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RAPID COMMUNICATION

A general strategy for the fabrication of high performance microsupercapacitors

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Abstract

We propose a generic strategy for microsupercapacitor fabrication that integrates layers of reduced graphene oxide (rGO) and pseudocapacitive materials to create electrode heterostructures with significantly improved cycling stability and performance. Our approach involves a combination of photolithography and a simple transfer method of free-standing reduced graphene oxide film onto an Au/patterned photoresist bilayer. The resulting stack (rGO/Au/patterned resist/substrate) is then used for the electrochemical deposition of various pseudocapacitive materials before the final step of lift-off. To prove the viability of this method, we have successfully fabricated microsupercapacitors (MSCs) with the following interdigitated electrode heterostructures: MnO_2/rGO, $Co(OH)_2$/rGO and PANI/rGO. These MSCs show better performance and cycling stability compared to the single layer, (i.e., rGO-free) counterparts. The interdigitated electrode heterostructures result in MSCs with energy densities in the range of 3–12 mW h/cm^3 and power densities in the range of 400–1200 mW/cm^3, which is superior to the Li thin film batteries (E=10 mW h/cm^3), carbon, and metal oxide based MSCs (E=1–6 mW h/cm^3) while device energy densities are in the range of 1.3–5.3 mW h/cm^3, corresponding power densities are in the range of 178–533 mW/cm^3. These results can be explained by a facilitated nucleation model, where surface topology of the rGO film creates a favorable environment for the nucleation and growth of pseudocapacitive materials with strong interfacial contacts and enhanced surface area. This approach opens up a new avenue in fabricating MSCs involving a variety of heterostructures combining electrical double layer carbon type with Faradaic pseudocapacitive materials for enhanced electrochemical performance.

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Introduction

The next generation of energy storage devices is expected to include devices fabricated in the planar format due to their compatible integration with microelectronic devices [1-3]. This reality has fostered the rapid development of on-chip energy storage devices such as thin film batteries and microsupercapacitors (MSCs) [4-7]. MSCs have become attractive owing to their high power densities and longer cycle life compared to thin film batteries, which suffer from poor rate capability and limited cycle lifetimes [4,6]. Additionally, due to their planar configuration, MSCs can exhibit higher charge-discharge rates compared to their conventional counterparts [6,7].

High surface area porous carbon based MSCs such as carbide derived [8], onion like[9], activated [10] and carbon nanotubes (CNTs) [11] were fabricated by employing conventional photolithography and various deposition methods including sputtering, electrophoretic, ink-jet printing and spray coating techniques. Further, conducting graphitic patterns involving 2D graphene and 1D CNTs were grown by chemical vapor deposition (CVD) to fabricate three-dimensional MSCs [12,13]. Of late, reduced graphene oxide (rGO), due to its high surface area, conductivity and functionality, has become an attractive material for energy storage applications [14,15]. For example, Gao et al., have used laser reduction to write reduced graphene oxide patterns over the GO thin films in order to fabricate rGO MSCs [16]. El-Kady et al., have demonstrated scalable fabrication of rGO MSCs by ordinary digital video disk (DVD) laser scribing technique [17]. Wu et al., have employed photolithography and oxygen plasma to create rGO based micropatterns and further demonstrated electrochemical performance of these MSCs [18]. As the mechanism of charge storage in these carbonaceous materials is of non-Faradaic type, these MSCs exhibited limited values of capacitance. Hence, in order to improve the capacitance values, pseudocapacitive materials such as metal oxides/hydroxides (RuO_2, MnO_2 and $Ni(OH)_2$) [19-21] and even conducting polymers (PPY, PANI) [22-24] which can undergo reversible redox reactions at their surfaces have been employed to fabricate micro-pseudocapacitors. However, pseudocapacitive materials suffer from poor cycling performance, which has been circumvented through the fabrication of hybrid electrodes composed of composites of rGO with pseudocapacitive materials [25-27]. The complimentary roles between these two components have been exploited where reduced graphene oxide serves not only as a conducting network for facile charge transport, but also as a mechanical support in improving cycling stability of these hybrid electrodes. Recently, there have been efforts in fabricating pseudocapacitive/reduced graphene oxide electrode heterostructures employing micromolding and filtration methods [28,29].

Patterning of pseudocapacitive/rGO heterostructures is of significant interest for achieving better electrochemical performance of MSCs. Here, we propose a simple and generic strategy for the fabrication of pseudocapacitive/rGO planar microsupercapacitor devices using a single step photolithography process. Free standing rGO films, obtained through vacuum filtration process, are transferred onto substrates having metal-coated patterned photoresist layer. The resulting stack (rGO/metal/patterned resist/substrate) is selectively coated by metal oxides (MnO_2 and $Co(OH)_2$) and conducting polymer (PANI) over the transferred rGO layer, followed by lift-off process. The result is a MSC with interdigitated patterns of different pseudocapacitive materials on rGO. As microsupercapacitor is comprised of a few microns thick film, electrochemical deposition can be a facile method, resulting in the mesoporous morphology of pseudocapacitve materials, required for maximum accessible surface area for the electrolyte ions. Avoiding binders or additives, while maintaining good interfacial contact through electrochemical deposition, ensures strong adherence with current collectors, helps in facile electron transfer across the pseudocapacitive/current collector interface. This in-plane design of hybrid electrodes with no separator ensures facile transport of ions, resulting in high scan rate abilities of heterostructured microsupercapacitor with improved cycling stability.

Experimental

Photolithography

Glass substrates (Fisher) were cut into 1 × 1 in. size, cleaned with a soap solution to remove the dirt followed by ultrasonication in acetone, isopropanol and deionized water sequentially for 5 min each and then dried by blowing nitrogen. Photoresist AZ9260 was spun coated at 3000 rpm for 60 s over the glass substrates to get 10 μm thick photoresist layer. Photoresist coated substrates were soft baked at 110 °C for 3 min. The exposure was done using EVG contact aligner at a constant dose of 1800 mJ/cm^2 through the Cr/Glass mask having the interdigitated patterns. After the exposure, samples were developed in AZ726 developer solution for 6 min, which has resulted in the formation of patterns in the photoresist layer. Metal layers of 200 nm Au/20 nm Ti were deposited by sputtering (Equiment Support Co., Cambridge, England) technique over the patterned photoresist layer. Before the lift-off process, rGO layer was transferred onto metal-coated patterned photoresist followed by electrodeposition of pseudocapacitive materials. In this study, we have employed interdigitated finger electrodes (width of each finger 100 μm, and spacing between the fingers is 50 μm); the total area of all the fingers is 0.25 cm^2.

RGO preparation and filtration

Graphite oxide was prepared from natural graphite source using a modified Hummers method [30]. Thus obtained graphite oxide was exfoliated in de-ionized (DI) water by sonicating using a bath sonicator (UP400S, Ultrasonic processor; Hielscher ultrasound Technology) for 1 h. The resulting graphene oxide was then reduced to graphene by following the method that was reported by Li et al. [31] Briefly, the homogeneous graphene oxide dispersion (5.0 mL) was mixed with 5.0 mL of water, 5.0 μL of hydrazine solution (35 wt% in water) and 100.0 μL of ammonia solution (28 wt% in water). The optimal hydrazine to graphene oxide weight ratio was 7:10 [31,32]. The mixture

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