

Shidong Fei · Jinhua Chen · Shouzhao Yao
Guohong Deng · Lihua Nie · Yafei Kuang

Electroreduction of α -glucose on CNT/graphite electrode modified by Zn and Zn–Fe alloy

Received: 17 March 2004 / Revised: 11 May 2004 / Accepted: 23 July 2004 / Published online: 15 June 2005
© Springer-Verlag 2005

Abstract Electroreduction of α -glucose to form sorbitol on Zn/CNTs and Zn alloy/CNTs electrodes has been investigated in this paper. Carbon nanotubes (CNTs) used in this paper are grown directly on graphite disks by chemical vapor deposition. Zn and Zn alloy are electrodeposited on the activated CNTs/graphite electrode by pulse galvanostatic method. The micrographs of Zn/CNTs and Zn alloy/CNTs electrodes are characterized by scanning electron microscopy. The results show that the current efficiency of α -glucose reduction on CNTs electrodes is much better than that on flat Zn electrodes. The order of the current efficiency on different electrodes is as follows: Zn/CNT (0.58) \approx Zn–Fe/CNT (0.57) > Zn–Ni/CNT (0.43) \approx Zn/graphite (0.42) > Zn (0.40). It indicates that CNTs have good potential application in electrosynthesis. Additionally, effects of some operating parameters, such as pH, temperature and α -glucose concentration, on the current efficiency of α -glucose reduction are also discussed.

Keywords Carbon nanotubes · Zn and Zn alloys · Electrodeposition · Glucose electroreduction

Introduction

Compared with conventional organic synthesis, there are many advantages in organic electrosynthesis, such as high purity and selectivity of product, simple process combined with low energy consumption and low pollution. Additionally, the most important is that electrosynthesis can be performed in a very wide potential

range, which make most oxidation and reduction reactions possible [1]. In general, the electrodes used in electrosynthesis should have good chemical and electrochemical stability, high conductivity, good electrocatalytic activity and selectivity, high surface area, etc. However, flat electrodes that result in low surface area are usually used in electrosynthesis [1, 2]. This is an obstacle to get a high current efficiency at a high applied current density. Several works have investigated the effect of the electrode structure on electrosynthesis and suggested that high available surface area of the electrodes could enhance the current efficiency and yield [3].

On the other hand, since 1991 [4], carbon nanotubes (CNTs) have attracted much attention because of their attractive electronic, chemical and mechanical properties [5–8], and were studied intensively in many fields such as field-emission devices [9, 10], atomic force microscope probes [11], gas and chemical sensors [12], composite materials [13], electrochemical supercapacitors [14], etc. Furthermore, high surface area, low resistance and good chemical and electrochemical stabilities in aqueous and non-aqueous solutions [15] suggest that CNTs are suitable materials as electrodes or supports for electrocatalytic active materials in electrosynthesis.

For the application in electrode, two kinds of CNTs electrodes have been developed: with [16] and without [17] binders. In the electrode without binders, CNTs are mechanically and electrically loose. When a binder is used, it brings impurities into the electrode and degrades the electrochemical performance. Furthermore, both methods result in a high contact resistance between the active materials (CNTs) and current collectors (graphitic). In this paper, CNTs are grown directly on graphite disks and are used for the first time as electrode in electrochemical synthesis. This not only simplifies the preparation of CNTs electrodes but also reduces greatly the contact resistance between CNTs and graphite.

In this paper, the electroreduction of glucose to sorbitol was chosen as an example to explore the potential application of CNTs/graphite electrode in electrosynthesis. The reduction of glucose to sorbitol, a compound

S. Fei · J. Chen (✉) · S. Yao · G. Deng · L. Nie · Y. Kuang
State Key Laboratory of Chemo/Biosensing and Chemometrics,
College of Chemistry and Chemical Engineering,
Hunan University, Changsha, 410082, P.R.China
E-mail: chenjinhua@hnu.cn
Tel.: +86-731-8821818
Fax: +86-731-8821818

with many uses in the foodstuff and related industries, has been investigated extensively [18–21]. In order to get high current efficiency, Zn, Pd, Cd, Th and their amalgams, which have high hydrogen overvoltage, are usually used as cathodic materials. Here, Zn and its alloys (Zn–Ni and Zn–Fe) are selected as the cathodic materials and electrodeposited on CNTs. The morphology of the electrode has been characterized by scanning electron microscopy (SEM). The electrochemical performance of the corresponding electrode has been investigated in detail. Additionally, effects of some operating parameters on the current efficiency have also been discussed.

