Carbon Nano-Onions Embedded CuO Nanosheets: An Excellent Stable Anode Material for Lithium Ion Battery

Zhongjing Hao#, 1, 2, Meng Qin#, 1, Yueming Li*, 1, Xiaojun Lv*, 2, Dafeng Zhang2 and Qiushi Wang2

1State Key Laboratory of Metastable Materials Science and Technology, College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, China
2Key Laboratory of Photochemical Conversion and Optoelectronic Materials and HKU-CAS Joint Laboratory on New Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China.
E-mail: liyueming@ysu.edu.cn

Abstract. Carbon nano-onions embedded CuO nanosheets was synthesized by hydrothermal method and this report reports the application of carbon nano-onions embedded CuO nanosheets in lithium ion battery anode materials. The introduction of carbon nano-onions leads to improved electrochemical performance. When applied to potential anode materials for lithium-ion batteries, the novel carbon nano-onions embedded CuO nanosheets deliver reversible discharge capacity of 709.7 mAh g⁻¹ at 0.1 A g⁻¹ and specific capacity of 167 mAh g⁻¹ at 5 A g⁻¹, much higher than those of the pure CuO nanosheets with same preparation conditions. In this paper, we demonstrate that the compositing of carbon nano-onions embedded CuO nanosheets is able to improve the performance significantly.

1. Introduction
Many electronic products, such as cell phones, notebook computers, and electric vehicles, use lithium-ion batteries because of their long cycle life, high energy density, environmental friendliness, and excellent rate performance. [1]. Graphite as an anode material has a limited specific capacity (372 mAh g⁻¹). Therefore, it is very important to find a high capacity anode material. In recent years, transition metal oxides (such as MnO2 [2], Fe3O4 [3], Fe2O3 [4], CuxO [5], NiO [6], SnO2 [7], Co3O4 [8], TiO2 [9]) Because of its high energy density and higher theoretical lithium ion storage capacity, it will be regarded as the most promising anode material, which has been studied by many scholars. Among various transition metal oxides, CuO is favored by some scholars because of its abundant yield, simple preparation process, stable chemical properties, low synthesis cost, high theoretical capacity (674mAh g⁻¹), and environmental harmlessness [10]. However, some of the inherent properties of CuO limit its practical application, for example, poor chemical stability, low electrical conductivity, and large and uneven volume changes during charging and discharging of lithium ions, resulting in rapid capacity degradation [11, 12]. The addition of some well-conducting carbon materials (such as graphene [13, 14] or carbon nanotubes [15]) to CuO is a good method to achieve a method of increasing stability. These conductive carbon materials can improve the inherent disadvantages of CuO and enhance the electronic conductivity of CuO by creating electron paths. Moreover, the conductive carbon can also act to buffer the volume change of the active particles, thereby alleviating the pulverization of the particles during charging and discharging, and ensuring good contact with the copper oxide active particles [16-18]. Compared to other forms of carbon, carbon nano-onions (CNO) can more effectively improve the electrical conductivity [19, 20]. Since
carbon nano onion itself has high conductivity and small particle size of 5-10 nm and 0-D nanostructure, these characteristics make it possible for them to form a conductive network evenly distributed over the entire electrode when making electrode materials, which will be very It is beneficial to improve the electrochemical stability of the battery [21].

In this report, a novel carbon nano-onions embedded CuO nanosheets has been prepared through a simple hydrothermal method. Compared with the copper oxide nanosheet electrode without the carbon nano-onion, the carbon nano-onion and the copper oxide nanosheet combine to function as a negative electrode material for a lithium ion battery, exhibiting a high capacity.

2. Experimental

2.1. Synthesis of CNO.
CNO was synthesized by thermal annealing using a nanodiamond raw material (average particle diameter of about 5 nm), then annealed in Ar atmosphere at a heating rate of 10 °C min⁻¹ and insulation 1300 °C for 1 hour.

2.2. Synthesis of CNO Embedded CuO Nanosheets.
First, in order to form a uniform liquid, CNO was added to a deionized aqueous solution (50 mL) for 30 minutes to maintain ultrasonic conditions. Second, 0.8 g of NaOH and 1.2 g of Cu(CH₃COO)₂·H₂O were added and stirring was continued for ten minutes. Third, the above solution was hydrothermal at 180°C for 12 hours, and naturally cooled to finally obtain a black precipitate which was washed with suction and deionized water for three times, and then dried at 80 °C for 12 hours. The CNO embedded CuO nanosheets composites with different amount of CNO synthesized by changing the amount of CNO (6, 12, 36mg), were named as CuO/CNO-1, CuO/CNO-2, CuO/CNO-3, respectively. The pure CuO was prepared used same procedure except no CNO was added.

