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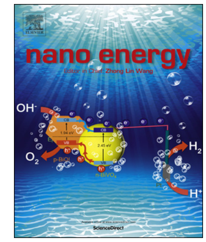

COMMUNICATION

Direct preparation and processing of graphene/RuO_2 nanocomposite electrodes for high-performance capacitive energy storage

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Abstract
Carbon materials are widely used in supercapacitors because of their high surface area, controlled porosity and ease of processing into electrodes. The combination of carbon with metal oxides results in hybrid electrodes with higher specific capacitance than pure carbon electrodes, which has so far limited the energy density of supercapacitors currently available commercially. However, the preparation and processing of carbon/metal oxide electrodes into supercapacitors of different structures and configurations, especially for miniaturized electronics, has been challenging. Here, we demonstrate a simple one-step process for the synthesis and processing of laser-scribed graphene/RuO_2 nanocomposites into electrodes that exhibit ultrahigh energy and power densities. Hydrous RuO_2 nanoparticles were successfully anchored

Abbreviations: EDLC, electrical double layer capacitor; LSG, laser-scribed graphene; GO, graphene oxide; ICP-AES, inductively coupled plasma atomic emission spectroscopy; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; TGA, thermal gravimetric analysis; SAED, selected area electron diffraction; CV, cyclic voltammetry; CC, galvanostatic charge/discharge; LED, light emitting diode

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to graphene surfaces through a redox reaction of the precursors, graphene oxide, and $RuCl_3$ using a consumer grade LightScribe DVD burner with a 788 nm laser. This binder-free, metal current collector-free graphene/RuO_2 film was then used directly as a hybrid electrochemical capacitor electrode, demonstrating much-improved cycling stability and rate-capability with a specific capacitance up to 1139 F g^{-1}. We employed these hybrid electrodes for building aqueous-based symmetric and asymmetric cells that can deliver energy densities up to 55.3 Wh kg^{-1}, placing them among the best performing hybrid electrochemical capacitors. Furthermore, this technique was used for the direct writing of interdigitated hybrid micro-supercapacitors in a single step for the first time, with great potential for miniaturized electronics. This simple approach provides a general strategy for making a wide range of composite materials for a variety of applications.

Introduction

The ever-increasing demand for smaller portable electronics has driven the need for efficient energy storage devices with continually shrinking footprints [1]. During the last few years, electrochemical capacitors have been successfully used as a powering medium for a camera flash, back-up power, regenerative braking, and a new generation of electric vehicles. Electrochemical capacitors offer significant advantages compared to conventional storage media, such as batteries and capacitors [2], providing significantly higher energy densities than conventional capacitors and higher power and longer cycle life than batteries [3,4].

Electrochemical capacitors can be separated into two general categories: electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store electrostatic charge at the interface between the electrode and electrolyte, where the charge accumulates on the electrode surface. The most important attributes of an EDLC electrode are high surface area and high porosity, as the amount of charge accumulation is related to the exposed surface area. Recent advances in carbon materials such as carbon nanotubes [5], graphene [6], and activated carbon (AC) [7] have led to their use as the active material in EDLCs. Graphene is one of the most attractive materials for such applications, owing to its remarkably high surface area, excellent electrical and thermal conductivity, electrochemical stability, and mechanical properties [8,9]. Recent studies have reported methods for fabricating 3-dimensional graphene via a laser scribing technique [10-16]. This method is especially advantageous as it allows patterning and fabrication of microsupercapacitors in a very simple fashion, while offering remarkably high electrochemical performance. While graphene-based EDLCs can provide a theoretical capacitance up to 550 F g^{-1} [11], this falls short for many practical applications, especially when compared to batteries.

Pseudocapacitors, which are based on redox reactions of the electrode material, can have up to 10 times higher capacitance than EDLCs, yet their wide-spread applications have been limited due to lower power density and poor cycling stability. In pseudocapacitors, only surfaces and near-surface sites can contribute to charge storage via redox reactions, where the electrode materials are commonly metal oxides [17] or conducting polymers. Among the metal oxides, RuO_2 has been widely studied as a material for pseudocapacitor applications due to its remarkably high specific capacitance (1300-2200 F g^{-1}) [18-22], highly reversible charge-discharge features, wide potential window, and high electrical conductivity (10^5 S cm^{-1}). For practical applications of RuO_2 as a pseudocapacitor electrode, power density and cycle life must be improved.

Much attention has been focused on developing a hybrid system where the merits of EDLCs and pseudocapacitors are combined to overcome the shortcomings of each individual technology. Such hybrid electrochemical capacitors offer improved energy and power densities, as well as improved cycling stability [23]. Carbon-metal oxide nanocomposites with high electronic conductivities have been of interest as electrodes for hybrid electrochemical capacitors with the proposition that they will benefit from the electrical conductivity of carbon and the high capacitance of metal oxides, thus providing systems with both higher energy density and higher power density. While previous studies of carbon-RuO_2 electrochemical capacitors have demonstrated improved overall performances, further improvements in the energy density are still required [18,24-30]. Another issue is the preparation of these electrochemical capacitors that often require multiple steps including post-processing, thereby limiting the potential of these methods for practical applications. Small-scale supercapacitors, known as micro-supercapacitors, have emerged as promising energy sources for powering microelectronics. Despite the significant progress, graphene/RuO_2 electrodes have been employed only in conventional parallel plate supercapacitors and have not yet been demonstrated in miniature interdigitated supercapacitors. This is because of the difficulty of fabrication and processing of hybrid materials into patterned microelectrodes. These hybrid micro-supercapacitors may, one day, be used to complement or even replace batteries and electrolytic capacitors in a variety of applications.

In this paper we propose a 3-dimensional hybrid electrochemical capacitor based on a carbon-RuO_2 nanocomposite. The nanocomposite is comprised of a 3-dimensional laser-scribed graphene (LSG) framework combined with hydrous RuO_2 nanoparticles via a one-step procedure where graphene oxide (GO)/$RuCl_3$ are simultaneously reduced (GO → LSG) and oxidized ($RuCl_3 \rightarrow RuO_2$) via a standard laser scribing technique [11]. By anchoring RuO_2 nanoparticles directly onto LSG, the 3-dimensional, highly porous graphene surface serves as an excellent conductor for fast electron transfer, while RuO_2