Experimental

Chemicals and instruments

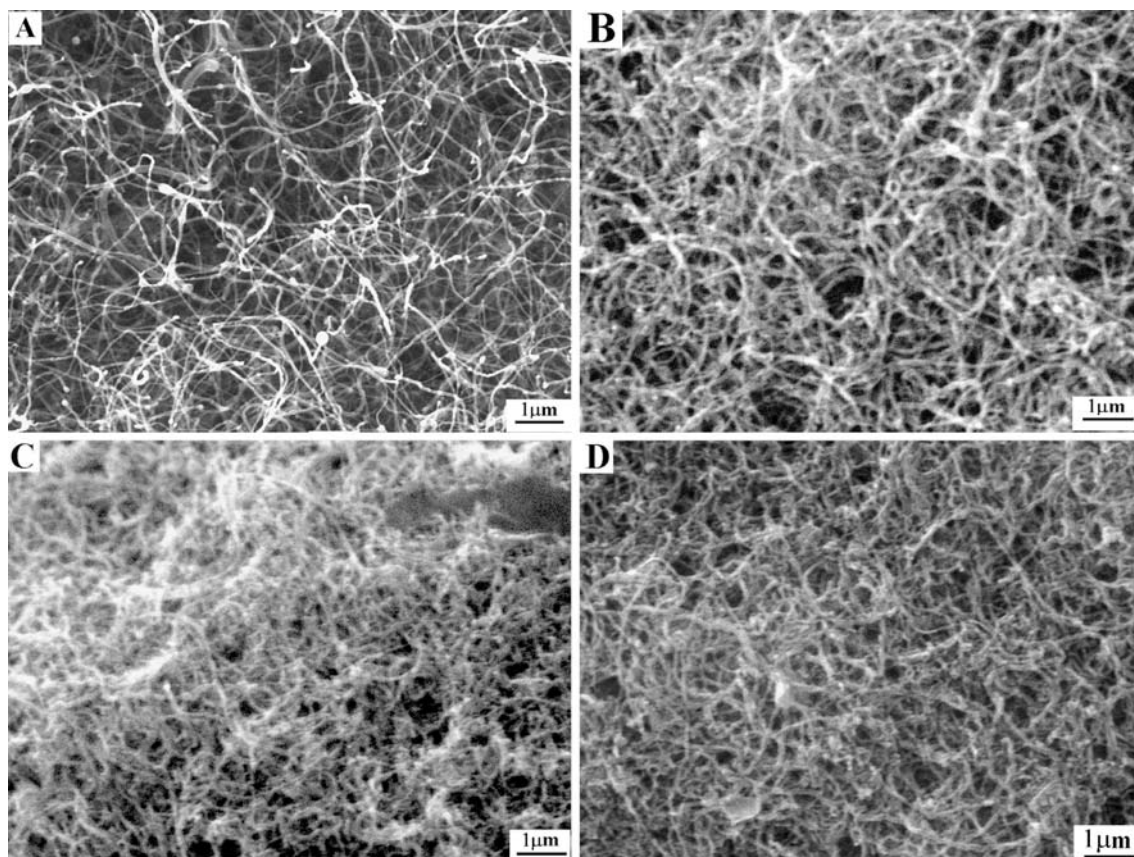
CNTs, grown directly on graphite disk (16 mm in length, 10 mm in width and 4 mm in height) by chemical vapor deposition, were used as working electrodes. The detailed description of the CNTs' synthesis has been

