Short Communication

Large-scale Synthesis of Cu₂O Nanocubes and Their Electrochemical Properties

Hongdong Liu[1], Zhongli Hu[1], Rong Hu[1,], Bitao Liu[1], Haibo Ruan[1,*] , Lei Zhang[2], Wei Xiao[1]*

[1] Research institute for new materials technology, Chongqing university of arts and sciences, Chongqing 402160, PR China
[2] College of life science, Chongqing normal university, Chongqing 401331, PR China
[*]E-mail: hurong_82@163.com, rhbcqu@aliyun.com

As an environmentally-friendly *p*-type semiconductor, cuprous oxide (Cu₂O) has exhibited potential applications, in particular sensors, solar cells, and Li-ion batteries. In this paper, uniform Cu₂O nanocubes were large-scale fabricated through a solution-based chemical precipitation method. The as-synthesized products were characterized by XRD and SEM. As anode materials for Li-ion batteries, Cu₂O nanocubes show excellent cycling performance, high capacity retention and coulombic efficiency.

Keywords: Cuprous oxide, Li-ion batteries, nanocubes, electrochemical performance

1. INTRODUCTION

Rechargeable Li-ion batteries are widely regarded as a potential power source for upcoming century become of the growing concern about energy crisis and environmental protection. The main advantages of the Li-ion batteries are its high energy density and lightweight, whereas its disadvantage is lower power which limits its application in some situations especially for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-4]. It is highly desired to develop better cathode and anode materials leading to enhanced electrochemical properties and economical Li-ion batteries[5, 6]. Therefore, several research groups have devoted to alternative anode materials with high capacities such as silicon-based materials [7], sulfide [8], lithium alloying metals[9] and transition metal oxides[10] in order to replace the conventional graphite anode materials[11-13]. Among these potential anode materials, cuprous oxide (Cu₂O) has attracted immerse attention as an anode material thanks to its non-toxicity, low-cost and reversible mechanism with Li⁺ [14-16]. Unfortunately, there are several

problems that limit the application of Cu_2O, including rapid capacity fading and poor cycling stability, which are caused by the large-volume change and low conductivity during cycling [17, 18]. To overcome these problems, the synthesis of micro- or nano-structured Cu_2O has become one of the most promising strategies. Until now, many kinds of micro- or nano-sized Cu_2O have been studied, for example, nanowires/nanorods, spheres, starfish-like and octahedral-shaped architecture, hollow/core-shell structure, and nanocubes[19-22]. According to previous studies[21, 23], Cu_2O nanocubes display superior Li-ion batteries' performance with excellent cycling performance, high capacity retention and coulombic efficiency. However, the preparation method of Cu_2O nanocubes is expensive and very difficult to industrially large-scale production.

Herein, we report a large-scale and economical method to synthesis Cu_2O nanocubes via a solution-based chemical precipitation method. As anode materials for Li-ion batteries, the as-synthesized samples show excellent cycling stability and reversibility.

2. EXPERIMENTAL

2.1 Synthesis

All the chemical reagents were of analytical grade and used as purchase without any further purification. In a typical synthetic procedure, 0.85 g of $CuCl_2 \cdot 2H_2O$ was dissolved in 500 mL of distilled water under vigorous stirring at 60 ^{o}C. When the solution became homogeneous, 50 mL of NaOH (2 M) was introduced to the solution. After stirring for 30 min, 50 ml of L-Ascorbic acid($C_6H_8O_6$) (0.6 M) was added slowly into the above solution under stirring. Then, the mixed solution was stirred for 3 h at 60 ^{o}C to form brick-red Cu_2O precipitates. Once being cooled to the room temperature naturally, the collected precipitates were centrifuged several times with de-ionized water and ethanol. Finally, the as-synthesized products were dried in vacuum at 60 ^{o}C for 24 h.

