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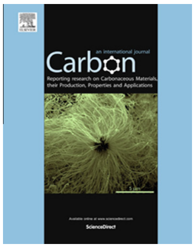

Monolithic carbons with spheroidal and hierarchical pores produced by the linkage of functionalized graphene sheets

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ABSTRACT

We report a novel monolithic porous carbon constructed by the hydrothermal self-assembly of graphene oxide sheets with poly (vinyl alcohol) as the linker in the formation process of a three-dimensional (3D) structure. All the pores in this carbon have circular cross-sections and range from micropores to mesopores to macropores and are formed by the gradual removal of trapped water. This 3D graphene network together with unique spheroidal and hierarchical pore structure with macropore openings at the surface allows fast ion and electron transport into the innermost micropores. The carbon not only exhibits excellent capability for removal of dye pollutants and oils but also shows a good performance as an electrode material in lithium ion batteries. Moreover, it is also proved to be an ideal buffer for expanded active materials in electrochemical energy storage.

1. Introduction

Porous carbons play vital roles in catalysis, environmental protection and energy storage [1,2] and their high porosity is usually obtained through an activation of carbon precursors [3] except for those derived by a template method [4,5]. The activation is intrinsically a chemical or physical process to etch structural defects in the carbon precursors and the resulting pore system is formed by the aggregation of disordered, defective and discontinuous (small size) graphene layers [6–8]. Thus, although having a high specific surface area (SSA), porous carbons produced by activation are normally characterized by a low electrical conductivity and a high resistance for ion transport. This feature restricts their use in many applications, for example, in electrochemical energy storage where high electron conductance and fast ion transport are needed and a foreign conductive additive is required [9].

The rise of graphene suggests a solution for the production of a carbon that has both a high SSA and excellent conductivity. Fully-isolated mono-layer graphene is predicted to have a theoretical SSA as high as 2630 $m^2\ g^{-1}$ [10], while powder-like graphenes (GNS) normally exist as a random aggregation of graphene layers and the overlayering of these layers hides most of the graphene surface, resulting in a relatively low measured value for SSA (far below the theoretical value) as discussed in our previous study [11]. Ruoff et al. developed a novel activation approach for preparing highly porous GNS, whose SSA is even higher than the theoretical value [12] and their work focuses on producing pores in individual

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sheets, which provide transport channels for foreign molecules that have access to the overlying graphene sheets. Ordered organization, through linking graphene sheets to three-dimensional (3D) pore systems, is another effective way to make more graphene surface accessible to foreign molecules, which is of importance for the practical application of graphene in macroforms. Cheng et al. were the first to develop a chemical vapour deposition (CVD) approach for producing a graphene-based 3D porous network by using Ni foam as a template [13]. Moreover, as an important alternative raw material, graphene oxide (GO) can offer an ideal platform for the assembly of such a porous system. Due to the existence of abundant oxygen-containing functional groups with epoxy and hydroxyl groups on their basal planes and carbonyl and carboxyl groups at their edges [14], GO sheets are easily assembled into membranes [15–17] and 3D macroassemblies [18–24] by a hydrogen bonding or dehydration process. Recently, our group has also successfully prepared graphene derived highly dense but porous carbons which have high volumetric capacitance for electrochemical capacitors up to 376 F cm^{-3} [25]. Thus graphene-based 3D assembly starting from GO was considered as an approach with great potential to realize macroscopic applications of graphene.

In this contribution we describe the production of a novel monolithic porous carbon by the linkage of functionalized graphene sheets with poly (vinyl alcohol) (PVA) as the linker under hydrothermal conditions. Such a carbon named reduced expanded porous graphene macroform (r-EPGM) is characterized by a unique hierarchical pore system, and all these pores are produced by the gradual removal of trapped water and have circular cross-sections ranging from micropores and mesopores to macropores. The macropore openings at the surface and the unimpeded channels along the spheroidal pore structure guarantee fast ion transport into the innermost micropores. With the fast ion transport and excellent electron conductance, which is the result of a fully interconnected graphene network, such a carbon shows potential versatile applications as a high-performance adsorbent and energy storage material.