reported in the literature [22, 23]. The SEM image of the CNTs used in this paper is shown in Fig. 1a. The diameter of the CNTs is about 50–100 nm. A platinum foil served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. CHI660A electrochemical workstation (CH Instruments, Inc.) was employed for electrodeposition of Zn and its alloy on the CNTs' surface and electrochemical studies of the electrodes using a standard three-electrode cell. On the other hand, galvanostatic electrolysis of α -glucose was carried out in a standard glass H-cell divided with an ion-exchange membrane (model, 3361; Shanghai Chemical Factory, China) and a platinum foil served as the counter electrode. A DF1738 DC regulated power supply (Ningbo Zhongce Electronics Co. Ltd, China) was used as the DC power source. All chemicals are of analytical grade. Freshly double-distilled water was used throughout. All experiments were carried out at ambient temperature.

Electrodeposition of Zn and its alloy on the CNTs' surface and electroreduction of α -glucose

Fig. 1 SEM images of (a) CNTs grown directly on the graphite disk; (b) Zn/CNTs deposited from 0.13 M ZnO + 3.0 M NaOH; (c) Zn–Fe/CNTs deposited from 0.13 M ZnO + 0.01 M FeSO₄ + 3.0 M NaOH + 0.17 M C₄H₄KNaO₆ and (d) Zn–Ni/CNTs deposited from 0.13 M ZnO + 0.06 M NiSO₄ + 3.0 M NaOH + 0.23 M TEA aqueous solutions

Zn and its alloys (Zn–Ni and Zn–Fe) were electrodeposited on the CNTs' surface by pulse galvanostatic method. $T_{on} : T_{off}$ was 1 ms : 9 ms. The average current density is 10 mA cm⁻². The electrodeposition bath is 0.13 M ZnO + 3.0 M NaOH solution for Zn film, 0.13 M ZnO + 0.06 M NiSO₄ + 3.0 M NaOH +



0.23 M TEA (Triethanolamine) solution for Zn–Ni film and 0.13 M ZnO + 0.01 M FeSO₄ + 3.0 M NaOH + 0.17 M C₄H₄KNaO₆ (potassium sodium tartrate) solution for Zn–Fe film. The electrodeposition experiment was carried out for 10 s. Before deposition of Zn and its alloy, the CNTs/graphite electrode was pretreated in 30 wt% HNO₃ aqueous solution for 30 min to remove the metallic iron particles that served as catalyst for the growth of CNTs. To further increase the electrochemical activity of CNTs in water solution [24], the CNTs/graphite electrode was then cycled in 0.5 M H₂SO₄ for 100 cycles under the potential range of –0.15 to 0.95 V at a sweep rate of 50 mV/s. After the deposition of Zn or its alloys, the samples were cleaned by double-distilled water. Then the electrochemical properties of the electrode and electroreduction of α -glucose to sorbitol were investigated by cyclic voltammetry, linear sweep voltammetry and galvanostatic method. The current efficiency was obtained according to iodimetric analysis method and calculated by the following equation [25]:

$$\eta = (V_1 - V_2) \times C \times \frac{M}{W} \quad (1)$$

where η is the current efficiency; V_1 and V_2 are the volumes of standard iodine solution consumed during iodine titration after and before glucose electro-reduction, respectively; C is the concentration of standard iodine solution (C is 0.05 M in this paper); M is the molecular weight of sorbitol and W is the theoretical yield of sorbitol.

For comparison, Zn was also electrodeposited on the graphite electrode and the electrochemical properties of the Zn/graphite and flat Zn electrodes have also been investigated. All the potentials were referred to SCE.

The morphologies of Zn and its alloy/CNTs electrodes were investigated by SEM (JSM 5600LV, operating at 20 kV).

