Research paper

One-step activation towards spontaneous etching of hollow and hierarchical porous carbon nanospheres for enhanced pollutant adsorption and energy storage

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ABSTRACT

Traditionally, porous carbon can be realized through chemical activation as well as templating with different materials for generation of hierarchical pores. However, the former method often results in the loss of the carbon's initial structure, while the latter is known to be complex and requires additional procedures to remove the templates. This work demonstrates one-step activation-excavation approach towards simultaneous etching of hierarchical pores with the preservation of its hollow framework for enhanced volatile organic compounds (VOCs) adsorption and supercapacitance performance. The improvement in activity in both applications stems from the micropores, mesopores and hollow interior for containment, selectivity of larger adsorbents and enhanced transport diffusion respectively for VOCs adsorption. Similarly, the hierarchical pore sizes and hollow cavity in supercapacitors serve the purpose of increased electroactive sites, provides shorter diffusion pathway and facilitates ion diffusion for improved capacitive rate. Thus, this facile and effective approach of producing hollow interior and hierarchical pores carbon nanostructures is promising for bifunctional pollutant removal and energy storage solutions.

1. Introduction

Porous carbon materials have attracted considerable attention due to their many different applications such as water remediation and energy storage [1,2]. Porous carbon has also been adopted as volatile organic compounds (VOCs) adsorbents for removal of toxic pollutants [3,4], catalyst supports [5] as well as electrode materials for electrical double-layer capacitors [6,7]. Furthermore, two-dimensional carbon material such as graphene with hierarchically multimodal pore-size distributions for electrooxidations has also become a hot topic of interest [8–10]. The high demand of porous carbon in the above-mentioned applications is attributed to its intrinsic properties such as high surface area, light-weight, low cost of the material, as well as the ease of obtaining various pore sizes [11]. Hierarchical pore structures, which consists of micro (< 2 nm), meso (2 nm – 50 nm) and macro (> 50 nm) pores, are especially beneficial to VOCs adsorption. Micropores are effective in the containment of VOCs while mesopores provides selectivity especially to adsorption of larger VOCs molecules and accelerates VOCs adsorption [12–15]. A hollow interior (macropores) has a

high surface to volume ratio leading enhanced transport diffusion, thereby improving the surface adsorption of VOCs. [16,17] In addition, a regularly shaped pore structure aids in decreasing the diffusion resistance of adsorbate molecules, thereby reducing the amount of time needed to adsorb the VOCs [12,18]. Similarly, the hierarchical pore structure is also favorable for enhanced supercapacitor performance as the micropores introduce abundant electroactive sites which are essential for high energy storage. Mesopores can be easily and rapidly accessed by electrolyte ions through porous channels, offering shorter diffusion pathways [19]. Moreover, the hollow interior (macropores) serves as ion-buffering reservoirs can effectively accommodate large number of ions, thus increasing the rate capability of the electrode [20]. As a result, synthesizing a hollow, hierarchical pore structures with regularly shaped pores is mandatory for superior performance of VOCs adsorption and supercapacitance.

In recent years, common methods of synthesizing porous carbon include chemical activation through the use of agents such as H_3PO_4, $ZnCl_2$ and KOH [21–23] and different templating methods such as hard templating with SiO_2, metallic templating or soft templating with

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surfactants [24–29]. The former methods result in structure containing both micropores and mesopores, however, the fundamental spherical structure of the carbon is often lost in the process of activation, leaving no room for the development of a hollow structure [6,21]. At the same time, maintaining regular pores shape might also be difficult due to the inconsistent etching of the carbon material [6]. The latter methods, on the contrary, allow the formation of hollow structure. However, such methods are known to be complicated and often involve the subsequent removal/etching of the core to obtain the required hollow structures [24–29]. As such, simultaneous etching of hierarchical pores with the preservation of its overall hollow frame structure remains particularly challenging stemming from the difficulty in identifying etchant with appropriate attrition capabilities.

Herein, this work presents an easy route using one-step chemical activation to simultaneously generate a hollow cavity and hierarchical pores structure for enhanced pollutant adsorption and energy storage. To the best of our knowledge, this is the first synthesis that demonstrates a convenient way towards readily controllable hierarchical pores and cavity of a carbonaceous material. Compared to other preparation methods, not only does this simple activation-excavation approach creates hierarchical pore sizes and hollow structure, the spherical structure of carbon spheres is not compromised, allowing it to act as a befitting scaffold for subsequent growth of heterostructure for enhanced VOCs degradation. As a proof of concept, the constructed carbon structure has exhibited superior VOCs adsorption due to presences of micro and mesopores, which contain and increase selectivity of adsorption of larger VOCs molecules respectively, while the hollow interior (macropores) promotes transport diffusion of VOCs. Supercapacitance measurements have also revealed superior or comparable capacitive performances compared to recent carbonaceous materials as the hierarchical porous channels act as electroactive sites, provides shorter diffusion pathway while the hollow structure facilitates ion diffusion. In addition, growth of TiO_2 nanosheets on the as-synthesized carbon leading to improved photocatalytic degradation has also been demonstrated. These findings may open a new straightforward avenue for the design and tailoring of highly porous, well-defined hierarchical and hollow carbon nanostructured materials promising for energy and environmental applications.