2.2 Materials characterization

The crystal structure and phase impurity of the samples were evaluated by X-ray powder diffraction (XRD, TD-3500X) with Cu Ka radiation at a scanning rate of 0.07 ^{o} s^{-1} between 10° and 80°. The morphology and the microstructure were examined by scanning electron microscopy (SEM, FEI Quanta 250, USA).

2.3 Electrochemical measurements

The electrochemical performance was tested using standard coin-type half cells. The working electrodes were firstly prepared by mixing 80 wt% of active materials, 10 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) dissolved in a certain amount of N-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. Subsequently, the slurry was uniformly coated onto the Cu foil and dried at 120 ^{o}C for 8 h under vacuum condition. The electrolyte was 1 M LiPF$_6$ with the mixture of

ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v). A metallic lithium foil was used as the counter electrode. All the half cells were assembled in an argon filled glove box. The charge/discharge measurements were carried out at the current density of 100 mA g^{-1} in the voltage range of 0-3 V using Battery Testing System (Neware BTS-610) at room temperature.
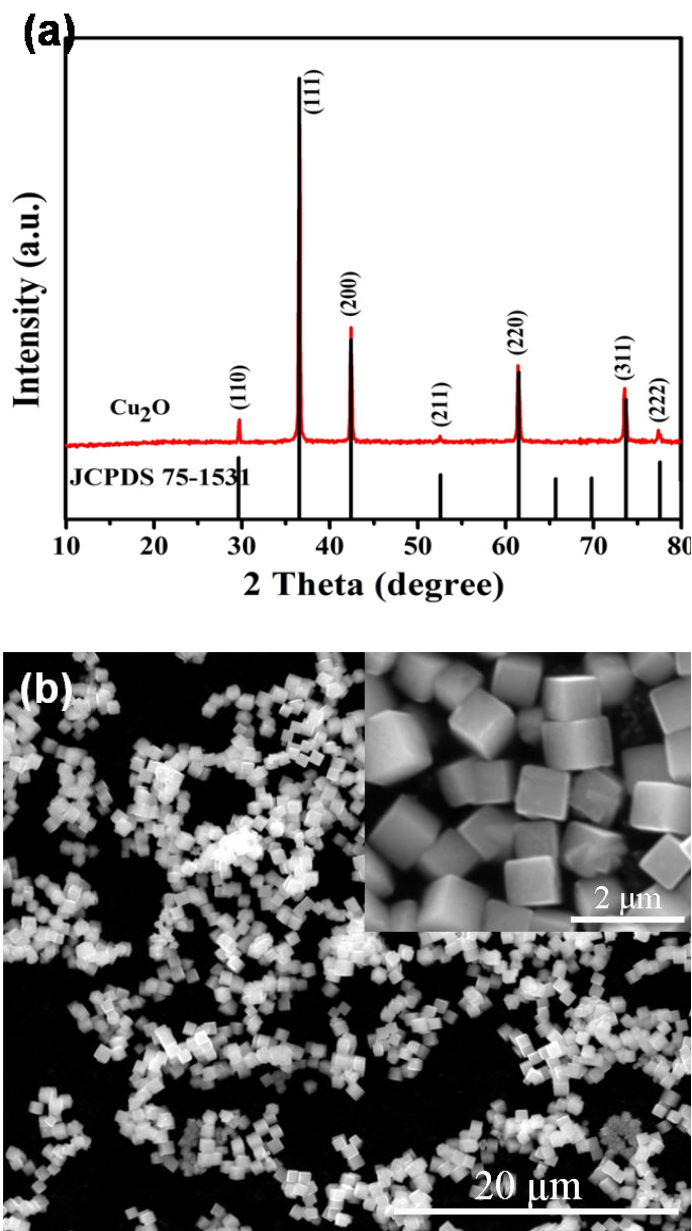
3. RESULTS AND DISCUSSION

Figure 1. (a) X-ray diffraction pattern of Cu$_2$O nanocubes, (b) SEM images of Cu$_2$O nanocubes.