2.3. Characterization.
Powder X-ray diffraction (XRD) was measured with a scattering angles from 10 to 80 °. Raman spectroscopy was carried out within 200 cm⁻¹ to 1800 cm⁻¹ using Ar⁺ laser excitation with a wavelength of 532 nm. Morphologies characterization was studied with scanning electron microscopy S-4800. The TEM images were obtained with JEM-2100F equipped with anoperating at 200 kV.

2.4. Electrochemical Measurements.
The active material, conductive Super P, and polyvinylidene fluoride (PVDF) binder with mass ratio of 8:1:1 and N-methylpyrrolidone (NMP) solvent were uniformly coated on copper. The foil is prepared as an anode material. The electrode was vacuum dried at 120 °C for 12 hours and then pressed into a battery for electrochemical testing. The active material mass load is 1.2 mg cm⁻². The lithium sheet is used as a cathode material, and the battery is assembled in a glove box that is insulated from air. Constant current charge/discharge measurements were made for different current densities using a Arbin battery test device over a voltage range of 0.01 to 3.0 V (vs. Li / Li +). Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy were performed using a P4000 electrochemical workstation (Princeton Applied Research, USA) in the range of 0.01 to 3 V (vs. Li / Li⁺).

3. Results and Discussion
The crystallographic information for the CuO, CuO/CNO-2 and precursor-CuO/CNO-2 was characterized by XRD, and the result was shown in Figure 1. The eleven diffraction peaks at 2θ values of 32.4, 35.4, 38.6, 48.6, 53.4, 58.2, 614, 66.1 and 68.0° can be indexed to monoclinic CuO with crystal planes of (110), (111), (202), (020), (202), (113), (311) and (220), which consistent with the JCPDS card NO. 48-1548 [22]. As can be seen from Figure 1, compared with the three materials, the crystallinity of CuO/CNO-2 before the hydrothermal reaction is not good, and the crystallinity of
CuO is the best. Additionally, there is no peak of CNO in the XRD patterns. This result may be attributed to the effect of small amount and small particle size (5-10 nm) of CNO.

To further prove the existence of carbon, the structure of the CuO/CNO-2 and CNO was studied by Raman Spectra (Figure 2). The composition of the product was further investigated by Raman spectroscopy. Three peaks at 298, 346, 632 and 1141 cm\(^{-1}\) (marked by “*”) are detected, consistenting with characteristic peaks of CuO [23-25]. It is found in the Raman spectrum that carbon has two characteristic peaks at about 1350 cm\(^{-1}\) (D band) and 1580 cm\(^{-1}\) (G band), demonstrating the presence of disordered carbon in the prepared material. Which is consistent with the peak of CNO [26].

Figure 1. Typical XRD patterns of the CuO, CuO/CNO-2 and precursor-CuO/CNO-2.

Figure 2. Raman spectra of CNO and CuO/CNO-2.

Figure 3 shows SEM images of precursor (a), the CuO (b) and the CuO/CNO-2 (c) and TEM images of the CNO (d), the CuO (e) and the CNO/CuO-2 (f). Figure 3 (a) shows the CuO/CNO-2 morphology before hydrothermal treatment, which shows an irregular particles morphology. However, after 12 hours of hydrothermal treatment, CuO sheets appeared (Figure 3 (c)). The particle size and morphology of CuO/CNO were characterized by using transmission electron microscopy (TEM). It can be seen from Figure 3 (d) that the carbon nano-onion before the composite with CuO nanosheets has a particle size of 5-10 nm, the inner layer is a diamond core, the outer layer is wrapped with several layers of graphite, and the inner layer of diamond supports the outer layer. The graphite layer is an effective electron path for lithium ion transport. Figure 3 (e) provides TEM micrographs of CuO comprising particles below 10 nm. The 0.253 nm spacing correspond to the (11 \( \bar{1} \) ) planes of monoclinic CuO. As seen at Figure 3 (f), CuO nanosheets and carbon onions still have partial been hybridized.
Figure 3. SEM images of (a) the CuO/CNO-2 before hydrothermal, (b) the CuO and (c) the CuO/CNO-2; TEM images of (d) the CNO, (e) the CuO and (f) the CNO/CuO-2; precursor-CuO/CNO-2.

