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MESOPOROUS CARBON SHEETS MADE OF EDGE-FREE GRAPHENE WALLS FOR ULTRA-STABLE SUPERCAPACITORS

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Introduction

Supercapacitors are rechargeable devices with advantages of high power density and long-term stability and a disadvantage of low energy density, compared with secondary batteries. Conventionally, activated carbons (ACs) have been used as an electrode material, but their insufficient stability restricts the voltage of a single cell (typically using an organic electrolyte) within 2.8 V. It is therefore necessary to stack a large number of cells to achieve required voltage (ca. 50 to 400 V) for practical applications. Thus, increase of single-cell voltage is crucial to reduce the stacking number, and thereby to make a whole module size more compact. A high-temperature stability is also required for many applications. The stability of supercapacitors highly depends on the structure of electrode material. It is known that single-walled carbon nanotubes are superior to ACs regarding the stability and achieve up to 4.0 V at room temperature[(1)]. Previously, we prepared graphene mesosponge (GMS), which is mesoporous carbon consisting of continuous graphene walls with a very small amount of carbon edge sites which are the origin of the corrosion reactions[(2)]. In this work, we try to make GMS into a seamless sheet and demonstrate its extraordinarily high stability as an electrode material.

Material

A seamless GMS sheet was prepared by using the templated method[(3)] as shown in **Fig. 1**. Al_2O_3 nanoparticles (TM300, Taimei Chemicals) with an average particle size of 7 nm were used as template. The Al_2O_3 powder was pressed to form a self-standing Al_2O_3 sheet. A very thin carbon with a thickness of 1~2 layers of graphene was uniformly deposited on the Al_2O_3 surface through the chemical vapor deposition (CVD) of CH_4, followed by template removal via chemical etching. The obtained carbon was annealed at 1800 °C to increase its crystallinity and to form a continuous graphene-framework.

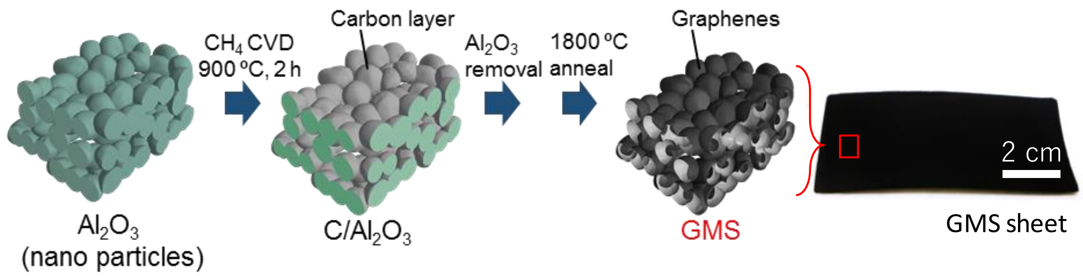

Figure 1. The preparation scheme of GMS and a photograph of a GMS sheet.

Characterization and Electrochemical measurement

As reference materials, activated carbon (AC, YP50F, Osaka gas chemical) and single-walled carbon nanotubes (SWCNT, Zeon Nanotechnology) were used. The BET surface areas of GMS, AC, and SWCNT are 1500, 1650 and 1300 m^2 g^{-1}, respectively. **Fig. 2** shows the total amount of desorbed gases (H_2, CO, CO_2, and H_2O) during each temperature programmed desorption (TPD) run. In the TPD analysis, graphene edge sites which are terminated by hydrogen or oxygen-functional groups release the aforementioned gases, and therefore, the total gas evolution represents a measure of the amount of carbon edge sites. While AC has a large amount of edge sites and release a significant amount of gases, SWCNT and GMS do not. Indeed, GMS has only 3% of edge sites AC has.

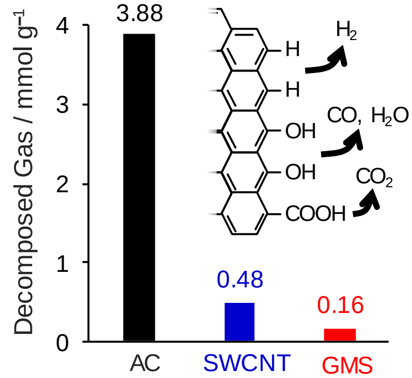

Figure 2. The total amount of desorbed gases from edge-sites during TPD.

The stability of GMS for supercapacitors was examined by using symmetrical two-electrode cells with a typical organic electrolyte (1.5 M Et_3MtNBF_4/PC). The cells were kept under a high voltage (3.5 V) and a high temperature (60 °C), and the capacitance decrease was monitored. These conditions are very harsh because general supercapacitors using activated carbon with the organic electrolyte are easily collapsed over 3 V at room temperature. The capacitances of cells were checked periodically by a galvanostatic charge/discharge measurement (5 mA/g) at 25 °C while the stability test was conducted. The capacitance retention of GMS is much better than those of AC and SWCNT (**Fig. 3**).

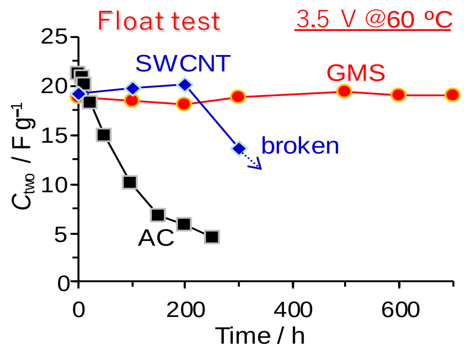

Figure 3. The capacitance change of each sample at 3.5 V and 60 °C.

The cycling stabilities of the samples at room temperature (25 °C) were also examined at a very high voltage (4.4 V) as shown in **Fig. 4**. AC shows quick capacitance drop at such a high voltage. SWCNT also cannot retain its capacitance, and the cell is broken over 500 cycles probably because of gas generation. Only GMS can retain its capacitance, indicating its ultra-high stability because of the edge free structure. The high-voltage operation at 4.4 V makes it possible to achieve 2.7 times higher energy density compared to conventional ACs. Our findings enable the development of highly durable and high-voltage type supercapacitors useful for many applications including automobiles.

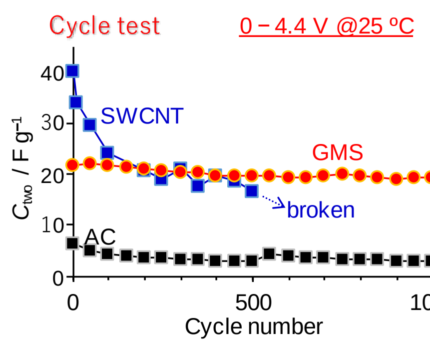

Figure 4. The capacitance change of each sample during cycle test at 4.4 V and 25 °C.

References

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