

# A novel method to enhance the conductance of transitional metal oxide electrodes†

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Transitional metal oxides hold great potential for high capacity anodes. However, the low electron conductivity of such materials leads to poor cycling stability and inferior rate capability. We reported herein the use of a novel hydrogen plasma technology to improve the conductance of metal oxides, which leads great success in improving the rate performance of CuO nanotube based anodes. This method has the potential to be widely adopted in the field of lithium ion batteries and supercapacitors.

Along with the rapid growth in the market for portable electronics and electrical vehicles, the need for developing better electrode materials towards high-performance lithium-ion batteries has been gaining more attention.<sup>1</sup> Oxides of transitional metals possess high charge storage capacity, thus these materials show great promise to be used for high-capacity anodes. Such materials, however, are generally poor conductors of electrons and ions and furthermore they exhibit large volume changes, which lead to poor electrode stability and inferior rate capability.<sup>2</sup> There are two major approaches directed to address these issues. The first method requires the downsizing of metal oxides to the nanoscale, or the construction of the metal oxide into a hierarchically porous structure to shorten the ion-diffusion length and accommodate the strain associated with lithium intercalation. Metal oxides with various structures such as nanocubes,<sup>3</sup> nanoflowers,<sup>4</sup> nanocages,<sup>5</sup> nanorings,<sup>6</sup> nanowires,<sup>7</sup> nanotubes,<sup>8</sup> *etc.* have been successfully synthesized, and these nanoscale metal oxides exhibit improved electrochemical performance in comparison to their bulk counterparts. In the second approach, conductive agents, such as carbon black,<sup>9</sup> carbon nanotubes,<sup>10</sup> graphene,<sup>11</sup> *etc.* have been introduced to enhance the conductivity of the electrodes. This strategy has shown great success for increasing the capacity and stability of metal-oxide based electrodes. However, the weak interaction between the metal oxide nanostructures and the conductive additive allows them to separate during charge/discharge

cycling, especially if a high current density is used. This results in inferior rate capability.

*In situ* composites can enhance the interaction between metal oxides and conductive agents.<sup>12,13</sup> However, it is difficult to control the intricate morphology of metal oxides by *in situ* synthesis.

Recently, Hicks *et al.* from the University of California in Los Angeles have developed a technique using downstream atmospheric pressure hydrogen plasma to reduce oxides on the surfaces of metals such as indium and copper.<sup>14–16</sup> In this work, we propose for the first time the application of atmospheric pressure hydrogen plasma towards improving the conductance of transitional metal oxide electrodes. Hydrogen plasma, generated by an Atomflo™ 400L from Surfex® Technology LLC, is a strong reductive gas rich in electrons, hydrogen atoms, metastables and H<sub>2</sub> molecules.<sup>17</sup> Through hydrogen plasma treatment, the surface layer of the metal oxides would be partially reduced into the corresponding metal, which will enhance the conductivity of the electrodes significantly. Unlike the add-in conductive agents, this conductive network is covalently bonded to the active materials, preventing the separation of the active material from the conductive network during cycling. Furthermore, the downstream hydrogen plasma treatment will not destroy the intricate metal oxide morphology formed by the synthesis method.

Copper(II) oxide was chosen as an example to prove the effectiveness of this method, since CuO has high theoretical capacity and suffers from poor cycle stability and rate capability.<sup>18,19</sup> Long CuO nanotubes were synthesized from the oxidation of copper nanowires, and binder-free electrodes were constructed using CuO nanotubes thereafter. The test results showed that CuO nanotubes show better electrochemical performance than copper oxide in particulate form. The cycling stability, however, still falls short of the expectation. Carbon nanotubes (CNTs) were introduced in the making of the electrodes to improve the capacity and cycling stability, and though

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some improvements are seen, the results were still unsatisfying. Treating the CuO nanotubes using the atmospheric pressure hydrogen plasma improved the rate performance of the anode greatly. The electrochemical results generated from the plasma treated anode greatly surpass those generated from CuO and CuO–CNT anodes. To the best of our knowledge, this capacity and rate capability outperforms the CuO-based electrodes ever reported.

