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Porous CuO nanotube electrode synthesized by *in situ* oxidation of copper foils exhibits superior pseudocapacitive and electrocatalytic performances.
Cost-Effective CuO Nanotube Electrodes for Energy Storage and Non-enzymatic Glucose Detection

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A facile strategy is developed to in situ synthesize low-cost, freestanding, binder-free CuO nanotube electrodes on a conducting Cu foil, totally eliminating non-active materials and extra processing steps. The synergy arising from the ameliorating structure, such as high porosity, large surface area and the ability for fast electron transport, the CuO nanotube electrodes can make an ideal multi-functional electrochemical device with excellent pseudocapacitive performance and a remarkable sensitivity to glucose as non-enzymatic biosensor (NGB). The electrodes deliver remarkable specific capacitances of 442 and 358 F g⁻¹ at current densities of 1 and 20 A g⁻¹, respectively. The capacitance loss after 5000 cycles is only 4.6% at 1 A g⁻¹, a reflection of excellent cyclic stability of the supercapacitor. The biosensor made from CuO nanotubes present an extremely rapid and accurate response to glucose in blood in a wide, linear range of 100 μM to 3 mM with a sensitivity of 2231 μA mM⁻¹ cm⁻². These interesting discoveries may open potentials for further developing new, multi-functional electrodes possessing both excellent energy storage and biosensory capabilities.

Introduction

Efficient energy storage and its economic use are central to the development of modern electronic products, transportation systems and medical devices. Supercapacitors (SCs) can offer higher power densities with longer cyclic lifespans than rechargeable batteries, and store higher energy densities than conventional capacitors, thus have been considered one of the most promising next-generation energy storage devices. A major bottleneck that hinders practical applications of existing SCs to date, however, is the lack of low-cost, high performance electrode materials. Porous nanostructures deposited directly on conductive metal substrates have been developed as electrodes possessing large active surface areas, capability to buffer the volume change during the charge/discharge process and short pathway for electron/ ion transport. Among various porous materials, mesoporous CuO has attracted considerable interest for SC application due to its low cost, excellent pseudocapacitive behavior, environmental benignity and practical availability.

On the other hand, biosensors are important for clinical diagnostics, biological and chemical analyses and environmental monitoring. Diabetes is a well-known global health care problem that seriously affects daily life of hundreds of millions of people. To dynamically monitor the concentration of glucose in the blood is an essential component of modern diabetes management, including clinical detection and therapy. In the past, the vast majority of glucose monitoring was carried out using enzymatic sensors because of their high selectivity, excellent sensitivity and low detection limit. However, enzymatic sensors suffer from not only the instability, but also the complexity and poor reproducibility. To address the above issues, significant research has been directed towards developing non-enzymatic sensors based on noble metals, such as Pt and Au, alloys and metal oxides. Compared with noble metals and alloys, CuO-based electrodes exhibited a higher electrocatalytic oxidation ability for glucose. Especially, nanostructured CuO possesses a large specific surface area, excellent electrochemical activity and high electron transfer reactions at a low overpotential, making it a promising candidate for non-enzymatic sensor applications. For instance, CuO nanowires demonstrated a high stability and good selectivity in glucose determination. CuO/graphene nanocomposites have also shown a good electrocatalytic activity for oxidation of glucose in an alkaline medium at room temperature.

