Supramolecular Hydrogels Directed Self-assembly of C, N-doping Hollow

CuO as High-performance Anode Materials for Li-ion Batteries Fucong Lyu,§

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Experimental Section

Chemical Regent

Copper nitrate trihydrate (Cu(NO₃)₂ \cdot 3H₂O), sodium hydroxide (NaOH),ascorbic acid and chitosan. All solution were prepared with ultrapure water.

Synthesis of Cu/Cu₂O particles and CuO hollow composites

The chitosan (CS) were first dissolved in ascorbic acid aqueous solution (3 wt%) to form a colorless and transparent solution (CS 10 mg ml⁻¹) (Figure S1a), with the ascorbic acid providing an acid environment for dissolving the CS as well as acting as a reductant. Subsequently 50ml NaOH (0.1M) aqueous solution was added slowly (drop-wise) into the chitosan solution. Then, dropping 15 ml $Cu(NO_3)_2$ (100 mg ml⁻¹) aqueous solution in the above solution and the Cu^{2+} ion triggered fast gelation and cross-linked with the chitosan molecule to form a yellow-green supramolecular hydrogel (Figure S1b). Over time (about 15 min), the Cu²⁺ were reduced by ascorbic acid and grew into nanoparticles, and with the help and the template effect of CS, these nanoparticles selfassembled into microparticles, which appeared as a brick-red solid matter in the hydrogel and then the hydrogel gradually transformed back into a liquid state (Figure S1c). After 30 min, a red precipitate (denoted as Cu/Cu₂O) deposited in the bottom of the vial and the hydrogel completely disappeared (Figure S1d). Finally, the precipitation was easily separated by centrifugation and dried at 80 °C in a vacuum oven for 10 h. The CS concentration dependent experiments were carried out through the same process. More importantly, the residual CS could be recycled by the addition of an alkaline solution to adjust the pH value to neutral or weakly alkaline. To obtain the CuO samples, the Cu/Cu₂O composites were placed in a porcelain boat and put it into a muffle furnace maintaining at the specific temperature (300, 400, 500 and 600 °C) for 2 h at a heating rate of 2 °C min⁻¹. For simplicity, the calcined samples at different temperature (300, 400, 500 and 600 °C) were denoted as CuO-X, which the X represent the specific oxidized temperature.

Preparation of Lithium Ion Battery Electrodes

The CuO-500 materials were fabricated by mixing 70 wt% CuO nanoparticles, 20 wt% cetylene black and 10 wt%carboxymethyl cellulose (CMC, Alfa Aesar) dissolved in H₂O to form a slurry, which was then pasted via doctor blade as the working electrode on an Cu foil (99.999%, 0.025 mm thick, Alfa-Aesar) and dried at 100 °C in a vacuum oven (RTP-500) for 10 h. For comparing the performance of the composites, CuO-300, CuO-400, CuO-600 and one kind of CuO derived from commercial Cu powders with a size of 0.2 μ m diameter as active materials were made from working electrode using the above-mentioned method, respectively. The electrochemical performance of the electrodes was evaluated using CR2032 coin-type cells assembled in an argon-filled glove box (UNILab2000). The Li metal was used as the counter and the reference electrode. A porous polypropylene separator (Celgard 2400, Hoechst Celanese) was used as the separator. The electrolyte consisted of a solution of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, V/V). Cyclic voltammogram (CV) measurements were performed on a Bio-logic VMP3 electrochemical workstation with a voltage range from 0.01 to 3 V at a scan rate of 0.1 mV

s⁻¹ and in the frequency range of 200KHz ~ 0.1 Hz at a 10 mV amplitude referring to open circuit potential, respectively. The cells were charged and discharged galvanostatically using a battery tester (CT2001A) in a potential range between 0.01 and 3.00 V. All of the electrochemical performance measurements were carried out in a two-electrode system and obtained at a constant temperature of 25 °C by using a homemade constant temperature and humidity chamber.

Characterization

These samples were characterized with scanning electron microscopy (SEM, FEI Nova NanoSEM 50, America) and high resolution transmission electron microscopy (HRTEM, FEI Titan G2 60~300 and Philips Tecnai F20). The EDS line scanning and spectra were performed with corrected scanning TEM. X-ray diffraction (XRD) measurements were conducted using a D8 Advance (Bruker) X-ray diffractometer with Cu Ka radiation (λ =1.5418 Å). Raman spectra were measured on a JobinYvon Labor Raman HR-800 using Ar-ion laser of 514.5 nm. Fourier transform infrared spectroscopy (FT-IR) spectra were documented with KBr pellets from a Bruker Model R 200-L spectrophotometer. For thermogravimetric analysis (TGA) (Mettler Toledo, TGA/SDTA851 e) in air at a scan rate of 10 °C min⁻¹ from room temperature to 800 °C. X-ray photoelectron microscopy (XPS) was performed on a ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al Ka (1486.6 eV) as the X-ray source set at 150 W and a pass energy of 30 eV for high-resolution scan, The base pressure was 3×10-9 mbar, and the binding energies were referenced to C1s line at 284.8 eV from adventitious carbon.