Ultra-long copper nanowires were synthesized by non-aqueous self-catalytic growth within liquid-crystalline medium of *n*-hexadecylamine (HDA) and hexadecyltrimethyl ammonium bromide (CTAB). The detailed synthesis procedure can be found in a previous publication by this group.<sup>20</sup> The nanowires were subsequently oxidized in air at 300 °C for 30 min to obtain CuO nanomaterial. Shown in Fig. 1a is an image of the as-prepared CuO taken at 1400 magnification with a scanning electron microscope (SEM). The lengths of the cylindrical nanomaterials as measured on the micrograph exceed 20 μm, while the diameters range from 50–200 nm, giving them an aspect ratio higher than 100 : 1. Closer inspection of the nanomaterials at 15 000 magnification is shown as an inset in Fig. 1a. The inserted image suggests that the CuO adopted a hollow core-shell structure, which is confirmed by the transmission electron micrograph shown in Fig. 1b. The diameter of the hollow core is measured to be 20–50 nm and the shell is about 10–30 nm in thickness. The formation of the tubular structure is attributed to the Kirkendall effect, in which copper and oxygen diffuse across the native oxide layer at the surface of the nanowire to propagate the growth of CuO. The diffusion rate of copper, however, is faster than that of the oxygen, which results in the formation of vacancies in the center of the nanostructure as Cu diffuses outward and forms CuO.<sup>21</sup> The hollow center of the tubular structure can better accommodate the strain associated with lithium intercalation.<sup>22</sup> Furthermore, the TEM image shows that nanocrystallites construct the shells of the nanotubes forming a rough exterior surface on the structures. The roughness provides additional contact area to the electrolytes in

battery applications, promising better lithium ion transport and ample reaction sites.

The CuO nanotubes were examined by X-ray diffraction (XRD) spectroscopy in order to determine the structure of the nanocrystallites, and the result is shown in Fig. 1c. All the peak assignments are associated to the attributes of a symmetrical monoclinic crystal system, which corresponds well with that of copper(II) oxide. The results from XRD suggest that the as prepared CuO crystallites are of high purity.<sup>23</sup>

Fig. 1d shows a SEM image of the CuO nanotube–CNT composites. In this image, the CuO nanotubes and CNTs intertwine to form a porous network structure. As reported, one dimensional nanostructures may allow more effective electron transport than their bulk and particulate counterparts.<sup>24</sup> The intimate contact between the CuO nanotubes and CNTs along their one dimensional structure provides excellent electron conductance, and the porous network structure they form facilitates the diffusion of electrolytes. The nano-scaled characteristic of CuO particles embedded in the nanotubes ensures high contact area between the active materials and the electrolytes. In addition, the hollow interior structure offers sufficient void space to alleviate the mechanical stress caused by volume changes. Therefore, the CuO nanotube–CNT composites are deduced to be excellent anode materials, which can provide high specific capacity and superior cycling stability.<sup>13</sup>

To examine their electrochemical performance, CuO nanotubes were used as the anode active materials in lithium ion batteries. A capacity of 640 mA h g<sup>-1</sup> was measured initially, and more than 82% of the electrode capacity was retained after 100 cycles of charge and discharge. Although this performance is much better than particulate copper oxide materials, the cycling stability is far below requirements for battery anodes.