As an important transition metal oxide, CuO has been synthesized using various methods such as hydrothermal method, electrodeposition, chemical bath deposition and electrostatic spinning. In order to prepare electrode of supercapacitor and biosensor using CuO powders as the active material, the CuO powder is generally mixed with binders and conducting additives to obtain a paste. Such obtained electrodes often suffer drawbacks of low active material utilization due to the presence of inaccessible regions to the electrolyte. It has been demonstrated that electrodes of one-dimension arrays standing on a conductive substrate usually holds larger electrochemical active surface area and higher utilization efficiency of the active materials than conventional powder electrodes. For example, Yang et al. reported a solution-immersion strategy for growing Cu(OH)₂/CuO nanotube arrays, which show
Thermogravimetric and differential thermal analysis (TG-DTA) was conducted at a heating rate of 10 °C min⁻¹ in air, and transmission electron microscopy (TEM, JEOL JEM-2010) and scanning electron microscopy (FESEM, JEOL JSM-7001F) was carried out on a polished Cu foil. The morphology was characterized by field emission scanning electron microscopy (SEM, LEO 1530) at room temperature. The surface of the materials was analyzed using Raman spectroscopy (Renishaw, England) with a confocal micro-Raman setup. The laser excitation was an Argon-ion laser at a wavelength of 532 nm. The resolution was 2 cm⁻¹, and the power was set at 0.5 mW to reduce damage to the samples. The samples were mounted on a temperature-controlled stage (DT Materials, UK) and the temperature was increased from 20 °C to 300 °C at a rate of 10 °C min⁻¹ in air. The Raman scattering measurement was carried out on a NanoRaman spectrometer (Renishaw, England) with a laser wavelength of 1.5418 Å. The Raman spectra were recorded at room temperature.

**Characterization**

**Results and discussion**

**Structures and morphologies**

**Experimental**

**Electrochemical analyses**

**Growth of CuO nanotubes on Cu Foil**

All the reagents were of analytical grade and used without further purification. The Cu foil was immersed in the aqueous solution containing 2.5 M NaOH and several times with ethanol and distilled water. The gold colour of the Cu foil gradually disappeared and the initial yellowish-brown colour changed to black. The CuO nanotubes were taken out of the solution, rinsed with deionized water, and dried in air. To obtain an electrochemical workstation, a three-electrode system was used as the working electrode, a Pt foil counter electrode, and a Ag/AgCl reference electrode. Linear-sweep voltammetry was performed using a CHI660E electrochemical workstation from 0 to 1 V at a scan rate of 5 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was recorded using an AC voltage of 5 mV at different frequencies. The samples were inserted into a CH100E electrochemical cell, and the working electrode was kept at a constant potential of 0 V vs. Ag/AgCl. Cyclic voltammetry (CV) was performed using a CHI660E electrochemical workstation from 0.1 to 1.2 V at a scan rate of 5 mV s⁻¹. A typical process: 10 mm x 10 mm Cu foil was immersed in 2.5 M NaOH and then the temperature was elevated to 200 °C and kept for another 2 h to promote the crystallization in a nitrogen atmosphere.

**Conclusion**

The CuO nanotube/Cu foil structure means extremely low contact resistance and high conductivity, low cost and high sensitivity. The CuO nanotubes can be scaled up for mass production. The whole process can be carried out at low temperature. The CuO nanotubes adsorb high performance materials with high specific activity and full utilization of electrode materials. The CuO nanotubes can be used as electrode materials for electrocatalytic reactions, providing excellent performance, cost-effectiveness, and high sensitivity. The CuO nanotubes were obtained by measuring several different positions for the same samples.
Fig. 1 (a) Schematic of the synthesis process of CuO nanotubes; (b-d) optical and SEM images of pristine copper foil, Cu(OH)₂ nanotubes on Cu foil, and CuO nanotubes on Cu foil.

Fig. 2 (a) XRD patterns of as-prepared Cu(OH)₂ and CuO nanotubes directly grown on Cu foil; and (b) Raman spectrum of CuO nanotubes.

cleaned Cu foil exhibited a rough surface with some directionality (Figs. S1a, b). After 5 min of treatment, solid nanorods started appearing sparsely on the surface (Figs. S1c, d). The nanorods became thicker and longer covering the surface in a directional manner with less blank surface after another 5 min of reaction (Fig. S1e). More interestingly, the solid rod tips started opening up at this stage (Fig. S1f). Finally, these nanorods were transformed entirely into nanotubes with irregularly-shaped ends after 20 min of reaction, which densely covered the Cu foil surface (Figs. S1g, h). These numerous nanotubes were grown in the form of a forest with ample space in between, such that the electrolyte could have full access to and direct contacts with the nanotubes for electrochemical reactions.