Figure S1. Digital images of the process of preparing the gel, which are formed using 10 mg mL⁻¹ chitosan



Figure S2. Digital images of the mass production.



Figure S3. The SEM images of (a) the Cu/Cu_2O , the corresponding (b) overlapping EDS elemental maps of Cu, O, C, N and EDS elemental mapping of (c) Cu (olivine), (d) O (green), (e) C (violet), and (f) N (rose-bengal) in the same area.



Figure S4. The digital images of different conditions in the experiment. From left to right, no CS in the solution, add 0.1 M NaOH after Cu²⁺ drop in the 10 mg ml⁻¹ CS solution, 1 mg ml⁻¹, 5 mg ml⁻¹, 10 mg ml⁻¹, 20 mg ml⁻¹ of CS solution.



Figure S5. The SEM images of different condition corresponding to Figure S1. (a) no CS in the solution, (b) add 0.1 M NaOH after Cu²⁺ drop in the 10 mg ml⁻¹ CS solution, different concentration (c) 1 mg ml⁻¹, (d) 5 mg ml⁻¹, (e) 10 mg ml⁻¹(same as the inset in Figure 3a), (f) 20 mg ml⁻¹ of CS solution.

We analyzed the morphological differences in the deposited samples in the absence of CS, without the formation of the supramolecular hydrogel, and at different concentrations of CS. As seen in Figures S3 and S4a, without the assistance of the CS molecule, the ascorbic acid takes a greater amount of time to reduce the Cu²⁺. In addition, the Cu²⁺ solution added directly to the CS solution did not easily form a hydrogel, and when NaOH was added drop-wise to the complex, a red precipitate formed immediately, which had similar morphology to the assembled nanoparticles of the Cu/Cu₂O composite but could not self-assemble into microspheres (Figures S3 and S4b). The concentration of CS had a great effect on the yield and morphology of the self-assembled microspheres. The lower the concentration of the CS solution, the lower was the yield of the Cu/Cu₂O composite (Figures S3). A CS solution having low concentration could form a microsphere with many polyhedral self-assembly nanoparticles (Figure S4d); however, too low or too high concentration of yield and morphology, we chose the 10 mg mL⁻¹ CS solution to produce the Cu/Cu₂O composite for further annealed experiments.



Figure S6. (a) The X-ray diffraction patterns, (b) Raman spectrum of Cu/Cu₂O microspheres and CuO hollow spheres oxidized at different temperature (300, 400, 500 and 600 °C), (c) FTIR spectrum of commercial Cu powder ($0.2 \mu m$), Cu/Cu₂O composites, CuO-300, and CuO-500.

As can be seen in Figure S5a, the Cu/Cu₂O microspheres mainly showed sharp peaks at 43.29° and 50.43° that can be assigned to the (111) and (200) reflections of Cu (ICCD No. 04-0836), and other relatively weak peaks centered at 29.55°, 36.46°, and 42.29° linked to the (111), (200), and (110) diffractions of Cu₂O (ICCD No. 65-3288). After treatment at 300 °C for 2 h, the character peak of Cu nearly disappeared while the intensity of Cu₂O increased and the character peaks of CuO emerged, which implies the oxidation of Cu. Increasing temperature resulted in all the Cu and Cu₂O being transformed to CuO. The chemical compositions of these samples were also determined by X-ray diffraction (XRD) measurements (Table S1).

The Raman spectra in Figure 4b shows the chemical conversion after the annealing process and further confirms the presence of the individual and mixed phases. The Cu/Cu₂O exhibited characteristic Raman bands at 207/410 and 150/221 cm⁻¹, which corresponded to the Cu and Cu₂O phases, respectively.^[1] Both the 207/410 and 150/221 cm⁻¹ peaks nearly disappeared in CuO-300, and the CuO-300 showed its characteristic peak at 292, 338, and 625 cm⁻¹, which corresponded to the Cu Ophase, which was consistent with the XRD results, while the oxidation process might occur from outside to inside of the nanoparticle, which made it difficult to observe the characteristic peak of Cu₂O. However, the XRD results demonstrated that many Cu₂O were still present in CuO-300. The wavenumbers of these CuO-X samples were lower than those reported in previous literature (295, 341, and 632 cm⁻¹)^{[4],[5]} owing to size effects, and increasing oxidation temperature from 300 to 600 °C resulted in the Raman peaks shifting to lower wavenumbers (e.g., 292, 291, 289, and 287 cm⁻¹, which corresponded to 300, 400, 500, and 600 °C, respectively) and became broader from 300 to 500 °C, indicating that grain size decreased.