Results and discussion

The micrographs of the Zn/CNTs and its alloys/CNTs electrodes

Figure 1 shows the micrographs of Zn/CNTs, Zn–Fe/CNTs and Zn–Ni/CNTs electrodes. From Fig. 1b–d, it can be observed obviously that Zn, Zn–Ni and Zn–Fe are dispersed uniformly on the surface of CNTs. Zn/CNTs, Zn–Ni/CNTs and Zn–Fe/CNTs composite have three-dimensional and porous structure. The interesting three-dimensional structure of the electrodes may result in large available reaction surface area for α -glucose reduction.

Electrochemical properties of the Zn/CNTs electrode

Electrochemical properties of the Zn/CNTs electrode have been investigated by linear sweep voltammetry.

Figure 2 shows that the cathodic polarization curves of flat Zn (Fig. 2a), Zn/graphite (Fig. 2b) and Zn/CNTs electrodes (Fig. 2c) in 0.1 M Na₂SO₄ (pH 11) aqueous solution with and without 0.1 M α -glucose. Compared with curve II in Fig. 2a, it can be found that the process (Fig. 2a, curve I) for glucose reduction ($\text{glucose} + 2\text{H}^+ \rightarrow \text{sorbitol} - 2\text{e}^-$) on flat Zn electrode starts at approximately –1.6 V. The cathodic polarization curve of Zn/graphite electrode (Fig. 2b) is very similar to that of flat Zn electrode (Fig. 2a). However, the current of hydrogen evolution on Zn/CNTs electrodes (Fig. 2c, curve II) is larger than that on flat Zn (Fig. 2a, curve II) and Zn/graphite electrodes (Fig. 2b, curve II) due to the high surface area of CNTs. On the other hand, the ratio of the currents at –1.8 V shown in curve I (with glucose) and II (without glucose) is 1.47 for Zn/graphite and 1.69 for Zn/CNTs electrodes. This implies that the reduction current of α -glucose is enhanced by CNTs.

Galvanostatic electrolysis of α -glucose was also carried out on these three electrodes and the corresponding current efficiencies are listed in Table 1. The current efficiency obtained on Zn/CNTs electrodes is higher than that on Zn/graphite and flat Zn electrodes. This is

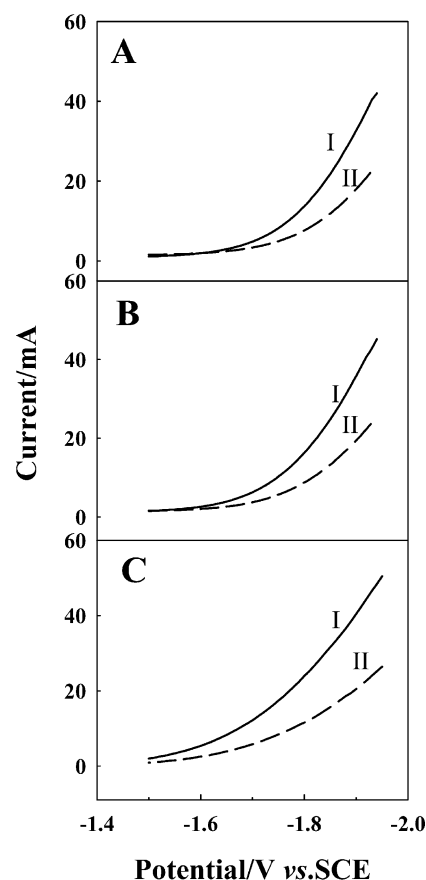


Fig. 2 Linear sweep voltammograms of α -glucose reduction at a flat Zn (a), Zn/graphite (b) and Zn/CNTs (c) electrodes in 0.1 M Na₂SO₄ aqueous solutions with 0.1 M glucose (curve I) and without glucose (curve II) (pH 11, temperature = 30°C, scan rate = 0.05 V/s)