The TEM image of a single CuO nanotube shows a porous structure with a uniform wall thickness (Fig. S2a). The lattice fringe spacings of 0.233 and 0.26 nm marked in Fig. S2b correspond to the (111) and (002) planes of monoclinic CuO, respectively. However, the lattice fringes were not continuous, which is consistent with the porous nature of the nanotube. The selected area electron diffraction (SAED) pattern (inset of Fig. S2b) indicates that the porous nanotubes had a relatively ordered internal structure with the same orientation.33, 34

Fig. 2a shows the powder XRD patterns of Cu(OH)₂ and CuO nanotubes in the wide angle region. Both materials showed two strong peaks at 43.3° and 50.4°, arising from the Cu foil (JCPDS file No. 65-9026). All the other diffraction peaks for Cu(OH)₂ nanotubes are indexed to orthorhombic Cu(OH)₂ (JCPDS file No. 35-0505). After heat treatment, the peaks located at 32.5°, 35.5°, 38.7°, 38.9°, and 48.7° are assigned to the (110), (002), (111), (200), and (202) planes of CuO phase (JCPDS file No. 45-0937), respectively. There were no other sharp peaks due to impurities, confirming high purity CuO nanotubes obtained in this study using the mild in situ reaction strategy. The high purity nanotubes were further evidenced by the Raman result, as seen in Fig. 2b. The broad peak with a relatively high intensity at 295 cm⁻¹ is assigned to A₁g band, while the two peaks at 342.8 and 628.5 cm⁻¹ are assigned to 2B₁g. The significant intensities of these peaks indicate a single phase and high crystallinity of CuO nanotubes, in good agreement with the previous reports.35, 36

The results from the thermogravimetric and differential thermal analysis (TG-DTA) of Cu(OH)₂ nanotubes are shown in Fig. S3. The gradual weight loss of 1.4% between 26 and 150 °C resulted from the removal of physically adsorbed and chemically bound water. The rapid weight loss of 12.4% between 150 and 180 °C is ascribed to the decomposition of Cu(OH)₂ to become CuO nanotubes. The DTA curve showed a strong heat absorption peak at ~170 °C, consistent with the decomposition of Cu(OH)₂ nanotubes.37 A further increase in temperature beyond 190 °C did...
ties.

Fig. 3 Nitrogen adsorption/desorption isotherms of (a) Cu(OH)\(_2\) nanotubes and (b) CuO nanotubes: the insets show the corresponding BJH pore size distributions.

not present any weight loss, indicating complete decomposition below 190 °C which is considered an appropriate calcination temperature.

The N\(_2\) adsorption/desorption isotherm curves were obtained to investigate the porous characteristics and textural properties.

According to the IUPAC classification of hysteresis loops,\(^{26}\) Fig. 3 plots type IV isotherms with type H3 hysteresis loops. They do not exhibit any limited adsorption at relative pressures from 0 to 1, proving the presence of a typical hierarchical porosity.\(^{39,40}\) An increase in slope at 0.6, especially for CuO nanotubes, corresponds to capillary condensation, typical of mesoporous materials, while the further increase in adsorbed volume at higher relative pressures indicates inter-particle porosity. The BET surface area was much larger for CuO nanotubes (109.02 m\(^2\) g\(^{-1}\)) than for Cu(OH)\(_2\) nanotubes (41.84 m\(^2\) g\(^{-1}\)). The average pore diameters of the two materials were positioned in the mesopore region: the maxima were centered between 3.76 and 6.54 nm for Cu(OH)\(_2\) nanotubes, and between 4.15 and 10.34 nm for CuO nanotubes. Such well-developed pore structures are advantageous for energy storage and electrocatalysis applications since large pore channels permit rapid electrolyte transport, while small pores offer more active sites for redox reactions.