2. Experimental

2.1. Sample preparation

2.1.1. *Preparation of r-EPGMs*

In order to investigate the role of PVA in the assembly process, a series of monolithic porous carbon with various PVA fractions were prepared. Here, we choose graphite oxide and PVA at a 30:1 *wt.* ratio as an example to describe the preparation process. Graphite oxide was prepared by a modified Hummers method [11] from graphite flakes. A GO colloidal suspension (2 mg mL^{-1}) was prepared by ultrasonication of graphite oxide in water for 2 h, followed by mild centrifugation (3800 rpm for 20 min) to remove thick layers. The homogeneous GO colloidal suspension (85 mL) and 282 μL of PVA solution (20 mg mL^{-1}) were mixed together with vigorous stirring. The mixture was then placed in a 100 mL Teflon-lined autoclave, and treated by a hydrothermal process in a muffle furnace (423 K) for 6 h. After the autoclave was cooled, the obtained cylindrical hydrogel was washed with distilled water and then dried by freeze-drying. Finally, r-EPGM was obtained by pyrolysis of the as-prepared dry sample at 1073 K for 3 h under an Ar atmosphere.

2.1.2. *Preparation of SnO_2/r-EPGMs*

The as-prepared r-EPGM was immersed in a $SnCl_2$ solution for 24 h. To avoid the hydrolysis of Sn^{2+}, a certain amount of HCl was added to the solution. The r-EPGM was then dried at 343 K overnight after removing it from the solution, followed by thermal treatment at 673 K for 3 h under an Ar atmosphere to guarantee the growth of SnO_2 crystals.

2.1.3. *Preparation of one-pot SnO_2/r-EPGMs*

Typically, 10 mL $SnCl_2$ solution (0.1 M) was added to 75 mL of the homogenous GO suspension (2 mg mL^{-1}) and stirred for 1 h. The solution was transferred to an autoclave and was treated at 423 K for 6 h. The cylindrical black product was then washed with distilled water and freeze-dried to remove water. One-pot SnO_2/r-EPGM was obtained after thermal treatment at 673 K for 3 h under an Ar atmosphere.

2.2. Samples characterization

The morphology of the sample was observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100F, Japan). Atomic force microscopy (AFM) images were obtained using a Nanoman II dimension 3100 instrument in tapping mode. X-ray diffraction (XRD) measurements were conducted at room temperature (Bruker D-8, Cu-Ka radiation, $\lambda = 0.154056$ nm). X-ray photoelectron spectroscopy (XPS) measurements were performed by an American PHI-1600ESCA system. Thermogravimetric analysis (TGA) was conducted using a Rigaku Thermo Plus TG 8120. Nitrogen adsorption/desorption isotherms were measured using a BEL-mini instrument and the samples were outgassed at 473 K for 10 h before the nitrogen adsorption measurements. The SSA, pore volume and pore size distribution (PSD) were obtained from the adsorption isotherm by the α_s and Brunauer–Emmett–Teller (BET) methods and density functional theory (DFT).

See details about liquid phase adsorption and electrochemical performance measurements in Supplementary Information.

3. Results and discussion

In our first attempt, GO sheets were used as the sole building blocks for the assembly of the porous material (as a hydrogel) in a hydrothermal environment, where these flexible sheets were interlinked in a 3D space by the dehydration reaction between –OH and –COOH groups at the edges of flexible GO planes. Freeze-drying was used to solidify the 3D microstructure and the obtained porous graphene macroform is denoted PGM. The PGM was then subjected to a thermal treatment and the obtained reduced PGM is denoted r-PGM. AFM observations (Fig. S1, ESI) indicate that the thickness of most GO sheets used here is ~1 nm, indicative of monolayers [26].