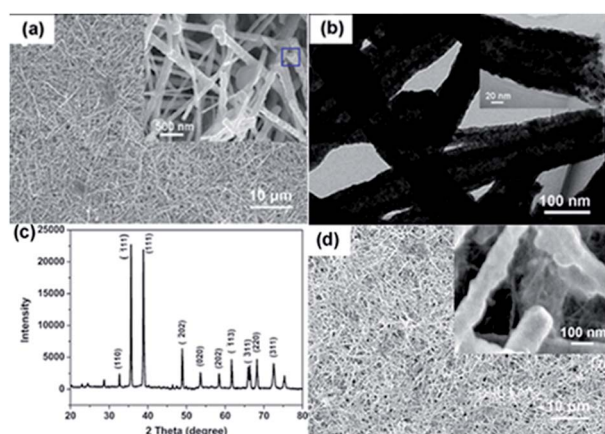


Fig. 1 (a) SEM image of the copper oxide nanotubes; (b) TEM image of the copper oxide nanotubes; (c) XRD pattern of the CuO nanotubes and (d) SEM image of the electrode based on CuO nanotube–CNT composites.

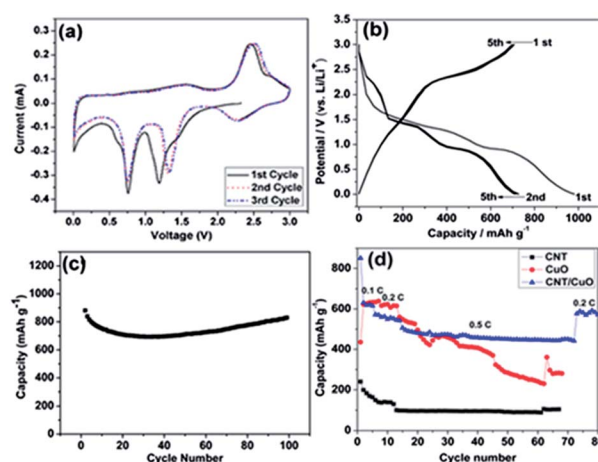


Fig. 2 (a) Cyclic voltammograms of the electrodes made of CuO nanotube–CNT composites at a potential scan rate of 0.5 mV s<sup>-1</sup>; (b) charge/discharge profiles of the CuO nanotube–CNT composites at a rate of 0.1 C; (c) cycling performance of the CuO nanotube–CNT composite electrode at a rate of 0.1 C and (d) rate performance of the electrodes made of CuO nanotubes, CNTs and CuO nanotube–CNT composites.

In order to improve the cycling stability of the CuO anode, CNTs were introduced. Fig. 2a shows the cyclic voltammograms of the CuO nanotube–CNT composite electrodes. Peaks at 1.19 V and 0.75 V are observed on the voltammogram. The former is known to be the result of CuO reduction to Cu<sub>2</sub>O, while the second one is due to the further reduction of Cu<sub>2</sub>O to Cu. Meanwhile, the only anodic peak is located near 2.5 V, corresponding to Li extraction from the crystal lattice of CuO. In the second cycle, a new cathodic peak appears at 2.26 V, which corresponds to the creation of Cu<sub>II</sub><sup>1-x</sup>Cu<sub>I</sub><sup>x</sup>O<sub>1-x/2</sub> (0 < x < 0.4) solid solution. The addition of CNTs does not change the position of the anodic and cathodic peaks as seen from Fig. S1,† implying that the introduction of CNTs does not change the electrochemical nature of CuO. In the second cycle, the peak intensity and integral area is decreased due to irreversible capacity loss, and the peak potentials are shifted. In subsequent cycles, the CV plots show good reproducibility, suggesting a high degree of reversibility of the battery cycling. The initial charge/discharge curves of the CuO nanotube–CNT composite electrode at a scan rate of 0.1 C are recorded in Fig. 2b. There are three pseudoplateaus (2.5–2.0, 1.35–1.25, and 1.0–0.02 V vs. Li<sup>+</sup>/Li, respectively) for the Li reaction with CuO, corresponding to the multistep electrochemical Li reaction process or additional sites for Li uptake.<sup>18</sup> This is in agreement with the three cathodic peaks in the above CV curves. The first discharge capacity of the CuO nanotube–CNT composite is about 980 mA h g<sup>-1</sup>, which is larger than the theoretical capacity of 670 mA h g<sup>-1</sup> based on a maximum uptake of 2 Li per CuO. This can be attributed to the electrolyte being reduced to form a solid electrolyte interphase (SEI) layer, and the reduction of the adsorbed impurities on CuO surfaces.<sup>25</sup> After the second cycle, the discharge/charge voltage profile was maintained at about 700 mA h g<sup>-1</sup>, indicating an excellent retention of the capacity. After 50 cycles, the capacity of the electrodes increased slightly, as seen from Fig. 2c. The increased capacity is attributed to the reversible formation and decomposition of a polymeric gel-like film on the surface of the nanotubes.<sup>26</sup>

