Supporting information

Preparation of CuO@humic acid@carbon nanotube composite material using humic acid as coupling agent and its lithium-ion storage performance

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1. Physical properties test method of electrode material

The products were characterized morphologically using a scanning electron microscope (SEM, Hitachi Su-70) and a transmission electron microscope (TEM, JEM-2100) at accelerating voltages of 10 and 200 kV, respectively. The X-ray photoelectron spectroscopy (XPS) of the products was measured by an X-ray photoelectron spectrometer (ESCALAB 250Xi spectrometer, Mg Kα radiation, hν=1253.6 eV). XRD patterns of the products were obtained using a Rigaku D/max 2500 X-ray diffractometer with Cu-Ka radiation, a scan range of $2\theta = 5°- 80°$, and a scan rate of 4°/min. Raman spectra of products were measured by a laser confocal micro-Raman spectrometer (Renishaw RM-1000 with a laser wavelength of 532 nm). Nitrogen adsorption/desorption isotherms of the samples at 77.3 K were first measured using the Micromeritics ASAP 2020M system, and then the specific surface area and pore size distribution of the samples were calculated using the Brunauer-Emmett-Teller (BET) model and the Barret-Joyner-Halenda (BJH) model, respectively. The thermo-gravimetric analysis (TGA) curves of the samples were obtained using a Netzsch

STA449C TG/DSC thermogravimetric analyzer by increasing the samples from room temperature to 800 °C at a ramp rate of 10 °C min^{-1} under an air atmosphere with an airflow rate of 50 mL min^{-1}.

2. Preparation method of lithium battery and the electrochemical property test method

The composite electrode material (CuO@HA@CNT or CuO@CNT or CuO@HA), acetylene black (conductive agent), and PVDF (binder) were mixed in the mass ratio of 8:1:1 and coated on the copper foil, followed by drying under vacuum oven at 80 ℃ for 10 hours, and finally cut into 12 mm diameter discs to obtain the working electrode. The polypropylene microporous membrane was used as the separator, the 1M LiPF6 solution (the volume ratio of dimethyl carbonate and vinyl carbonate was 1:1) was used as the electrolyte, and the lithium sheet was used as the counter electrode. The working electrode, counter electrode, separator and electrolyte were assembled into a CR2032 type coin cell using a tablet press in a glove box filled with argon gas (H_2O < 0.1 ppm, O_2 < 0.1 ppm) at room temperature, and the assembled cell was left for 24 h for electrochemical testing.

The galvanostatic charge/discharge (GCD) tests were performed with the Blue Electric Battery Test System (LANHE, Wuhan Blue Electric Electronics Co., Ltd.) at the current density from 0.1 to 2.0 A g^{-1} and in the voltage range of 0.005-3.0 V (vs Li/Li$^+$) to obtain cycling stability, rate capability and GCD curves. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed using an electrochemical workstation (PGSTAT302N, Aptar, Switzerland). The scan voltage range for CV testing was 0.005-3.0 V, and the scan rate was 0.1-1.0 mV s^{-1}. The EIS test was performed with a scan frequency of 10^5 Hz to 0.1 Hz and a sinusoidal perturbation voltage amplitude of 5 mV. The AC impedance spectra of the samples were tested before cycling and after 500 cycles (both in the fully charged state).

3. Method to get electrode's Li$^+$ diffusion coefficient (D_{Li+})

According to Equation S1, a linear fitting curve of Z' (real part of Q_w impedance) versus $\omega^{-1/2}$ was obtained as shown in Figure 5e. The electrode's Li$^+$ diffusion coefficient (D_{Li+}) was then obtained by substituting the value of σ (Warburg coefficient) into Equation S2 [1-3].

$$Z'=R_s+R_{ct}+\sigma\omega^{-1/2} \tag{S1}$$

$$D_{Li+}=R^2T^2/(2A^2n^4F^4C^2\sigma^2) \tag{S2}$$

where R, T, A, n, F, and C corresponded to the gas constant, temperature, effective working area, number of electrons under the charged status, Faraday's constant and ion concentration, respectively.

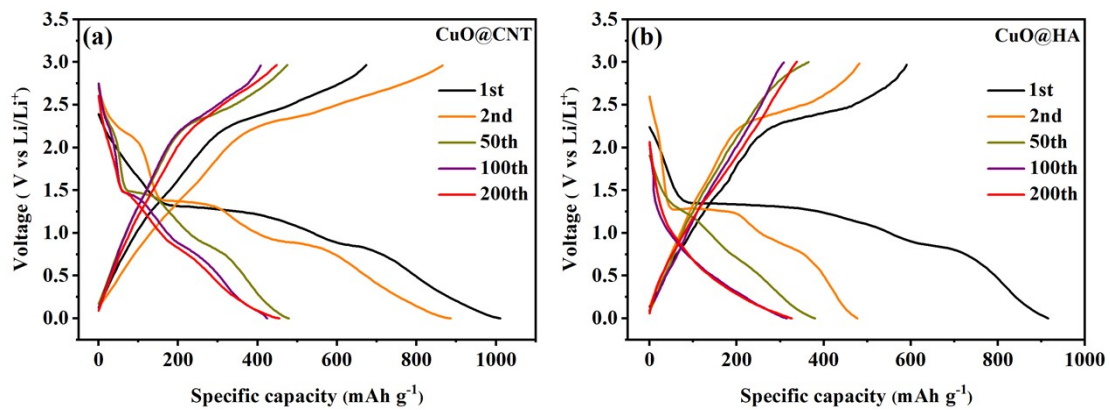**4. Figure S1 GCD curves of (a) CuO@CNT and (b) CuO@HA at 0.1 A g^{-1}**

Figure S1 GCD curves of (a) CuO@CNT and (b) CuO@HA at 0.1 A g^{-1}.

References

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