2. Experimental methods

2.1. Synthesis of resorcinol formaldehyde (RF)-resin spheres

20 ml of deionized (DI) water was added into 8 ml of pure ethanol (Merck) and stirred at 500 rpm for 10 s. Following which, 0.15 g of resorcinol (Acros Organics) and 0.1 ml of ammonia (Acros Organics) was added to the above solution and left to stir until complete dissolution. 0.21 ml of formaldehyde (Sigma Aldrich) was then added and the solution was left to stir for 24 h. The mixture was transferred to the Teflon-lined autoclave with a capacity of 50 ml and heated at 100 °C for 24 h. The precipitate obtained was washed three times with DI water followed by one time with ethanol *via* centrifuging. The resulting product was eventually dried at 60 °C and collected for further use.

2.2. Synthesis of activated carbon spheres (ACs)

0.1 g of the as-prepared RF-resin spheres was added to different mass of potassium hydroxide (KOH, Acros Organics). Carbon nanospheres (CNs) were obtained without adding KOH and annealed at 600 °C in a N_2 gas environment with a ramping rate of 5 °C min^{-1}. Porous carbon nanospheres (PCNs) and hollow carbon nanospheres (HCNs) structures were obtained by adding 0.1 g and 0.15 g of KOH respectively and annealed at the same temperature conditions as CNs. After annealing, the powder was washed several times with DI water until the pH reached ~7. The product was dried at 60 °C and collected for further use.

2.3. Synthesis of AC@TiO₂ sheets

5 mg of the as-prepared CNs, PCNs or HCNs were each added to 20 ml of pure ethanol (Merck), followed by 200 μl of diethylene-triamine (DETA, Alfa Aesar) and 40 μl of titanium tetraisopropoxide (TTIP, Sigma Aldrich). The mixture was left to sonicate and stir for 5 min. The solution was then transferred to a Teflon-lined autoclave with a capacity of 50 ml and heated at 200 °C for 20 h. The product was washed three times with ethanol, then eventually dried at 60 °C and annealed at 450 °C for 2 h in a N_2 gas environment with a ramping rate of 2 °C min^{-1}.

2.4. Materials characterization

The scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 7001F field-emission operating at 15 kV. The EDX characterization was performed with an Oxford Instruments Energy Dispersive X-ray (EDX) System. The crystalline structures were analyzed using transmission electron microscopy (TEM, FEI Tecnai F20X-TWIN) operated at 200 kV and X-ray diffraction (XRD, D5005 Bruker X-ray diffractometer equipped with graphite-mono-chromated Cu Kα radiation at λ = 1.541 Å). Raman measurements were measured using a microscope (WITecCRM200) with 532 nm (2.33 eV) excitation wavelength and laser power below 0.3 mW. Fourier transform infrared (FTIR) spectra of the products were recorded on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Brunauer–Emmett–Teller (BET) measurements were conducted using Quantachrome Nova 2200e with N_2 as the adsorbate at liquid nitrogen temperature. The specific surface area (S_{BET}) was calculated according to the multiple-point Brunauer-Emmett-Teller (BET) method at relative pressure P/P$_0$ = 0.01-0.1. Porosity distributions were calculated by the Quenched Solid Density Functional Theory (QSDFT) and Barrett–Joyner–Halenda (BJH) method. The total pore volume was obtained from the volume of N_2 adsorbed at a relative pressure of P/P$_0 \approx$ 0.99. The concentration of VOCs was measured by gas chromatography mass spectrometry (Shimadzu GCMS-QP2010 Ultra). Time-resolved photo-luminescence measurement was performed upon excitation of 350 nm fs pulses with average power of 5 mW. The measurement was employed with a mode-locked Ti:sapphire laser (Chameleon Ultra II, Coherent) working at repetition rate of 80 MHz and pulse duration of 140 fs. The second harmonic generation of 700 nm output from the laser was employed to excite the samples. The photoluminescence of the samples was filtered by a 500 nm long pass filter and collected and the PL spectra were detected by a CCD (Princeton Instrument, PIXIS100). The time-resolved PL was performed by using a photon-counting photo-multiplier (PMA, Picoquant). The emission centered at 550 nm was purified by a monochrometer (SpectroPro 2300i, Princeton Instrument). The PL decay dynamics were achieved by a time-correlated single photon counting module (TCSPC Picoharp 300, Picoquant).

2.5. Electrochemical measurements

The electrochemical properties of the HCNs were investigated in a three-electrode configuration at 25 °C using saturated calomel electrode (SCE) as the reference electrode and Pt foil as the counter electrode in aqueous 6 M KOH electrolyte. The working electrode was prepared by mixing 80 wt% HCNs, 10 wt% carbon black (XC-72) and 10 wt% polyvinylidene fluoride (PVDF) using ethanol to produce a homogeneous paste. The paste was then coated onto nickel foam and dried overnight at 60 °C. All electrochemical measurements (cyclic voltammetry (CV) and galvanostatic charge discharge (GCD)) were conducted on a CHI 660E electrochemical workstation. The CVs curves were obtained between −0.2 V to −0.8 V potential window at scan rates of 10, 20, 30, 40, 50, 75 and 100 mV s^{-1}. The GCD was acquired between −0.2 V to −0.8 V at current densities of 1, 2, 4, 8 and 10 A g^{-1}. The cycling stability test was performed by galvanostatically charging and discharging for 10000 consecutive cycles at 4 A g^{-1}.