As discussed above, the introduction of CNTs can improve the cycling stability of CuO nanotube electrodes efficiently. However, these add-in CNTs did not show much success on improving the rate performance of the CuO nanotube electrodes. As seen in Fig. 2d, a capacity of 620 mA h g<sup>-1</sup> is maintained at a 0.2 C charge/discharge rate but the capacity decreased considerably when the charge/discharge rate was elevated to 0.5 C. The rate capability was slightly improved after introducing CNTs, and a capacity of 450 mA h g<sup>-1</sup> was maintained after 70 cycles. Unfortunately, further elevating the charge/discharge rate leads to considerable capacity loss. At a 1 C charge and discharge rate, only a capacity of 290 mA h g<sup>-1</sup> is maintained after 50 cycles. This is because the microstructure of the CuO nanotubes would deform during cycles of charge/discharge, which causes the CNTs to detach from the CuO nanotubes. This detachment will reduce the electron conduction significantly.

In order to solve this problem, we employed a surface-reduction method to enhance the conductivity of the CuO

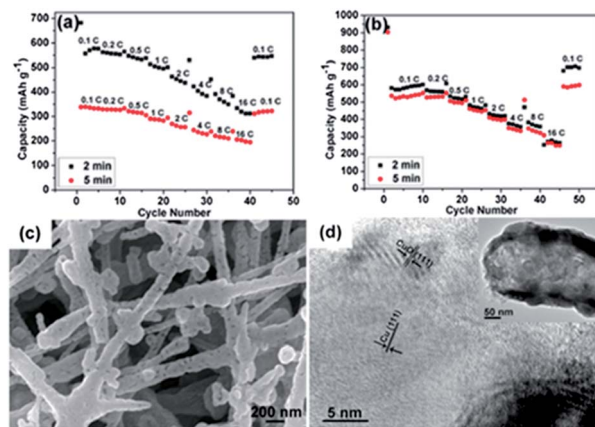


Fig. 3 (a) Rate performance of CuO nanotube electrodes treated by H<sub>2</sub> plasma; (b) rate performance of CuO nanotube–CNT composite electrodes treated by H<sub>2</sub> plasma; (c) SEM image of a CuO nanotube electrode treated by H<sub>2</sub> plasma and (d) TEM image of the CuO nanotube electrode treated by H<sub>2</sub> plasma.

nanotube networks (Fig. 3). The nanotube network is simply positioned on a 250 °C hot plate and treated with hydrogen plasma for several minutes under ambient atmosphere. Then the electrodes were put into a glove box and made into coin cells immediately. After H<sub>2</sub> plasma treatment, the electrode turns red, testifying the reduction of CuO to Cu. As seen from the SEM image, a mass of pores appeared on the surface of the tubes after H<sub>2</sub> plasma treatment. The TEM image showed the maintenance of the hollow interior structure, and the fringes in the HRTEM image were indexed to both Cu and CuO, confirming the partial reduction of the active materials. Elemental analysis of a single CuO nanotube was conducted by STEM-EELS to further prove its partial reduction by H<sub>2</sub> plasma. As shown in Fig. S2,† the oxygen content of the nanotubes decreases after 5 minutes of treatment, especially on the outer surface, which verified the surface reduction of CuO nanotubes by H<sub>2</sub> plasma treatment. Electrochemical impedance spectroscopy was performed on the electrodes with and without H<sub>2</sub> plasma treatment (Fig. S3†). This discloses that the size of the semicircle decreased apparently after H<sub>2</sub> plasma treatment, indicating the decrease of the impedance. As expected, the rate performance of the electrode with H<sub>2</sub> plasma treatment was greatly improved. Although the initial capacitance is lower than that of pure CuO nanotube electrodes due to the loss of active materials *via* surface reduction, their rate capability was incredibly enhanced. A capacity of around 500 mA h g<sup>-1</sup> was maintained after running at a 1 C rate for the CuO nanotube electrode treated with H<sub>2</sub> plasma treatment for 2 min. This is a remarkable enhancement compared with the continuous decay of the capacity at a 0.5 C rate for the CuO electrode without treatment. 54% of the capacity was still maintained when the charge/discharge rate was gradually elevated to 16 C. To our knowledge, most studies on CuO-based anodes have performed the cyclability tests at low charge/discharge rates (within 5 C). For that reason, the 310 mA h g<sup>-1</sup> capacity obtained at 16 C in this study is remarkable for the CuO