contributed to the good properties and high surface area of CNTs, besides high hydrogen evolution potential of Zn. As reported in literature [19], the current efficiency of glucose reduction decreases obviously with the increase of the current density ascribed to hydrogen evolution. In this paper, due to high specific surface area of Zn/CNTs electrodes, the real current density on Zn/CNTs electrodes is much lower than that on flat Zn and Zn/graphite electrodes at the same applied current. This results in lower over-potential and higher current efficiency of α -glucose electroreduction. On the other hand, for glucose reduction on solid electrode, the mutarotation of glucose from the irreducible cyclic hemiacetal form to the open chain aldehyde form is carried, and then the open chain aldehyde is electrochemically reduced to sorbitol [20]. The corresponding scheme is shown in Fig. 3. For Zn/CNTs electrodes, with the evolution of hydrogen, an alkaline zone is formed in the whole three-dimensional structure of the electrode and should be larger than that at the flat Zn and Zn/graphite electrodes. This large alkaline zone is beneficial to the conversion of cyclic hemiacetal of glucose to the electro-reducible form (the open chain aldehyde) during glucose electroreduction. This implies that the current efficiency of glucose reduction may be improved by three-dimensional Zn/CNTs electrodes. Additionally, small Zn particles with high dispersion on CNTs may be more active for α -glucose reduction than bulk Zn.

In the practical opinion, the long-term stability of electrode materials for electrosynthesis is very important. The stability of Zn/CNTs electrodes has been investigated by cyclic voltammetry in 0.1 M Na₂SO₄ (pH 11) aqueous solution and the corresponding results are shown in Fig. 4. The oxidation and reduction of Zn can be observed at -1.1 and -1.5 V (SCE), respectively. Compared with curves I and II in Fig. 4, it can be seen that the peak currents of oxidation and reduction of Zn decrease significantly (about 50%) after the electrode was used in galvanostatic electrolysis of glucose for 4 h. The main reasons may be that the dissolution of Zn on CNTs happens during glucose electrolysis. Additionally, from Fig. 4, the starting current for curve I is much more negative than that for curve II. This implies that the dissolution of Zn in curve I is easier than that in curve II, which may result from the change of surface state of Zn during glucose electroreduction. Therefore, the stability of Zn/CNTs electrodes should be improved.

Table 1 Influence of cathode materials on the current efficiency of α -glucose electroreduction by galvanostatic method (α -glucose = 0.1 M, Na₂SO₄ = 0.1 M, pH 11, current density = 1 A/dm², temperature = 30°C)

Electrode	Flat Zn	Zn/graphite	Zn/CNTs	Zn-Ni/CNTs	Zn-Fe/CNTs
Current efficiency	0.40	0.42	0.58	0.43	0.57

