Layer-by-layer assembled reduced graphite oxide/PDDA thin film as a model to evaluate the capacitance of a single layer of graphene

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The theoretical surface area of an isolated single-layer of graphene ($2,630$ m^2 g^{-1}) is the major driving force for the glowing interest for application towards electrochemical capacitors. Unfortunately, graphene has a strong tendency to aggregate due to the interaction of individual sheets, leading to specific surface area much lower than activated carbon and limited access of electrolyte. The reported specific capacitance of reduced graphite oxide nanosheet (or simply 'graphene') electrodes prepared by exfoliation and reduction of graphite oxide ranges from 100 to 250 F g^{-1}.[1] The dispersed capacitance values is due at least in part to the difference in synthetic procedures, including degree of exfoliation, reduction, re-stacking, as well as the starting materials and electrolyte used etc. In order to realize an electrochemical capacitor using graphene-related material, it is essential that the factors governing the capacitive behavior be clarified. In addition information on the capacitance of a single layer of graphene should be elucidated.

Based on the reported specific capacitance of the edge plane of graphite (c.a. 50-70 µF cm^{-2}) and basal plane (~3 µF cm^{-2}),[2] the lateral size of reduced graphite oxide nanosheets (rGOns) is expected to be at least one of the factors affecting the electrochemical properties. The size of rGOns can be controlled by using different starting material.[3,4] For example, rGOns derived from platelet carbon nanofibers (PCNFs) affords rGOns with average diameter of 150 nm while that derived from natural graphite gives rGOns with average size of ~3 µm. The small-sized rGOns derived from PCNF gives approximately 60% higher specific capacitance compared to rGOns from natural graphite.[4] Ultrasonic treatment is another approach to control the size of rGOns. We have successfully derived rGOns with equivalent diameter (D_e) of 920, 370, and 280 nm from the same starting material.[5] The capacitance of H$_2$-reduced rGOns increased with decreasing D_e. Specific capacitance of rGOns with the smallest D_e of 280nm was 242 F g^{-1} in H$_2$SO$_4$ and 205 F g^{-1} in Na$_2$SO$_4$. The area specific capacitance based on the S_{BET} value of 283 m^2 g^{-1} is much higher than conventional activated carbons, even in neutral electrolyte where the capacitance can be considered to be purely double-layer charging.

Although rGOns powder affords high area specific capacitance, the low electrochemically accessible surface area limits its gravimetric capacitance to values comparable with activated carbon. To overcome this disadvantage, we have attempted to achieve an ionically accessible structure by layer-by-layer assembly of reduced graphite oxide nanosheets and poly-diallyldimethyl ammonium. As shown in Fig. 1, monotonous increase in capacitance was observed with increasing number of rGOns layers (H$_2$-reduced), indicating that the entire surface of rGOns is fully accessible for charge storage. The specific capacitance per layer was 115 µF cm^{-2} in H$_2$SO$_4$ and 66 µF cm^{-2} in Na$_2$SO$_4$, in excellent agreement with the data obtained for rGOns powder (Fig. 2). The electrochemically active surface area of 10 layers of (PDDA/rGOns) is anticipated to be ~1,300 m^2 g^{-1} based on the degree of overlap (50%) observed by AFM studies of a monolayer of GOns (Fig. 3). The gravimetric capacitance per layer of rGOns derived from these numbers is quite promising; 1,500 F g^{-1} in acid and 860 F g^{-1} in neutral electrolyte.

[1] L.L. Zhang, R. Zhou, X.S. Zhao, *J. Mater. Chem.*, **20**, 5983 (2010).
[2] J. Randin, E. Yeager, *J. Electrochem. Soc.*, **118**, 711 (1971).
[3] J. Sato, K. Higurashi, K. Fukuda W. Sugimoto, *Electrochemistry*, **79**, 337 (2011).
[4] J. Sato, Y. Takasu, K. Fukuda, and W. Sugimoto, *Chem. Lett.*, **40**, 44 (2011).
[5] Z. Lei, T. Sakai, W. Sugimoto, **submitted**.

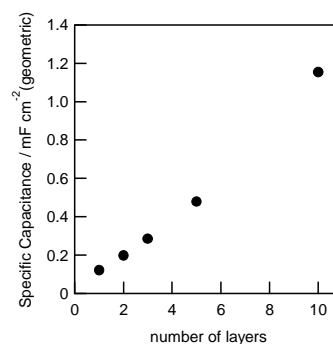**Figure 1**. Geometric capacitance of multi-layered (PDDA/rGOns). Reduced with H$_2$ at 200°C. Electrolyte: 0.5 M H$_2$SO$_4$, v=20 mV s^{-1}, E=0.2-1.2 V vs. RHE.
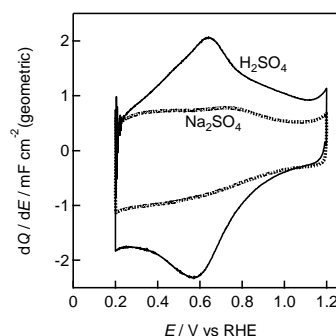
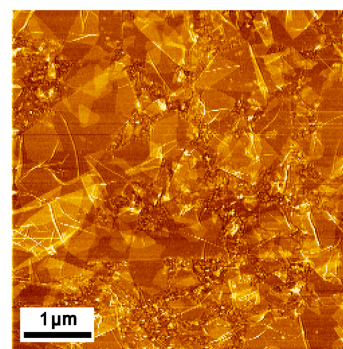**Figure 2**. Cyclic voltammogram of (PDDA/rGOns)$_{10}$ in 0.5 M H$_2$SO$_4$ and 0.5 M Na$_2$SO$_4$ at v=20 mV s^{-1},

Figure 3. Typical AFM image of (PDDA/rGOns) monolayer.