

Porous crumpled graphene with hierarchical pore structure and high surface utilization efficiency for supercapacitor

Zhihong Tang^{a,b,*}, Xiaodong Li^{a,c}, Tianren Sun^a, Shuling Shen^{a,b}, Xiu Huixin^{a,b}, Junhe Yang^{a,b}

^a School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai, 200093, China

^b Shanghai Innovation Institute for Materials, Shanghai, 200444, China

^c Semiconductor Lighting Research and Development Center, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, 100083, China

ARTICLE INFO

Keywords:

Porous crumpled graphene
Hierarchical pore structure
High surface utilization efficiency

ABSTRACT

As a promising active material for supercapacitor, graphene suffers serious restack, which reduces the surface area utilization of electrodes. Porous crumpled graphene (PCG) with hierarchical pore structure is designed in this paper. The spherical morphology of porous crumpled graphene effectively prevents it from restack, and thus dramatically promotes the utilization of pores on the graphene sheets. As electrode in supercapacitor, the specific capacitance per surface area is as high as $20.7 \mu\text{F cm}^{-2}$ due to the high surface utilization efficiency, which is much higher than that of the traditional activated carbon ($6.0 \mu\text{F cm}^{-2}$) and porous graphene ($6.5 \mu\text{F cm}^{-2}$), approaching the theoretical value of $20.9 \mu\text{F cm}^{-2}$.

1. Introduction

Electrical double layer capacitor (EDLC) is an energy storage device that stores energy by physisorption of electrolyte ions on the inner surface of porous carbon materials [1–5]. It has been demonstrated both theoretically and experimentally that several factors significantly affected the electrochemical performances of carbon materials including effective surface area accessible to electrolyte ions, electrical conductivity and pore volume. Graphene was considered as a promising material for supercapacitors because of large theoretical surface area and high conductivity [6–9]. However, graphene tended to aggregate due to the soft skeleton and therefore limited electrolyte ions accessible surface greatly, and then lowered the surface utilization of graphene for supercapacitor electrode [6,10]. Turning 2D into 3D crumpled graphene ball was proved an effective method for avoiding graphene from aggregation and therefore improving its electrochemical performance [11,12]. Actually, the crumpled graphene is not composed by a single layer graphene, but several layers. Therefore, the surface area is still low for a supercapacitor with high performance.

To create pores in the partially stacked graphene, Ruoff et al. used KOH to activate graphene-based spheres, the spherical structure of which was destroyed after activation [13]. Although the resulting sample had much high surface area ($3290 \text{ m}^2 \text{ g}^{-1}$), the surface utilization efficiency was only 31.1% of the theoretical value of graphene. It was speculated that the maintenance of spherical structure after activation may be useful to enhance the surface utilization furthermore and

boost the electrochemical performance.

Based on our previous work on crumpled graphene, we explored an effective strategy for preparing porous crumpled graphene with hierarchical pore structure and opened pores [14]. Our new material is thought to be able to combine the functions of crumpled structure and micropores very well and thus the specific capacitance per surface area is as high as $20.7 \mu\text{F cm}^{-2}$ (close to theoretical value of graphene, $20.9 \mu\text{F cm}^{-2}$).

2. Experimental

The experimental details were provided in supporting information. Briefly, aerosol containing graphene oxide (GO) sheets and KOH, generated by an ultrasonic atomizer, were blown into a preheated tube furnace (250°C) by using N_2 as carrier gas, the crumpled GO balls with homogeneously distributed KOH were obtained after flying through the heating zone. Then, the dried powders were heated under argon at 800°C for 1 h. The sample was washed by deionized water to neutral. As comparison, the crumpled graphene oxide (CGO) without KOH was prepared by the same method, and then KOH was coated on the wall of CGO by dispersing CGO into KOH solution. Activation was performed at the same condition and the sample was named a-CG.

3. Results and discussion

Fig. 1 schematically illustrated the formation process of PCG and the

* Corresponding author. School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai, 200093, China.
E-mail addresses: zhtang@usst.edu.cn (Z. Tang), jhyang@usst.edu.cn (J. Yang).