CV curve of CuO / CNO-2 at 0.1 mV s$^{-1}$ was shown in figure 4(a). It can observe from the curve that during the first scan, the prominent peak at the 1.02V position is due to the formation of the Cu$_2$O mesophase and the associated structural damage. The other two small cathode peaks at 0.87 V and 0.70 V correspond to further reduction of Cu$_2$O to metal Cu$^0$ in the Li$_2$O matrix, possibly with decomposition of the electrolyte solution. Decomposition of the electrolyte solution results in the formation of inorganic by-products in the form of polymer layers and solid electrolyte interfaces (SEI) [27-29]. The above conversion reaction can be seen as $2\text{CuO}+4\text{Li}^++4e^-\rightarrow\text{Cu}_2\text{O}→2\text{Cu}^0+2\text{Li}_2\text{O}$. In the anode scan, the oxidation peak at 2.46V appears to be the oxidation reaction of Cu$^0$ to Cu$^{2+}$ (Cu$^++\text{Li}_2\text{O}\rightarrow\text{CuO}+2\text{Li}^++2e^-$) [30], which is reserved in subsequent cycles. Since the second cycle, the phenomenon that the cathode peak potential is shifted to a higher voltage of 1.21 V proves that an irreversible phase transition occurs in the first cycle. In the anode scan, the oxidation peak appeared at 2.58V. A large number of previous articles have also proved that the electrochemical reaction has the appearance of a cuprous oxide intermediate phase and a similar mechanism [31-33]. As is well known, in the second and third cycles, the CV curves of the materials become overlapping and the area increases slightly, demonstrating that this material provides excellent reversibility in electrochemical reactions. Figure 4 (a) shows that the area of the third circle of CuO/CNO-2 is slightly larger than that of the second circle, which proves that the capacity didn’t decrease. However, the integrate area of the third circle of CuO is smaller than the second circle, which proves that the pure copper oxide capacity is decreasing.

Figure 4. CV curve of (a) CuO/CNO-2, (b) CuO at 0.1 mVs$^{-1}$.
As shown in Figure 5 (b), the rate capabilities of bare CuO, CuO/CNO-1, CuO/CNO-2 and CuO/CNO-3 were tested from 0.1 to 5 A g\(^{-1}\). The capacity retentions of CuO/CNO-2 were 709.7, 643.4, 549, 458.9, 327 and 167.2 mAh g\(^{-1}\) from 0.1 to 5 A g\(^{-1}\) (Figure 5 (a)), respectively, exhibiting a better performance than those of bare CuO (196.3, 124.5, 89.9, 72.3, 55.6, and 26.4 mAh g\(^{-1}\)), CuO/CNO-1 (456.2, 331.1, 230.5, 164.9, 115.2 and 58.6 mAh g\(^{-1}\)) and CuO/CNO-3 (515.2, 410.1, 282.2, 186.0, 103.5 and 40.4 mAh g\(^{-1}\)) upon increasing the current densities. This performance is excellent compared to the best values reported previously among Copper oxide and carbon materials for anode used in lithium ion battery [1, 13, 34-41] (Figure 5 (c)).

The above data demonstrate that the combination of CNO and CuO nanosheets greatly improves the cyclic performance and capacity. Main roles of the carbon shells of CNOs is that the multi-layered graphite carbon shell enables Li ion transport to be faster and more efficient, resulting in a significant increase in transmission capacity [42]. Therefore, too little carbon is not enough to play the role discussed above. But too much carbon is not good either. Since the theoretical specific capacity of carbon is lower than that of copper oxide, the amount of mixing will reduce the total capacity.

4. Conclusions

In all, carbon nano-onions (CNO) embedded CuO nanosheets has been prepared by hydrothermal method. As a potential anode material, compared with bare CuO nanosheets, the CNO embedded CuO nanosheets exhibits high reversible capacity and better rate performance. Accordingly, this research suggests that the introduction of CNO was an effective method to improve the performance of electrode material used as lithium-ion batteries.

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6. References

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