The Fourier transform infrared spectroscopy (FTIR) spectra of the commercial Cu powder, the Cu/Cu₂O, CuO-300, and CuO-500 samples were recorded to provide direct evidence for interactions between Cu and heteroatoms. In the spectrum in Figure 4c, the frequency of the Cu-O stretching vibration experienced a peak shift from 642 to 634 cm⁻¹, with intensity increasing again that indicated the existence of Cu₂O, and the broad band at 3445 cm⁻¹ (attributable to CS v_{OH} and v_{NH} absorptions) in Cu/Cu₂O composites clearly demonstrated the existence of CS.^[6] Moreover, the major evidence for the interaction of CS and Cu, and Cu₂O in Cu/Cu₂O composites was a new vibration appearing and shifting to 1620 cm⁻¹ (attributable to amide II band) compared to results of a previous study.^[7] When the annealing process at 300 °C was applied, the strong bands observed at 531, 478, and 428 cm⁻¹ could be attributed to the Cu-O stretching vibration of CuO and illustrated that Cu, as well as Cu₂O, oxidize to CuO. In addition, the peak at 612 cm⁻¹ underwent a blue shift and intensity increase that proved a section of Cu could oxide to Cu₂O only at low calcination temperatures.^[8] The broad band at 3445 cm⁻¹ and peaks at 2352 cm⁻¹ and 2325 cm⁻¹ could explain the decomposition and carbonization of CS. We also investigated the infrared activity of CuO-500, and showed that the peak at 612 cm⁻¹ contributed to the disappearance of Cu_2O , indicating the absence of Cu₂O. Additionally, the peaks related to CuO mixed into one broad peak. Furthermore, from Cu/Cu₂O to CuO-500 the peak at 2352 cm⁻¹ and the peak at 2325 cm⁻¹ suffered a red shift to 2341 cm⁻¹ with intensity decrease. These variations revealed that some Cu-N formed during the annealing procedure.^[9]

Samples	Cu	Cu ₂ O	CuO	
Cu/Cu ₂ O	\checkmark	\checkmark	—	
CuO-300	\checkmark	\checkmark	\checkmark	
CuO-400	_	\checkmark	~	
CuO-500			~	
CuO-600	_	_	\checkmark	

Table S1. Chemical compositions for Cu/Cu_2O , CuO-300, CuO-400, CuO-500 and CuO-600 determined by XRD.



Figure S7. SEM images of (a) CuO-300 particles, (b) CuO-400 particles, (c) CuO-600 particles.

Table	S2.	Elemental	compositions	for	Cu/Cu ₂ O,	CuO-300,	CuO-400,	CuO-500	and	CuO-600
determ	ined	by SEM E	DS mapping.							

Samples	Cu (at%)	O (at%)	C (at%)	N (at%)
Cu/Cu ₂ O	81.28	1.49	14.39	2.84
CuO-300	51.31	35.73	10.61	2.35
CuO-400	49.09	38.65	10.14	2.12
CuO-500	44.67	43.80	9.79	1.74
CuO-600	46.86	44.64	6.58	1.92

Table S2 summarizes the elemental compositions of Cu/Cu₂O and different temperatures oxidized samples determined by SEM EDS mapping, as the oxidation of Cu/Cu₂O preceding the amount of O at% sharply increased and Cu at% decreased. At higher annealing process temperatures, oxidation of Cu/Cu₂O was more complete, and the O at% was nearly approximate to the Cu at% when the temperature was 500 °C. In addition, the amount of C and N atoms originating from the CS molecule gradually decreased with increasing annealing temperature and showed a content of approximately 9.79 and 1.74%, respectively, at 500 °C. The amount of C and N might not loss too much even though the proportion of C and N decrease obviously because of the introduction of O resulted in increase of the total mass during the oxidation of Cu/Cu₂O. Our results revealed that the content of C and N changed little, maybe because the majority of the CS molecule was inserted into the Cubased materials and was not exposed to the air, with this organic matter not being able to easily convert to CO₂ and could only carbonize and remain in the sample. However, too high temperatures influence this protection by causing the loss of C and numerous crashing of the hollow structure (Figure S6c).



Figure S8. XPS spectra of Cu/Cu₂O and CuO-500 (a) survey scan, (b) comparison of Cu 2p, High resolution XPS spectra and simulations of Cu/Cu₂O composites and CuO-500 (c) Cu 2p, and (d) N 1s.

