An interleaved porous laminate composed of reduced graphene oxide sheets and carbon black spacers by in situ electrophoretic deposition†

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Although the graphene-based materials have a great potential to be used for various energy storage devices, the expected performance of graphene has not been achieved yet seemingly due to the lack of interconnected porosity and actively-exposed surface area that should be developed in the re-stacked graphene electrodes. Herein we used an electrophoretic deposition (EPD) method to fabricate a binder-free porous supercapacitor electrode composed of reduced graphene oxide (RGO) sheets and conductive carbon black (CB) particles. Applying EPD for an electrostatically-stabilized aqueous mixture of RGO and CB nanoparticles, the electrophoretic squeezing force in EPD induced the RGO sheets to align in the in-plane direction along with the CB particles placed in the interlayers of RGO. The developed ladder-like interleaved composite structure allowed a desirable porosity network and conductive path for a facile movement of ions and electrons. Controlling the ratios of concentrations (C_{RGO}/C_{CB}) and/or zeta potentials (ζ_{RGO}/ζ_{CB}) of the RGO and CB nanoparticles in aqueous mixtures, different nanostructures of the interleaved RGO/CB laminates could be fabricated. Thoroughly tested as a supercapacitor electrode in an organic electrolyte (TEA BF₄), the developed RGO/CB electrodes provided excellent performance of the specific capacitance of 218 F g⁻¹ at a scan rate of 1 mV s⁻¹ (133.3 F g⁻¹ at a current density of 2 A g⁻¹), energy density of 43.6 W h kg⁻¹ and power density of 71.3 kW kg⁻¹. It is believed that an ideal performance of intrinsic graphene properties could be exerted by the unique nanosstructure of binder-free interleaved graphene laminates as developed by the scalable in situ EPD process for large-volume production.

Introduction

Graphene is believed to be an ideal carbon electrode material for various electrochemical energy storage devices like electrical double layer capacitors (EDLCs) because it has large surface area and excellent electrical conductivity.1–3 although graphene has been tested as a supercapacitor electrode material usually mixed with other carbon materials,4,5,6 conducting polymers,7,8 or transition metal oxides.9 However, practical application of graphene still faces challenges mostly in the steps of electrode fabrication, where the graphene-sheet mixture are prepared in the liquid media and subsequently re-assembled as a solid-state electrode membrane. In this preparation step, an appropriate nanoscale structure should be developed for accommodating ions and electrons to the active surface of graphene sheets. It is believed that the exposed surface area and the well-connected open porosity of the re-stacked graphene sheets should be ensured to achieve excellent performance and long-term durability of EDLC.7,12–15,17

More specifically, the graphene-based materials such as graphene oxide (GO) and reduced graphene oxide (RGO) sheets have a strong tendency to restack themselves very densely during drying processing due to the large surface area and the strong van der Waals force. If this spontaneous and compact restacking of RGO sheets occurs, the desired supercapacitor performance may not be exerted although the intrinsic surface area of graphene-based materials is large.13 For supercapacitor electrodes, the interconnected pore network should be guaranteed for ions and electrolytes to move in a facile way. In this sense, conductive particles have been incorporated as a spacer in the restacked graphene layers and tested as supercapacitor electrodes for the purpose of providing porosity.12,16 In this approach, the compact restacking of graphene sheets was likely interrupted by the incorporated conductive particles. However, the binder materials (or adhesive glues) were inevitably used in those paste-coating methods and they might very well cover the RGO surface and/or block the open porosity network.