



Electrostatic assembly of graphene oxide with Zinc-Glutamate metal-organic framework crystalline to synthesis nanoporous carbon with enhanced capacitive performance

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ABSTRACT

We demonstrated a protocol of incorporating the graphene oxide sheets on the surface of Zinc-Glutamate metal-organic framework (MOF) microcrystalline by electrostatic attraction and carbonizing this composite to synthesis the nanoporous carbon. The etching of facets in Zinc-Glutamate MOF microcrystalline by the graphene oxide sheets was observed and the possible mechanism of this etching had been elucidated. Excitingly, the Supercapacitor electrodes from this hierarchically porous carbon exhibit fast frequency response and ultrahigh charge/discharge rate up to 2 V/s, high specific gravimetric and volumetric capacitances of 318 F/g and 299 F/cm³ at the scan rate of 20 mV/s, outstanding cycling stability of 90% capacitance retention after 5000 cycles at the currency of 5 A/g in aqueous alkaline electrolytes.

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1. Introduction

Compared with the carbonaceous materials prepared using the conventional precursors, MOF-derived Nanoporous carbons have significant advantages in terms of a simple synthesis with inherent diversity affording precise control over porous architectures, pore volumes and high surface areas [1,2]. However, the common linking organic ligands and solvents in the synthesis of MOFs are petroleum-based compounds which are costly and generally detrimental to environment and health [3]. It is anticipated that MOFs made solely from natural feedstock and green solvents could not only bring environmental compatibility, but favour an easy and sustainable scale up [4]. Very recently, we reported a spontaneous growth of Zinc-Glutamate MOF (a scarce 3D metal ion-amino acid frameworks) microcrystallines in water with the precursor of monosodium glutamate (microbial fermentation based) and exploited the supercapacitor electrode performances of its derived porous carbon [5].

It was well-known that the partial breakdown of the MOF frameworks and incorporation of heteroatoms to carbon lattice

could not be avoided during the carbonization step, resulting in the decreased conductivity of as-prepared Nanoporous carbons, thus limited the rate performance for supercapacitors [6]. Recently, the two-dimensional graphene oxide (GO) with controllable surface chemistry emerged as a promising candidate for the fabrication of supercapacitor materials due to its high stability in suspension and excellent electric conductivity after being reduced. Nevertheless, graphene oxide often suffers from irreversible sheets-to-sheets restacking due to the strong inter-layer van der Waals force, resulting in the deterioration of its high specific surface area [7]. Thanks to the complementary features between graphene oxide and MOFs structures, two fabricating strategies are often deployed; that is, coating the graphene oxide sheets on the surface of MOFs or directly growing MOFs above the graphene oxide flakes [8,9]. In this work, it was discovered that Zinc-Glutamate MOF microcrystallines exhibits a positive zeta potential (12.5 mV) in the water dispersion and it could be coated with negative water suspension of GO sheets immediately at room temperature. After the carbonization of this MOF-GO composite under inert atmosphere, electrochemical measurements of the obtained nanoporous carbon as supercapacitor electrodes show outstanding performance.

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2. Experimental

2.1. Synthesis of MOF crystals

In a typical procedure, 8.45 g monosodium glutamate (purity >99.9%, Rongxin Food Company) and 6.02 g Zinc acetate dehydrate (AR grade, Sinopharm Chemical Reagent Co., Ltd) were mixed in 50 ml deionized (DI) water and stirred vigorously at 40 °C. After the zinc salt powder dissolved completely in 3 min, the obtained white sediment (3.94 g) was collected by filtration and washed with DI water and anhydrous ethanol for three times, then dried at an oven at 105 °C.

2.2. Coating the GO sheets on MOF crystals

Graphene oxide was synthesized from natural graphite flakes (300 μm, Qingdao Graphite Company) according to the modified Hummers' method and washed with DI water intensively until neutrality (Fig. S1) [10]. After ultrasonicated for 0.5 h, 50 ml Brown red GO suspension with the concentration of 1 mg/ml was formed; 3.45 g aforementioned white MOF powder was poured into the GO suspension with magnetic stirring for 5 min at room temperature. Finally, the coffee sediment was collected and dried in the air at 105 °C.

2.3. Pyrolysis of MOF-GO composite

The coffee sediment was placed in a porcelain boat, and flushing with N₂ flow (99.99% purity) for 10 min, heated in a horizontal tube furnace up to 800 °C, 900 °C, 1000 °C at a rate of 5 °C min⁻¹ under the N₂ flow and maintained at respective temperature for 2 h. The obtained black sample was immersed with 1 M HCl solution to remove soluble or insoluble substances, subsequently rinsed with adequate amount of DI water. Finally, the sample was dried at 110 °C for 12 h to achieve products, denoted as S800, S900, S1000. The yield of carbonaceous material is 20%–30%.