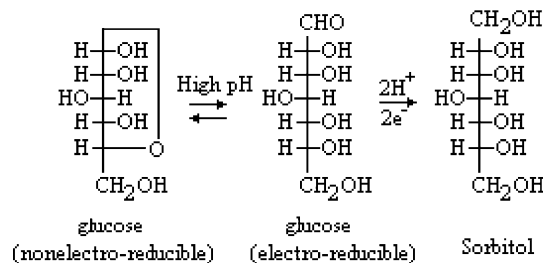


Fig. 3 The scheme of α -glucose mutarotation and electroreduction

Electrochemical properties of Zn alloys/CNTs electrodes

In order to improve the stability of Zn/CNTs electrodes, Zn alloys (Zn-Fe and Zn-Ni) deposited from alkaline bath solutions, were used as the electro-active materials. The electrochemical properties of Zn-Ni/CNTs and Zn-Fe/CNTs electrodes have also been investigated. From Fig. 5, it can be seen that the curves of Zn-Ni/CNTs (Fig. 5a) and Zn-Fe/CNTs (Fig. 5b) electrodes are similar to that of Zn/CNTs electrodes (Fig. 2c). The hydrogen evolution current on Zn-Ni/CNTs electrodes (Fig. 5a, curve II) is larger than on Zn/CNTs electrodes (Fig. 2c), which may be attributed to Ni in alloy [26], while the increase of hydrogen evolution current on Zn-Fe/CNTs electrodes (Fig. 5b, curve II) is not much in contrast with that on Zn/CNTs electrodes (about 7%). Figure 6 shows a CV of Zn-Fe/CNTs electrodes in 0.1 M Na₂SO₄ (pH 11) aqueous solution. After 8 h electrolysis, a decrease of the peak currents of the oxidation and reduction of the active material (Zn-Fe) can also be observed. However, compared with Zn/CNTs electrodes (Fig. 4), it can be concluded that Zn-Fe/CNTs electrodes has good electrochemical stability for α -glucose reduction. A similar result can also be observed for Zn-Ni/CNTs electrodes (the CV is not shown here). The current efficiencies for electroreduction of α -glucose on Zn-Fe/CNTs and Zn-Ni/CNTs electrodes are obtained and also shown in Table 1. It can be observed that the current efficiency on Zn-Fe/CNTs electrodes is much higher than that on Zn-Ni/CNTs

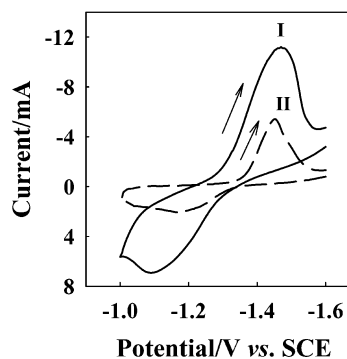


Fig. 4 Cyclic voltammograms at Zn/CNTs electrode before electrolysis (curve I) and after electrolysis for 4 h (curve II) in 0.1 M Na₂SO₄ solution (pH 11, scan rate = 0.1 V/s)

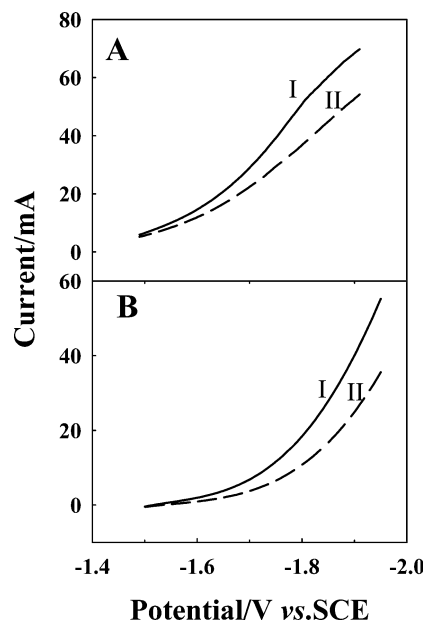


Fig. 5 Linear sweep voltammograms of α -glucose reduction at Zn–Ni/CNTs (a), Zn–Fe/CNTs (b) electrodes in 0.1 M Na_2SO_4 aqueous solutions with 0.1 M glucose (curve I) and without glucose (curve II) (pH 11, temperature = 30°C, scan rate = 0.05 V/s)

electrodes. Therefore, Zn–Fe/CNTs electrode is selected to investigate the effects of some parameters (such as temperature, pH, etc.) on the electroreduction of α -glucose to sorbitol.

Effects of some operating parameters on the electroreduction of α -glucose to sorbitol at Zn–Fe/CNTs electrodes

It was reported that current efficiency of electrosynthesis was affected by pH, temperature, electrolyte compositions, etc. [20]. The effect of pH on the current efficiency

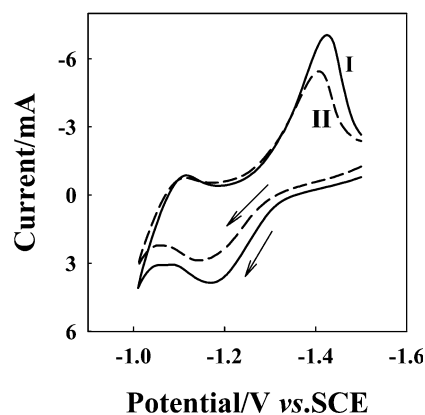


Fig. 6 Cyclic voltammograms at a Zn–Fe/CNTs electrode before electrolysis (curve I) and after 8 h electrolysis (curve II) in 0.1 M Na_2SO_4 solution (pH 11, scan rate = 0.1 V/s)