anodes. Prolonging the time of H<sub>2</sub> plasma treatment to 5 min led to better rate capability, which reflected the 60% retention of the initial capacity after running at a rate of 16 C. However, almost half of the capacity was compromised due to the reduction of the active materials. CuO nanotube–CNT composite electrodes showed similar improvement of their rate capability after H<sub>2</sub> plasma treatment for 2 min. Differently, the capacity was not compromised considerably with the prolonging of the treating time. We believe that the CNTs wrapped around the CuO-nanotubes affected the further reduction of the CuO nanotubes inside, as seen from Fig. S4.† The reduced drop of the oxygen content peak confirmed the protecting effect of the CNTs (Fig. S2†). Continuously prolonging the treating time led to further decrease of the capacity of the CuO nanotube electrode, while it was maintained above 500 mA h g<sup>-1</sup> when CNTs were introduced.

Two main reasons are responsible for the enhanced rate capability; one is the improved conductivity of the electrodes, and the other is the massive formation of pores on the tubes. After H<sub>2</sub> plasma treatment, a thin layer of Cu formed on the surface of the tubes and constituted a conductive network through the electrode (Fig. 4), which facilitates the transport of electrons significantly. Moreover, the reduction of CuO to Cu led to the shrinkage of the crystallites, which explained the pores that appeared on the tubes. These pores together with the hollow interior promised better Li ion transport and better accommodation of the strain associated with lithium intercalation. Reliable transport pathways of electrons and Li ions are decisive criteria that govern the cycling stability and rate capability. This work develops an effective method to make effective pathways for electrons and Li ions, and could be expanded to other electrode materials. Electrodes based on Fe<sub>2</sub>O<sub>3</sub> and NiO nanoparticles have also been fabricated and treated with H<sub>2</sub> plasma. Great enhancement of the conductance of these electrodes after treatment again proved the efficiency of this method.

In this work, hydrogen plasma treatment was used to enhance the electrochemical performance of metal oxide electrodes for the first time. Long CuO nanotubes were synthesized and treated with hydrogen plasma for several minutes. After treatment, a thin layer of the CuO nanotubes was reduced and a continuous conductive network formed. In addition, massive pores appeared on the surfaces of the nanotubes after treatment. Such a structure provided effective transport pathways for

electrons and Li ions, and therefore led to electrodes with excellent cycling stability and rate capability. This work creates a simple novel way to enhance the conductance of electrodes, and can be expanded to other transitional metal oxide active materials.

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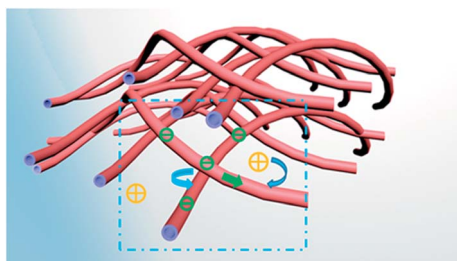


Fig. 4 Schematic diagram of the electrode made with Cu/CuO nanotubes.

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