Helical Carbon Tubes Derived from Epitaxial Cu-MOF Coating on Textile for Enhanced Supercapacitor Performance

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EXPERIMENTAL SECTION

Materials and Instruments

All of the chemicals were used after purchasing without further purification. A piece of commercial cotton T-shirt (TS) and commercial carbon cloth (CC) were first cleaned using distilled water in an ultrasonic bath and dried before activation. And then the T-shirt and the commercial carbon cloth were treated with a mixture of 0.1M NaOH aqueous solution and hydrogen peroxide (30%) with a volume ratio 3:1 at 80 °C for 30 min and then cleaned with deionized water and dried under nitrogen flux for the next preparation.

The Powder X-ray diffraction (PXRD) analysis was performed on a MiniFlex2 X-ray diffractometer using Cu−Kα radiation (λ = 0.1542 nm) in the 2θ range of 5−30° with a scanning rate of 1° min⁻¹. IR data were recorded using a Bruker Vertex 70. Scanning electron microscope (SEM) images for the morphology of samples were measured by JSM6700. X-ray photoelectron spectroscopy (XPS) spectra for the samples were measured by ESCALAB250Xi. Transmission electron microscope (TEM) images recorded for the samples were used by JEM-2010F. The BET was measured at liquid nitrogen temperature (77 K) after dehydration under vacuum at 100 °C for 12h using ASAP 2010 analyzer. Raman spectra were collected on LabRAM HR instrument with a 532 nm excitation laser. Electrochemical measurement was carried out by the CHI760e electrochemical workstation (Shanghai Chenhua Instrument China)

Fabrication of HKUST-1@TS and HKUST-1@CC

HKUST-1@TS and HKUST-1@CC used in the present work were grown using the
liquid-phase epitaxy (LPE) pump method and were fabricated using the following diluted ethanolic solutions: copper acetate (1mM), BTC (1,3,5-benzenetricarboxylic acid) (0.4mM). The immersion times were 15 min for the copper acetate solution and 20 min for the BTC solution. Each step was washed with pure ethanol to remove residual reactants. A total of 80 growth cycles were used for HKUST-1 grown on TS and CC in this work.

Fabrication of TS-800, HKUST-1@TS-800, HKUST-1@CC-800 and CC-800

The HKUST-1@TS, HKUST-1@CC, TS and CC were put into a tube furnace and kept at 800 °C for 5 hs and then cool down to room temperature with a continuous nitrogen gas flow in a speed of 10 °C/min.

Electrochemical measurement

The electrochemical tests were carried out in the CHI760e electrochemical workstation (Shanghai Chenhua Instrument China) using a three electrode electrochemical mode in 6 M KOH aqueous solution at room temperature where Pt wire served as the counter electrode and Ag/AgCl as the reference electrode, the HKUST-1@TS-800 and HKUST-1@CC-800 were directly selected as the working electrode without any ancillary materials. The electrochemical behaviors of the prepared electrodes were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) measurements, cycling performance and electrochemical impedance spectroscopy (EIS). CV curves were measured in a potential range from -1.0 to 0 V at different scan rates (10-100 mV/s) and GCD processes were performed according to the above mentioned potential range at various current densities. The cycling performances
were conducted between -1.0 V and 0 V at a current density of 5mA/cm$^2$. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range from 0.01 Hz to 100 kHz by applying an AC voltage with an amplitude of 5 mV. The areal capacitance ($C_A$) is calculated according to the following equation:

$$C_A = I \cdot \Delta t \cdot A^{-1} \cdot \Delta V^{-1} \text{ (mF cm}^{-2}\text{)}$$

The volumetric energy density (E) and powder density (P) are defined according to the following equation:

$$C_V = I \cdot \Delta t \cdot A^{-1} \cdot D^{-1} \cdot \Delta V^{-1} \text{ (mF cm}^{-3}\text{)}$$

$$E = C_V \cdot \Delta V^2 \cdot 7200^{-1}\text{ (mW h cm}^{-3}\text{)}$$

$$P = E \cdot 3600 \cdot \Delta t^{-1} \text{ (mW cm}^{-3}\text{)}$$

where $C_A$ (mF cm$^{-2}$) and $C_V$(mF cm$^{-3}$) is the areal capacitance and the volumetric capacitance, respectively. $I$ (A) represented discharge current, $\Delta t$ (s), $A$ (cm$^2$), $\Delta V$ (V) and $D$ (cm) designated total discharge time, the geometric surface of electrode material, potential drop during discharge and the thickness of the samples, respectively.
Figure S1. The XPS spectra of HKUST-1@TS-800.
**Figure S2.** The SEM EDS spectra of HKUST-1 @TS-800.
Figure S3. IR spectra of CC, HKUST-1@CC and HKUST-1@CC-800.
Figure S4. (a) The photos of bare carbon cloth (CC), HKUST-1@CC and HKUST-1@CC-800; (b) The SEM images of bare CC; (c) The SEM images of HKUST-1@CC-800.
Figure S5. SEM element mapping of HKUST-1@CC-800.
There are two main bands (D and G bands) in the Raman spectra. The peak area ratio of the D band to G band ($I_D/I_G$) could be used as an indicator for the crystallinity of carbon. Figure S4 showed the $I_D/I_G$ of TS-800 and HKUST-1@TS-800 was much higher than the sample of CC-800 and HKUST-1@CC-800 respectively in the Raman spectra, demonstrating TS-800 and HKUST-1@TS-800 can enhanced electrical conductivity and benefited the charge transport in supercapacitors, leading to higher capacitance.\(^1\)

Figure S7. The setup of electrochemical measurement.
Figure S8. CV curves of HKUST-1@CC-800 with different scan rates.
Figure S9. GCD curves of HKUST-1@CC-800 with different current densities.