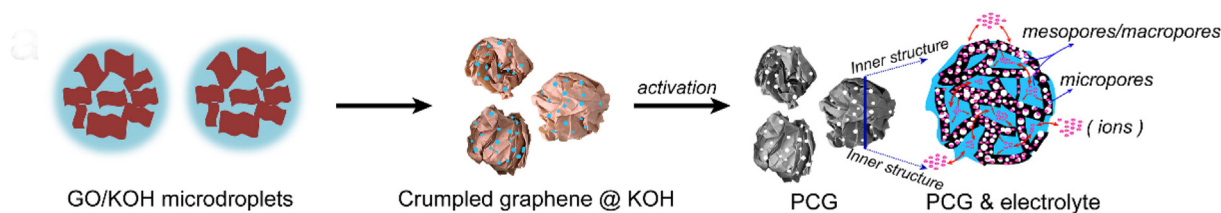


Fig. 1. Schematic illustration of the preparation of PCG.

ions diffusion route. It was thought that the formation of PCG involved three steps. First, the microdroplets containing GO and KOH were generated by ultrasonic. During the water evaporation, KOH distributed uniformly on the surface of GO, whilst the GO was squeezed by the capillary force during the water evaporation, whereby GO with uniformly dispersed KOH was crumpled. Second, the samples were calcined at high temperature to make KOH react with CGO wall to form the micropores on the wall. Finally, PCG was obtained by washing activated sample with DI water. When PCG was assembled into electrode, macropores could be formed among PCGs. After infiltration of electrolyte, the macropores can act as electrolyte reservoir, remarkably shortened the ion diffusion distance from bulk electrolyte to micropores on the PCG wall in electrode. Therefore, the pores in the PCG can be effectively utilized. The advantage of our methods was that KOH was loaded during the formation of GO spheres, thus KOH particles are very small because of the limited space between GO layers, which can effectively suppress the growth of KOH particles. If KOH was coated on crumpled GO spheres in separated steps, as shown in Fig. S1, large KOH particles will be formed. After heat treatment at high temperature, the wall of CGO was so seriously destroyed that the crumpled structure cannot be maintained. As a result, mesopores and macropores were dramatically decreased.

Scanning electron microscopy (SEM) image in Fig. 2(a) gave an overview of PCG, which clearly showed the spherical structure with average size of 400 nm. Observed more carefully, the ripples of PCG looked more like wrinkles than ridges, which was definitely different from the crumpled graphene (Fig. S2). The detailed structure of PCG was observed by transmission electron microscopy (TEM) (Fig. 2(b)), a semitransparent structure was observed, which maybe caused by the loosely packed graphene sheets induced by the reduction of capillary force of the evaporation of water exerted to the partially reduced GO after the KOH addition [15]. The high magnification TEM image of PCG was collected to check the surface structure (Fig. 2(c)), abundant micropores on the surface were found. It was worth noting that PCG can be dispersed very well in water only by gentle hand-shaking (Fig. 2(a) inset), which could be deduced the sample could be well wetted by water electrolyte, further facilitated the electrolyte permeation. In contrast, the crumpled structure of a-CG was totally collapsed and turned into relatively large bulk carbon material, which was believed to be an aggregation of the debris of the broken crumpled graphene (Fig. 2(d) inset). TEM image of the sample shown in Fig. 2(e) further proved the disappearance of the crumpled structure of a-CG. In addition, the water dispersibility of a-CG was very poor even after ultrasonic processing for 15 min (Fig. 2(d) inset). Compared with a-CG, PCG had good water wettability, opened micropores on the graphene sheets, combined with the high conductivity of graphene, it was predicted that the PCG would have good electrochemical performance as supercapacitor electrodes.