2.4. Structure characterization

Zeta potential distribution was performed in a Malvern (ZEN3600) with a disposable zeta cell. Thermo-gravimetric (TG) analyses were conducted on a NETZSCH (209F1 Libra) analyzer with a temperature ramp of 10 °C min⁻¹ under the Ar flow. The morphology and micro-texture of the final carbons was characterized using a Field emission scanning electron microscope (FESEM, Supra 55) with "Oxford" energy dispersion spectrum (EDS) and Transmission electron microscopy (TEM, JEOL-2010 microscope at 200 kV). The specific surface area and pore structure of the porous carbon samples were determined by cryogenic N₂ adsorption-desorption isotherms (Quantachrome Autosorb-iQ) after being vacuum-dried at 150 °C overnight. The specific surface areas were calculated by the BET (Brunauer–Emmett–Teller) method. Micropore surface area (Smicropores) was derived from the slope (the linear t range: 0.4–0.6) of the t plot, wherein t is the statistical layer thickness of carbon black, given by $t = 0.88(P/P_0)^2 + 6.45(P/P_0) + 2.98$ Å. The total pore volume (Vt) was calculated from the adsorbed N₂ amount at a relative pressure of 0.99. Cumulative pore volume and pore size distribution were calculated by using a slit/cylindrical nonlocal density functional theory (NLDFT) model and Barrett–Joyner–Halenda (BJH) method. The X-ray powder diffraction (XRD) patterns in the Bragg's angle (2θ) range of 10° to 80° were collected using a D/max 2500 PC (Rigaku) diffractometer with monochromatic Cu Kα radiation of wavelength 0.1541 nm and at a scanning speed of 2° min⁻¹. Raman spectra were recorded on a Thermo Fisher DXR Raman microscope equipped

with a CCD detector at an excitation wavelength of 532 nm and the power of 7 mW. X-ray photoelectron spectra (XPS) were obtained on a VG ESCALab MK II X-ray photoelectron spectrometer with an exciting source of Mg Kα (1253.6 eV). In the XPS spectra, all binding energies were referenced to the C 1s neutral carbon peak at 284.5 eV and the elemental compositions were determined from peak area ratios correction for each element.

2.5. Electrochemical measurements as supercapacitor electrodes

The electrode was prepared by mixing well the active materials (80 wt%), carbon black (15 wt%, Super P), and poly (tetrafluoroethylene) (PTFE) binder (5 wt%, Daikin) with anhydrous ethanol as solvent. In the case of using 6 M KOH solution as the electrolyte, the above slurries were pressed onto a nickel foam (1 cm * 1 cm) at the pressure of 15 MPa. The resultant electrodes were placed in a vacuum drying oven at 105 °C for 12 h. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) tests were carried out using a conventional one-component three-electrode glass cell, in which Platinum foil (1 cm²) and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The experiments were performed using an electrochemical analyzer (CHI 660 B, USA) under ambient conditions. In both cases, all the mass of electrode was weighed out with the electronic balance (Shimadzu, ATY224, 0.1 mg) and the typical mass load was about 1.5 mg/cm² in each working electrode.

Specific capacitances derived from galvanostatic tests can be calculated with the following equation (1):

$$C_g = \frac{I \Delta t}{m \Delta V} \quad (1)$$

where C_g (F/g) is the specific capacitance; I (A) is the discharge current; Δt (s) is the discharge time (after iR-drop correction); ΔV (V) is the potential window; and m (g) is the mass of active materials loaded in the working electrode.

Specific capacitances derived from cyclic voltammetry (CV) tests can be formulated by integrating the corresponding curves and then are divided by the scan rate as the following equation (2): v is scan rate, V_a and V_b are the initial and final potential.

$$C_g = \frac{1}{mv(V_b - V_a)} \int_{V_a}^{V_b} IdV \quad (2)$$

The volumetric capacitance is calculated according to the following equation (3):

$$C_v = C_g \times \rho$$

$$\rho = \frac{1}{Vt + \frac{1}{\rho_{carbon}}} \quad (3)$$

C_v (F/cm³) is the volumetric capacitance, C_g (F/g) is the gravimetric capacitance, ρ (g/cm³) is the particle density, Vt (cm³/g) is the total pore volume and ρ_{carbon} (g/cm³) is the true density of carbon materials (2 g/cm³).

3. Results and discussion

Fig. 1 illustrates the fabricating process of the Nanoporous carbon by electrostatic assembly of GO colloid and Zn-Glu MOF microcrystallines. The crystallographic structure of the coffee sediment powder are determined by powder X-ray diffraction

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