X-ray photoelectron microscopy (XPS) measurements were used to obtain further information about the elemental bonding configurations of these samples. The survey spectrum of the Cu/Cu₂O and CuO-500 particles revealed that the indexed peaks corresponded to the presence of C, O, N, and Cu atoms (Figure S5a), again illustrated the successfully C, N doping in the electrode materials. A high binding energy region between 926 and 970 eV of two selected samples showed the response from the Cu 2p spin-orbit split, and Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core levels at 932.7 and 952.5 eV, respectively, in Cu/Cu₂O composites, which indicated the presence of Cu metal.^[10] The presence of CS did not affect the Cu 2p signal, which was a similar result to that obtained from the literature.^[11] In addition, the slight intensity satellite peaks (~939–946 and 963 eV) and fitting curves for Cu 2p_{3/2} and Cu 2p_{1/2} line confirmed the presence of Cu(I) species in Cu/Cu₂O.^[12] These satellite peaks sharply increased and additional shoulder peaks appeared at approximately 933.6 and 953.6 eV and the component peaks at 932.7 and 952.5 eV shifted to higher binding energy in the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of CuO-300 (Figure S5b), indicating that oxidization could be triggered when a temperature of 300 °C was applied to the samples. These values in conjunction with the XRD pattern and Raman spectra further explained the coexistence of Cu, Cu₂O, and CuO in CuO-300. The intensity of the satellite peaks further increased and the peaks of Cu 2p_{3/2} and Cu 2p_{1/2} shifted entirely to higher binding energy centered at 933.6 and 953.6 eV, respectively, in CuO-500, demonstrating that the Cu phase disappeared and was mainly oxidized to CuO. Fitting of the complex Cu 2p spectra demonstrated the difference between the additional component of Cu $2p_{3/2}$ (933.6 eV) and Cu $2p_{1/2}$ (953.6 eV) levels was approximately 20 eV, which was in agreement with standard values for CuO.^[7] These observations are representative XPS signatures of the presence of Cu(II) derived metal-oxides and the components at 934.1/943.7 eV could be contributed to the Cu-N.^[13] We did not observe obvious N 1s peaks at 399.7 eV (Figure 6b) from CS in Cu/Cu₂O according to references reported in the literature,^[14] which might be because CS were mainly wrapped in the Cu/Cu₂O particles and the small amount of CS on the surface of the particles could not cause a strong signal. However, we obtained an obviously different N 1s signal from CuO-500, which indicates the CS had undergone a chemical reaction during the annealing carbonization. A deconvolution procedure applied to the N 1s levels lead to separation of four sub-peaks centered successively at 398.9, 400.5, 401.2, and 405.8 eV that could be assigned to pyridine N, pyrrolic N, quaternary N, and pyridine N-oxide, respectively.^[13b, 15] This might result from the oxidizing conditions of the carbonization process and oxidation when annealing in ambient air.^[16] Both FTIR and XPS measurements further verify the formation of Cu-N bonds during the annealing process, which also explained the Cu at% being higher than the O at% after the Cu species was entirely converted to CuO.

	Press Press				
materials	proportion	Cu	0	С	Ν
Cu/Cu ₂ O	at %	60.82	10.79	25.64	2.76
	wt %	88.26	3.90	6.96	0.88
CuO-500	at %	38.17	41.28	19.69	0.87
	wt %	72.88	19.71	7.05	0.36

Table S3. Elemental compositions for Cu/Cu₂O and CuO-600 determined by XPS.

we can analyzed the component of the materials based on the calculation and simulation of the peaks area. For example, in Cu/Cu₂O, the O from CS and Cu₂O, however, the C and N just came from CS, so based on the atomic proportion of the C or N and the formula of CS (($C_6H_{11}NO_4$)n), so we can calculated that the content of CS was about 10.13 wt%.



Figure S9. (a) The first charge–discharge voltage profiles of CuO-500 at 100 mA g^{-1} from 0.01 to 3.0 V versus Li/Li⁺, (b) comparison of cycle performance of CuO-300, CuO-400, CuO-500, CuO-600, and CuO-0.2 μ m derived from 0.2 μ m commercial Cu powder.



Figure S10. Electrochemical impedance spectra (EIS) of the CuO electrodes (a) before cycle and fully discharge state at 20th, 100th and 200th cycle, (b) before cycle and fully charge state at 20th, 100th and 200th cycle.



Figure S11. SEM images of (a) CuO-500 particles after fully discharged at 500th cycle. (b) is the corresponding high resolution SEM image of the marked particle as indicated in (a) with red square

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