To identify the crystal structure and phase impurity of the Cu$_2$O nanocubes, XRD experiment was tested. Fig.1a shows the XRD pattern of the samples and the standard card of Cu$_2$O. It is observed

that all the diffraction peaks of 2θ values at 29.67°, 36.52°, 42.41°, 52.54°, 61.42°, 73.58° and 77.50° can be well attributed to (110), (111), (200), (211), (220), (311) and (222) planes of the cubic phase of Cu_2O (JCPDS 75-1531), respectively. There is no other noticeable peaks belonged to the impurities, which indicates that high purity Cu_2O has been synthesized successfully.

SEM was performed to determine the morphology and microstructure of the as-synthesized products. As shown in Fig.1b, the SEM image of low magnification shows that the samples present a cubic structure with a relative uniform size. The high magnification SEM pattern inserted in Fig.1b reveals that the edge length of Cu_2O nanocubes is about 800 nm.

Half cells were assembled to evaluate the electrochemical performance of the Cu_2O nanocubes using galvanostatic charge/discharge tests. Fig.2a displays the initial three charge/discharge cycles at the current density of 100 mA g^{-1} between 0 and 3 V. The initial discharge capacity of Cu_2O nanocubes is 473 mAh g^{-1}, which is higher than the theoretical capacity. However, the charge capacity decreases to 148.81 mAh g^{-1} in the first cycle, and the coulombic efficiency is 31.45%. High initial capacity loss of 324.35 mAh g^{-1} is attributed to the formation a solid electrolyte interface (SEI) layer and electrolyte decomposition, which is commonly reported about most anode materials[24-26]. The SEI layer is a passivation film of electrical insulation and ion conduction on the Cu_2O surface caused by the electrolyte decomposition, which can consume limited Li^+ and increase the interface resistance between electrode and electrolyte [27-29]. In the following cycles, the reversible capacity is almost stable and the coulombic efficiency is enhanced. In addition, in the first discharge cycle, there are two potential plateaus at about 1.2 V and 0.9 V, indicating the formation of SEI layer and the reduction of Cu_2O to Cu, respectively. In the first charge cycle, only two weak potential plateaus are observed. And no obvious changes of the discharge and charge potential plateau in the subsequent cycles except the potential plateau at about 1.2 V is disappeared, which suggesting that the Cu_2O electrodes become more reversible and stable.