The pore structure of PCG was analyzed by N_2 adsorption/desorption. Fig. 3(a) exhibited a type-IV isotherm with a pronounced hysteresis with the relative pressure ranging from 0.4 to 1.0 and a high adsorption amount of N_2 at low pressure region, implying the existence of a large number of micro- and mesopores in PCG [16,17]. Meanwhile, the pore size distribution calculated by density functional theory (DFT) indicated the continuous distribution of well-defined micropores,

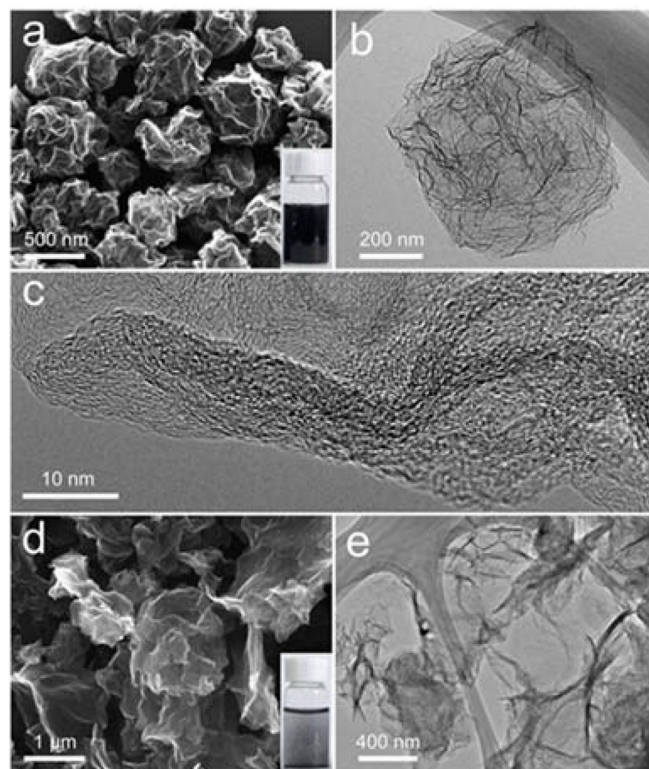


Fig. 2. (A) SEM image of the PCG, PCG can be well dispersed in water by gentle hand-shaking (inset); (b) TEM image of the PCG; (c) HRTEM image of the edge of PCG; (d) SEM image of the a-CG and a-CG cannot be well dispersed in water by 5 min ultrasonic processing accompanied with gentle hand-shaking (inset); (e) TEM image of the a-CG.

mesopores and macropores (range: 0.5–100 nm) (Fig. 3(b)), further confirming that hierarchy pore structure was formed in the PCG. It should be mentioned that the specific surface area of PCG was calculated to be $582 \text{ m}^2 \text{ g}^{-1}$ by Brunauer-Emmett-Teller (BET) method, and the pore volume of PCG was as large as $1.54 \text{ cm}^3 \text{ g}^{-1}$, which proved the existence of mesopores and macropores in the sample. To further explore the relationship between pore width and specific surface area (SSA), the differential and cumulative surface area V.S. pore width was illustrated, as shown in Fig. S3(a). The micropores contributed 41.5% of total SSA and the mesopores (2–50 nm) was 56.3% of total SSA. As comparison, as shown in Fig. 3(c, d), the nitrogen adsorption-desorption isotherm of a-CG also had a high adsorption amount at low relative pressure and a hysteresis in the P/P_0 range of 0.4–1.0, but the pore size distribution calculated by the DFT method indicated the pore width of a-CG was mainly less than 10 nm (Fig. 3(d)). And Fig. S3(b) also suggested that the high SSA was mainly benefited from the pores less than 10 nm. The main reason was that when KOH was mixed with GO in precursor solution, which would distributed uniformly in crumpled graphene, which was attributed to the high speed of water evaporation and the limited space between crumpled graphene [18]. Therefore, carbon atom could react with KOH homogeneously at high

Download English Version:

<https://daneshyari.com/en/article/6531557>

Download Persian Version:

<https://daneshyari.com/article/6531557>

[Daneshyari.com](https://daneshyari.com)