The wettability test result shown in Fig. S4a presented a very low CA of 18.57° on the surface of Cu(OH)\(_2\). The CA with the CuO surface remained very low, 27.01° (Fig. S4b). The low CAs are attributed to the hydrophilic nature of both Cu(OH)\(_2\) and CuO along with mesopores covering their surfaces,\(^{11}\) confirming excellent wettability of the nanotubes by aqueous electrolyte when they are employed as the electrode.\(^{42}\)

Excellent energy storage performance

The above ameliorating surface properties of the porous CuO nanotubes, including extremely large BET surface area, pore volume and excellent wettability, offered significant synergy on pseudocapacitive performance of the electrode, as shown in Fig. 4. The CV curves of the three different electrode materials obtained at a scan rate of 10 mV s\(^{-1}\) (Fig. 4a) clearly indicate that the capacitive current of neat Cu foil was much lower than those of Cu(OH)\(_2\) and CuO nanotube electrodes, confirming a negligible capacitance contribution of the Cu foil to the composite electrodes. The CuO nanotube electrode exhibited more distinct redox peaks and a much larger enclosed area of the CV curve than those of the Cu(OH)\(_2\) electrode. These findings imply that the former electrode would have a higher capacitance than the latter as the specific capacitance is proportional to the area of the CV curve.\(^{43}\) The CV profiles given in Figs. 4b and 4c reveal that the capacitance characteristics of both the nanotube electrodes are obviously different from that of the ideal rectangular shape for electric double-layer capacitance, suggesting their capacitances originating primarily from the Faradic redox reactions. The redox reactions involve in the transition between Cu\(^+\) and Cu\(^{2+}\) species associated with OH ions.\(^{44}\)

\[
\text{Cu}_2\text{O} + 2\text{OH}^- \leftrightarrow 2\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \tag{1}
\]

With increasing scan rate, the current density increased while the shape of the CV curves remained largely unchanged except for the small shift of the peak position, presenting prominent electrochemical reversibility and apparent high-rate performance. The specific capacitances (\(C_s\)) were calculated from the CV curves according to the equation:\(^{55}\)

\[
C_s = \frac{\int J dV}{\nu A V m} \tag{2}
\]

where \(I\) (A) is the response current, \(V\) (V s\(^{-1}\)) is the potential scan rate, \(\Delta V\) (V) is the potential window, and \(m\) (g) is the mass of the active electrode material. It is noted that the specific capacitance of the CuO nanotube electrode gradually decreased from 564 to 419 F g\(^{-1}\) when the scan rate was changed from 5 to 100 mV s\(^{-1}\) (Fig. 4d). The Cu(OH)\(_2\) nanotube electrode presented an essentially similar trend with lower capacitances by 80-90 F g\(^{-1}\) than the corresponding values of the former electrode. The reduction in capacitance at high charge/discharge rates means that all active species of the electrode did not involve in the redox process.

The galvanostatic charge/discharge curves obtained at a current density of 1 A g\(^{-1}\) (Fig. 4e) gave discharge times 5.04, 226.2 and 265.2 s for the Cu foil, Cu (OH)\(_2\) and CuO nanotube electrodes, respectively. This finding further demonstrates that Cu foil had a negligible capacitance while the CuO electrode exhibited better electrochemical performance than the Cu(OH)\(_2\) electrode. Both the curves of the Cu(OH)\(_2\) and CuO electrodes were not ideal straight lines, suggesting the dominance of the pseudocapacitive behavior. In addition, the sudden potential drop in the initial discharge period was caused by internal resistance of the electrodes.\(^{45}\) Figs. 4f and g show the galvanostatic charge/discharge...
Fig. 4 (a) CV curves of three electrode materials measured at 10 mVs⁻¹; CV curves of (b) Cu(OH)₂ and (c) CuO nanotube electrodes at different scan rates; (d) plots of specific capacitance of Cu(OH)₂ and CuO nanotube electrodes vs scan rate; (e) galvanostatic charge/discharge curves at 1 A g⁻¹; galvanostatic charge/discharge curves of (f) Cu(OH)₂ and (g) CuO nanotube electrodes at different current densities; (h) plots of specific capacitance of Cu(OH)₂ and CuO nanotube electrodes vs current density; and (i) cyclic performance of electrodes at 1 A g⁻¹.

curves of the Cu(OH)₂ and CuO electrodes at different current densities, respectively. The specific capacitances \( C_s \) were calculated at different applied current densities using the following equation:

\[
C_s = \frac{I \Delta t}{\Delta V m}
\]