To further confirm the electrochemical performance of the Cu_2O nanocubes, the cycling performance was carried out at the current density of 100 mA g^{-1} between 0 and 3 V in Fig.2b.
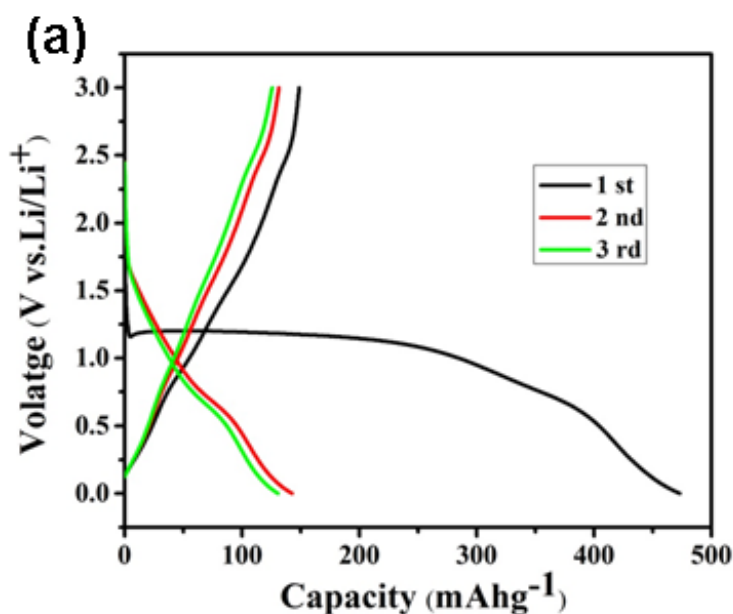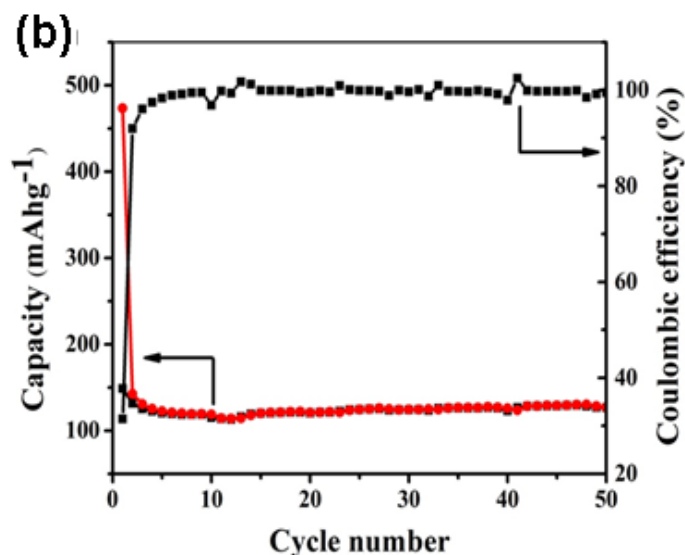
Figure 2. (a) Charge-discharge voltage profiles of Cu_2O nanocubes during initial three cycles at the current density of 100 mA g^{-1},(b) Capacity and coulombic efficiency at the current density of 100 mA g^{-1} over 50 cycles.

The initial discharge capacity is 473 mAh g^{-1} which is high than the previously reported cubic shape Cu_2O (390 mAh g^{-1})[21], subsequently, the discharge capacity rapidly decreases to 142 mAh g^{-1} at the second cycle and maintains around 126 mAh g^{-1} during the subsequent cycles. A reversible capacity of 127 mAh g^{-1} is much high than 82.40 mAh g^{-1} of spherical Cu_2O[30], with almost 85 % of capacity retention even after 50 cycles. Besides, it shows a high coulombic efficiency of over 98 % except the first five cycles. These results indicate that Cu_2O nanocubes maintain good cycling stability and high coulombic efficiency.

4. CONCLUSIONS

In summary, we have successfully prepared Cu_2O nanocubes with edge lengths of 800 nm by a chemical precipitation method. As anode materials for Li-ion batteries, Cu_2O nanocubes exhibit excellent electrochemical cycling performance, capacity retention, and coulombic efficiency. The results show that the first discharge capacity of the Cu_2O nanocubes is 473 mAh g^{-1} at 100 mA g^{-1}, and is still maintained 127 mAh g^{-1} with almost 85 % of capacity retention even after 50 cycles, indicating that Cu_2O nanocubes maintain good cycling stability and high coulombic efficiency.

