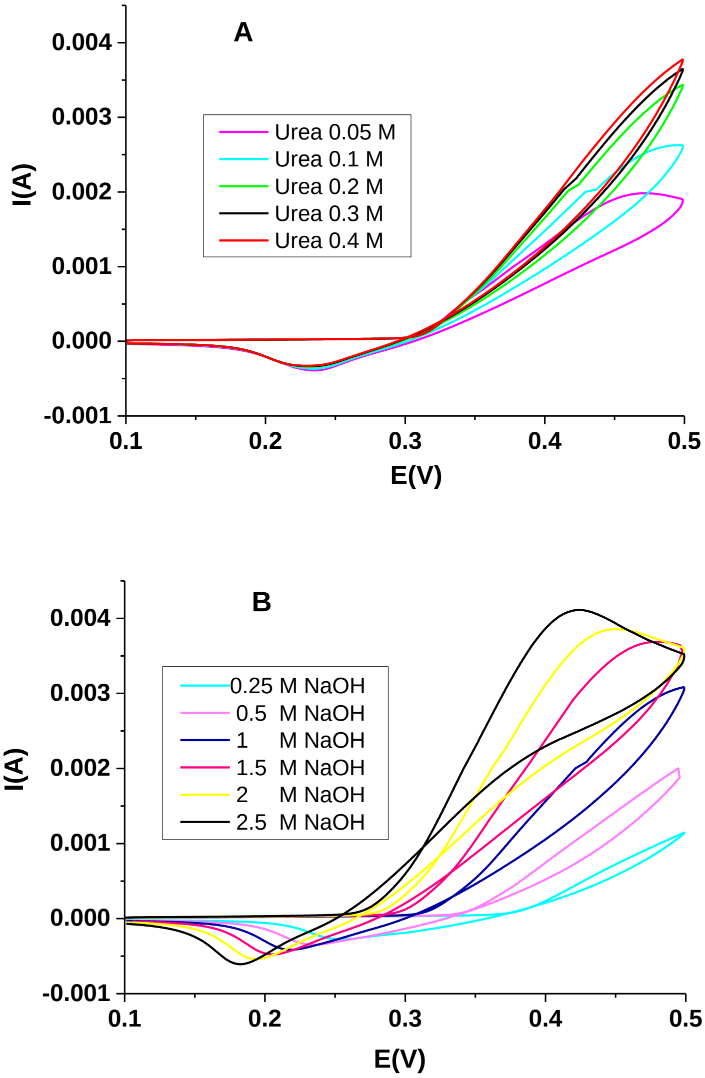


Figure 6. The CVs of Ni@C/GCE in 1M NaOH solution at different urea concentration (A), and CVs of Ni@C/GCE in different NaOH solution containing 0.1M urea (B) .

The effect of different NaOH concentration on the electro-oxidation of urea at Ni@C/GCE was also investigated. Figure 6B shows the CVs of Ni@C/GCE in different NaOH solution containing 0.1M urea. As can be seen from the figure, with increasing NaOH concentration from 0.25-2.5M, the oxidation current has an obvious increase and reduction current has little increase. Moreover, the the redox peak potential and the oxidation onset potential are all negatively moved. The negatively moved oxidation onset potential and increased oxidation current indicated the high NaOH concentration was favor of urea electro-oxidation. But excessive NaOH could not further enhance the urea oxidation.

4. CONCLUSION

In this work, Ni@C microspheres with Ni-btc (btc=benzene-1,3,5-tricarboxylate) microspheres as precursor was prepared. The Ni@C microspheres are modified to the glassy carbon electrode and the electrocatalytic performance for urea oxidation is investigated in alkaline solution. Experimental results showed that Ni@C microspheres have excellent urea electro-oxidation performance with high catalytic current and low initial potential in the reaction process. The effects of different scan rates, urea concentration and NaOH concentration on the electro-oxidation of urea were also investigated. A diffusion-controlled electrode reaction process for the oxidation of urea was obtained.

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