of glucose electroreduction has been investigated on Zn–Fe/CNTs electrodes and the corresponding result is shown in Fig. 7. The current efficiency increases with the increase of pH and a plateau can be observed at high pH value (pH \geq 11). This may be ascribed to the character of glucose electroreduction: high pH is helpful to the mutarotation of glucose, which results in the increase of current efficiency. On the other hand, at high pH, glucose isomerization occurs and fructose and mannose will be formed, which results in the decrease of current efficiency [20].

On the other hand, the effect of temperature on current efficiency is shown in Fig. 8. It can be found that the current efficiency increases with the increase of temperature and the maximum of the current efficiency was obtained at about 40°C. The reason may be as follows: both the rate of the mutarotation of α -glucose and the evolution of hydrogen increases with the increase of temperature. At low temperature (< 40°C), the current efficiency is affected mainly by the rate of the mutarotation of α -glucose and increases with the increases of temperature. However, hydrogen evolution is dominant at high temperature (> 40°C) and results in the decrease of the current efficiency [20].

Besides, the effect of the α -glucose concentration on the current efficiency is shown in Fig. 9. The current efficiency increases with the increase of α -glucose concentration and a maximum appears at around 0.1 M. This result is similar with that obtained in other works [20, 27]. At low concentration, the reduction of α -glucose is diffusion controlled and the dominant reaction on electrode is hydrogen evolution. This results in a relative low current efficiency. With the increase of the α -glucose concentration, the diffusion rate of α -glucose to electrode surface increases, which results in the increase of the electroreduction rate of α -glucose and the current efficiency increases.

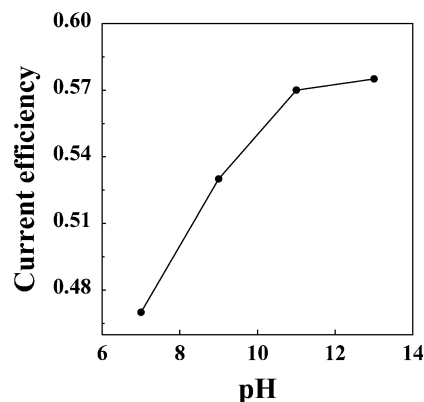


Fig. 7 Effect of pH on the current efficiency of α -glucose reduction on Zn–Fe/CNTs electrode by galvanostatic method (α -glucose = 0.1 M, Na_2SO_4 = 0.1 M, current density = 1 A/dm², temperature = 30°C)

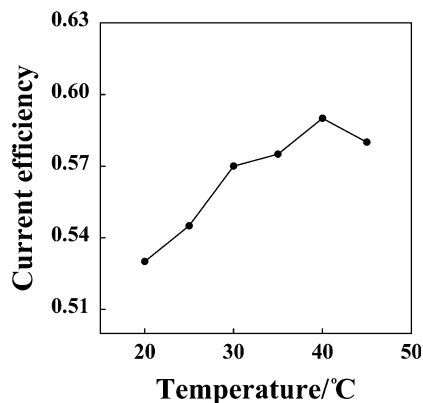


Fig. 8 Effect of temperature on the current efficiency of α -glucose reduction on Zn-Fe/CNTs electrode by galvanostatic method (pH 11, α -glucose = 0.1 M, Na_2SO_4 = 0.1 M, current density = 1 A/dm²)

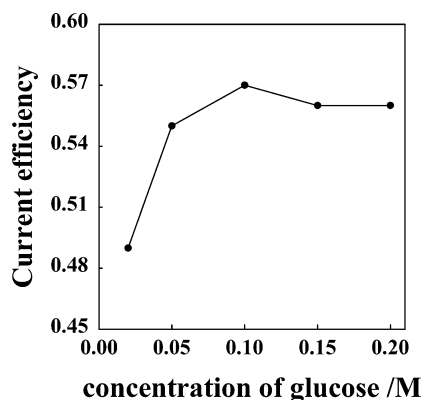


Fig. 9 Effect of α -glucose concentration on current efficiency of α -glucose reduction on Zn-Fe/CNTs electrode (pH 11, Na_2SO_4 = 0.1 M, current density = 1 A/dm², temperature = 30°C)