References

1. W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng, K. Muellen, *Advanced Materials*, 25 (2013) 2909.
2. S. Liu, J. Xie, Q. Su, G. Du, S. Zhang, G. Cao, T. Zhu, X. Zhao, *Nano Energy*, 8 (2014) 84.
3. N. Wang, X. Ma, H. Xu, L. Chen, J. Yue, F. Niu, J. Yang, Y. Qian, *Nano Energy*, 6 (2014) 193.
4. A. Chen, C. Li, R. Tang, L. Yin, Y. Qi, *Physical Chemistry Chemical Physics*, 15 (2013) 13601.
5. H. Geng, Q. Zhou, Y. Pan, H. Gu, J. Zheng, *Nanoscale*, 6 (2014) 3889.
6. H. Geng, Q. Zhou, J. Zheng, H. Gu, *Rsc Advances*, 4 (2014) 6430.
7. C.K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nature Nanotechnology*, 3 (2008) 31.
8. C.W. Lee, S.-D. Seo, H.K. Park, S. Park, H.J. Song, D.-W. Kim, K.S. Hong, *Nanoscale,* 7 (2015) 2790.
9. S. Iwamura, H. Nishihara, Y. Ono, H. Morito, H. Yamane, H. Nara, T. Osaka, T. Kyotani, *Scientific Reports,* 5 (2015).
10. Y. Sharma, N. Sharma, G.V.S. Rao, B.V.R. Chowdari, *Journal of Power Sources*, 173 (2007) 495.
11. S.-H. Yu, D.E. Conte, S. Baek, D.-C. Lee, S.-K. Park, K.J. Lee, Y. Piao, Y.-E. Sung, N. Pinna, *Advanced Functional Materials*, 23 (2013) 4293.
12. Y. Chen, B. Song, L. Lu, J. Xue, *Nanoscale*, 5 (2013) 6797.
13. X. Dong, L. Li, C. Zhao, H.-k. Liu, Z. Guo, *Journal of Materials Chemistry* A, 2 (2014) 9844.
14. Y.H. Lee, I.C. Leu, S.T. Chang, C.L. Liao, K.Z. Fung, *Electrochimica Acta*, 50 (2004) 553.
15. L.J. Fu, J. Gao, T. Zhang, Q. Cao, L.C. Yang, Y.P. Wu, R. Holze, H.Q. Wu, *Journal of Power Sources,* 174 (2007) 1197.
16. J.H. Shin, S.H. Park, S.M. Hyun, J.W. Kim, H.M. Park, J.Y. Song, *Physical Chemistry Chemical Physics,* 16 (2014) 18226.
17. X. Shen, S. Chen, D. Mu, B. Wu, F. Wu, *Journal of Power Sources*, 238 (2013) 173.
18. Y. Zhang, X. Wang, L. Zeng, S. Song, D. Liu, *Dalton Transactions*, 41 (2012) 4316.
19. K. Chen, D. Xue, *Crystengcomm*, 15 (2013) 1739.
20. A. Li, H. Song, J. Zhou, X. Chen, S. Liu, *Crystengcomm*, 15 (2013) 8559.
21. C.Q. Zhang, J.P. Tu, X.H. Huang, Y.F. Yuan, X.T. Chen, F. Mao, *Journal of Alloys and Compounds*, 441 (2007) 52.
22. W. Liu, G. Chen, G. He, W. Zhang, *Journal of Nanoparticle Research*, 13 (2011) 2705.
23. I.C. Chang, P.-C. Chen, M.-C. Tsai, T.-T. Chen, M.-H. Yang, H.-T. Chiu, C.-Y. Lee, *Crystengcomm*, 15 (2013) 2363.
24. Z. Xing, Z. Ju, J. Yang, H. Xu, Y. Qian, *Electrochimica Acta*, 102 (2013) 51.
25. H.-C. Tao, X.-L. Yang, L.-L. Zhang, S.-B. Ni, *Journal of Physics and Chemistry of Solids*, 75 (2014) 1205.
26. M. Cai, H. Qian, Z. Wei, J. Chen, M. Zheng, Q. Dong, *Rsc Advances*, 4 (2014) 6379.
27. S. Yuan, X.-l. Huang, D.-l. Ma, H.-g. Wang, F.-z. Meng, X.-b. Zhang, *Advanced Materials*, 26 (2014) 2273.
28. S. He, J. Li, J. Wang, G. Yang, Z. Qiao, *Materials Letters*, 129 (2014) 5.
29. C. Wang, J. Xu, R. Ma, M.-F. Yuen, *Materials Chemistry and Physics*, 148 (2014) 411.
30. Z. Hu, H. Liu, *Journal of Materials Science-Materials in Electronics*, 26 (2015) 5405.