(3)

where \( I \), \( \Delta t \), \( \Delta V \) and \( m \) refer to the constant discharge current, the total discharge time, the potential window and the mass of the electroactive materials, respectively. When the current density was changed from 1 to 20 A g⁻¹, the specific capacitance of the CuO nanotube electrode gradually decreased from 442 to 358 F g⁻¹ and likewise from 377 to 221 F g⁻¹ for the Cu(OH)₂ electrode, with remarkable capacity retention ratios of ~81% and ~59%, respectively (Fig. 4h). The higher the current density used, the more difference in capacitance between the two electrodes. This result further confirms that the porous CuO electrode with a larger surface area was more competent to boost electron transport when charged/discharged at faster rates. The common capacitance decrease resulting from the increase in current density is likely caused by the increase in potential drop due to the electrode resistance and the relatively less utilization of the active material at high current densities.

The long-term cyclic stability of the electrodes was measured at a current density of 1 A g⁻¹ (Fig. 4i). Interestingly, the specific capacitance of both electrodes increased in the first several hundred cycles, which can be attributed to the gradual activation of the electrodes before reaching the full activation. The capacitance retention of the Cu(OH)₂ and CuO electrodes after 5000 cycles was 95.4% and 91.9% of the maximum value, respectively. The pseudocapacitive behavior is associated primarily with redox reactions of the cations in electrode materials. Thus, the charge storage mechanisms of both the electrodes in SCs should be similar.

Judging from the fact that both electrodes have the same Cu²⁺ and similar nanotube structures, they should show similar electrochemical performance. Because the Cu(OH)₂ electrode possessed a relatively smaller surface area and lower porosity than the CuO counterpart, the kinetics of the ions would be slower with an inevitably lower capacitance. The difference in electrochemical performance of these two electrodes can also be understood from the Nyquist plot (Fig. 5a). The two impedance spectra were similar, being composed of one semicircle component
Fig. 5 (a) Electrochemical impedance spectra (EIS) of electrodes at open circuit potential; and (b) schematic of charge storage advantages of porous CuO nanotube electrodes.

each at high frequencies and a linear component each at low frequencies, further demonstrating the long-term electrochemical stability of these electrode materials. The internal resistance \((R_i)\) is the sum of the ionic resistance of electrolyte, the intrinsic resistance of active materials and the contact resistance at the active material/current collector interface, and can be obtained from the intercept of the plots on the real axis. The semicircle of the Nyquist plot corresponds to the Faradic reactions and its diameter represents the interfacial charge transfer resistance \((R_{ct})\).

The inset of Fig. 5a gives an equivalent circuit used to fit the EIS curves to measure \(R_i\) and \(R_{ct}\), where \(Z_m\) and CPE are the Warburg impedance and the constant phase element, respectively. The results are shown in Table S1, confirming much lower \(R_i\) and \(R_{ct}\) values for the CuO electrode than the Cu(OH)\(_2\) electrode. Furthermore, the CuO electrode presented a higher slope and a shorter line in the low frequency region, suggesting faster OH\(^-\) diffusion rates and smaller variation of diffusion paths. All these observations are directly related to the better overall electrochemical properties of the CuO electrode than the Cu(OH)\(_2\) counterpart as discussed above with reference to Fig. 4.

Summarizing, the mechanism of charge transfer in the CuO nanotube electrode is schematically shown in Fig. 5b. The CuO nanotubes offer reliable one-dimensional pathways for charge carrier transport. The open-end nanotube structure combined with a large surface area and ample empty space in-between allows the relief of strains induced during the charge/discharge process and provides extremely large reaction sites between the active materials and the electrolyte.

To further demonstrate the long-term stability of the CuO nanotube electrode, the changes in morphology and impedance after 5000 cycles at 1.0 A g\(^{-1}\) were evaluated and the results are shown in Figs. S5 and S6. It is clearly seen that the nanotube forest was largely intact and attached firmly onto the Cu foil current collector after the repeated phase conversion reactions (Fig. S5). There was virtually no change in the detailed nanotube structure. When the Nyquist plots obtained after 1 and 5000 cycles are compared (Fig. S6), the \(R_i\) of the CuO electrode showed only a negligible increase from 1.71 to 1.83 \(\Omega\), manifesting an excellent conductivity of the electrolyte and a very low internal resistance of the composite electrode (Table S2). The \(R_{ct}\), however, increased slightly more after 5000 cycles, probably as a result of the gradual formation of solid electrolyte interface films. Nevertheless, the CuO nanotube electrode remained remarkable cyclic stability, as seen from Fig. 4i.