Conclusion

Electroreduction of α -glucose on Zn/CNTs and Zn alloy/CNTs electrodes has been investigated in this work. CNTs used in this paper are grown directly on graphite. Zn and Zn alloy are electrodeposited on the activated CNTs/graphite electrodes by pulse galvanostatic method. The micrographs of Zn/CNTs and Zn alloy/CNTs electrodes are characterized by SEM. The results show that current efficiency for α -glucose reduction on modified CNTs/graphite electrodes is much better than on flat electrodes and Zn-Fe/CNTs electrodes has good

electrochemical stability for α -glucose reduction. These results suggest that CNTs possess potential applications as electrode or catalyst supports in electrosynthesis.

Acknowledgments This work is supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry under the grant 2001-498 and by the National Natural Science Foundation of China under the grants 50172014 and 20275009.

References

1. Ma CA (2002) Introduction to synthetic organic electrochemistry. Science Press, Beijing
2. Shen Y, Atobe M, Li W, Nonaka T (2003) *Electrochim Acta* 48:1041
3. Trasatti S (2000) *Electrochim Acta* 45:2377
4. Iijima S (1991) *Nature* 345:56
5. Wang J, Musameh M (2003) *Anal Chem* 75:2075
6. Collins PG, Bradley K, Ishigami M, Zettl A (2000) *Science* 287:1801
7. Seifert G, Kohler T, Frauenheim T (2000) *Appl Phys Lett* 71:1313
8. Ajayan PM (1999) *Chem Rev* 99:1787
9. Collins PG, Zettl A, Sando H, Thess A, Smalley RE (1997) *Science* 278:100
10. Heer WAD, Chatelatin A, Ugarte D (1995) *Science* 270:1179
11. Wong SS, Woolley AT, Joselevich E, Cheung CL, Lieber CM (1998) *J Am Chem Soc* 120:8557
12. Joseph W, Mustafa M (2003) *Anal Chem* 75:2075
13. Dresselhaus MS (1992) *Nature* 385:195
14. Hughes M, George ZC (2002) *Chem Mater* 14:1610
15. Nugent JM, Santhanam KSV, Rubio A, Ajayan M (2001) *Nano Lett* 1:87
16. Ma R, Liang J, Wei B, Zhang B, Xu C (1999) *Bull Chem Soc Jpn* 72:2563
17. Niu C, Sichel EK, Hoch R, Moy D, Tennent H (1997) *Appl Phys Lett* 70:1480
18. Pintauro PN, Johnson DK, Park K, Baier MM, Nobe K (1984) *J Appl Electrochem* 14:209
19. Park K, Pintauro PN, Baizer MM, Nobe K (1985) *J Electrochem Soc* 132:1850
20. Kassim AB, Rice CL (1981) *J Appl Electrochem* 11:261
21. Anantharam V, Pintauro PN (1994) *J Electrochem Soc* 141:2742
22. Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou RA, Wang G. (1996) *Science* 274:701
23. He ZB, Chen JH, Liu DY, Tang H, Deng W, Kuang YF (2004) *Mater Chem Phys* 85:396
24. Eraymundo P, Cazorla AD, Linares SA, Delpeux S, Frackowiak E, Szostak K, Beguin F (2002) *Carbon* 40:1597
25. Lin GF (1997) *Handbook of food additives*. Chemical Industry Press, Beijing
26. Hu CC, Tsay CH, Bai A (2003) *Electrochim Acta* 48:907
27. Lu ZG, Wen LR, Zhang JS (2001) *Chin J Fine Chem Intermed* 31:30