**Sensitive biosensory capability**

The electrochemical performance of the CuO nanotube electrode as a non-enzymatic glucose biosensor was also investigated. Fig. 6a shows the linear-sweep voltammogram of the electrode in 0.1M KOH solution measured at a scan rate of 0.05 Vs\(^{-1}\). Broad catalytic current peaks with a peak potential of about +0.5 V were observed, which might correspond to the \(\text{Cu}^{2+}/\text{Cu}^{+}\) redox couple. The amperometric response linearly increased with increasing glucose concentration at all applied potentials. Furthermore, glucose oxidation occurred in the potential range of 0.4-0.8 V, where the oxidation wave for \(\text{Cu}^{2+}/\text{Cu}^{+}\) was demonstrated.

All these observations prove that the CuO electrode was electrocatalytically active for glucose oxidation. Fig. 6b shows a typical amperometric response curve of the electrode when the glucose concentration was successively increased in a stepwise manner. The electrode exhibited a stable and immediate amperometric response to the changes in glucose concentration. As expected, the signal noise increased with increasing glucose concentration due to the accumulation of adsorbed intermediate species on the electrode surfaces. The corresponding calibration curve is plotted in Fig. 6c, where a linear region was found between the concentrations 100 \(\mu\)M and 3 mM with an equation: \(I (\text{mA}) = 0.1267 + 2.231C \text{ (mM)}\) and a correlation coefficient of 0.999. The electrode presented an excellent sensitivity of 2231\(\mu\)A\text{mM}\(^{-1}\) cm\(^{-2}\) and a low detection limit of 1.07 \(\mu\)M (with a signal/noise ratio = 3). It should be noted that the detection limit is at least three orders of magnitude lower than the normal blood glucose level of 4.4-6.6 mM, indicating that the CuO nanotube electrode is perfectly suited to electrochemical detection of blood glucose. Note that the sensitivity of our present sensing system is higher than that of other CuO materials, as shown in Table S3. To test the stability and reproducibility of the sensor, we performed 20 successive measurements at a glucose concentration of 0.1 mM. It was found that the relative standard deviation (R. S. D.) was 2.3 %, indicating an acceptable reproducibility.

Another important analytical factor of a glucose sensor is the ability to discriminate the interference species from the real sample, such as ascorbic acid (AA), urea, lactose, uric acid (UA), and sodium chloride (NaCl), all of which usually coexist with glucose.
in human blood. In view of the fact that the concentration of glucose in human blood is more than 30 times the interfering species, the interference experiment was carried out by successive addition of 0.1 mM of glucose and 0.01 mM of interfering species in the 0.1 M KOH solution. As shown in Fig. 6d, a distinct glucose response was observed while the responses to the interfering species were negligible compared to glucose addition. This observation confirms a satisfactory anti-interference ability of the CuO nanotube-based glucose sensor.

Conclusions

We present a facile strategy for in-situ synthesis of low-cost, free-standing, binder-free CuO nanotube electrodes on a highly conductive Cu foil. The electrode material offered many advantages, including highly porous structure, large surface area, abundant empty space, short and fast electron transport paths and total elimination of both inactive materials and extra processing steps. These advantages make them ideal electrodes for SCs and NGBs. The electrode exhibited excellent electrochemical properties, including a remarkable specific capacitance of 382 F g\(^{-1}\) at a current density of 10 A g\(^{-1}\) and a response to glucose at a linear range of 100 μM to 3 mM with an outstanding sensitivity of 2231 μA mM\(^{-1}\) cm\(^{-2}\). The above findings may open up a new avenue for practical application of CuO nanotube electrodes in the next-generation SCs and NGBs.

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Notes and references
