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Performance evaluation of Asymmetric Supercapacitor based on Cobalt manganite modified graphene nanoribbons

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ABSTRACT

An aqueous, high potential asymmetric supercapacitor (ASC) is developed using cobalt manganite ($CoMn_2O_4$) modified graphene nanoribbon (GNR). Combining $CoMn_2O_4$/GNR and GNR as different electrodes of supercapacitor in Na_2SO_4 electrolyte, the ASC device exhibited 1.9 V wide potential window for charge storage along with significantly improved capacitive performance than symmetric counterpart. When cycled reversibly in 0-1.9 V, the ASC demonstrates high energy density 84.69 Wh Kg^{-1} (more than four times of the symmetric cell) at high power density 22 kW Kg^{-1} due to elegant synergism between different electrodes. Additionally, it exhibits long term stable cycling performance with 96% capacitance retention and ~ 97.5% columbic efficiency. These outstanding results pave their way for promising applications in high energy storage systems.

1. Introduction

Demand of supercapacitor devices is increasing particularly from the applications that require high pulsed power density and long cycling life [1,2]. Bridging batteries and conventional capacitors in energy and power density, supercapacitors can be used as backup power sources in specialized applications like hybrid electric vehicles, industrial equipments, power back up, military devices and portable electronics [3,4]. Charge storage mechanism in supercapacitors is classified into two i.e. electrical double layer capacitance (EDLC), where electrical energy is stored in the form of adsorbed ions at electrode/electrolyte interface, and the pseudo-capacitance in which the redox transitions are utilized. Supercapacitor electrode employs three main classes of materials which include carbonaceous material, transition metal oxides and conducting polymers [4–6]. Commercially, most supercapacitor devices are based on EDL charge storage and therefore high surface area carbon materials have been extensively investigated. By virtue of large surface, significantly large EDL formation takes place and consequently these material possesses high power density however lack in energy density [7]. Enhancing energy density to meet the demands without forfeiting power delivery and cycle life is a major challenge due to limited operating potential [8]

Recently, considerable research efforts have been devoted to various asymmetric supercapacitor (ASC) systems employing two different electrodes with comprehensive working potential range leading to notable improvement in energy density such as activated carbon (AC)//$Ni(OH)_2$ [9], carbon nanotube (CNT)//MnO_2 [10], RGO//MnO_2/RGO [11], Graphene//MnO_2 [12]. However, these devices still have restricted performance in terms of sacrificed power density. Mostly utilized anode materials i.e. activated carbons have high hydrogen evolution potential leading to large negative potential range with low average capacitance resulting in imbalanced synergism [13]. Moreover, AC has limited accessibility of hydrated ions to the pores smaller than 0.5 nm (lesser than hydrated ions) retarding their relaxation time constant [14,15]. Instead, graphene nanoribbon (GNR), a quasi one dimensional form of graphene is employed for the first time as an anode material for high performace supercapacitors.

To bring dynamic synergistic effect in ASC, it is important to choose the cathode with efficient kinetics of redox reactions. Kinetics may be boosted by functionalized electrode materials capable in offering high electronic and ionic conductivities, active charge storage sites and desired microstructures. However, it is not possible for a single material to exhibit all desired characteristics and therefore binary or ternary nanocomposite have been investigated [16,17]. Low electrical conductivity, poor cycling stability at high current densities and less mechanical stability of

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the electrode material is shown to improve by making binary composites of metal oxides such as Ni-Co, Co-Mo, Co-Ru oxides ensuring fast redox reactions [18,19]. Among them, Mn-Co oxide has been used promisingly as supercapacitor electrode due to the high capacitance and richer redox reactions over unitary Mn or Co oxide [20]. Recently, Ma et al. studied the effect of Co doping in MnO_2 and showed improved microstructural uniformity with increase in Co content thereby enhancing the MnO_2 performance [21]. Chang et al. prepared manganese cobalt oxide by anodic deposition and inhibited the dissolution of MnO_2 [22]. High specific capacitance for cobalt doped manganese oxide prepared by potentiodynamic method on stainless steel substrate was also reported by Prasad et al. [23]. Synthesis of multilayered films of cobalt nanowires with MnO_2 nanosheets was carried out and a high specific capacitance of 507 Fg^{-1} with long cycling life was reported [24]. Role of conducting carbon support to nanostructure transition metal oxide was investigated and found out that besides providing a conducting path, support also act as buffer to accommodate large volumetric alterations during charge discharge cycling to prevent any strain in the material [25]. In case of carbonaceous material, Graphene nanoribbon (GNR), a quasi one dimensional form of graphene, exhibit tunable electrical properties through dimension confinement or functionalization [26,27]. It not only provides a platform for the growth of transition metal oxides but also offer a conducting network resulting in high performance supercapacitor [28].

In this work, we report the synthesis of graphene nanoribbon supported $CoMn_2O_4$ nanofibers ($CoMn_2O_4$/GNR) using microemulsion method. $CoMn_2O_4$/GNR which is then employed as an cathode for asymmetric supercapacitor with GNR as anode. Corresponding ASC of $CoMn_2O_4$/GNR//GNR exhibits high energy density 84.69 Wh Kg^{-1} in a large potential range 1.9 V. Excellent cycling life stability is also demonstrated with relaxation time 67 μs imparting high power delivery capability to the cell.

2. Experimental

Cobalt chloride ($CoCl_2.6H_2O$), Manganese chloride ($MnCl_2.4H_2O$), Sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4), Potassium permanganate ($KMnO_4$), Sodium sulphate (Na_2SO_4), Phosphoric acid (H_3PO_4), Hydrogen peroxide (H_2O_2), isopropyl alcohol (IPA) and isooctane were purchased from Merck. MWCNTs were purchased from Shenzhen Nanotech Port, Co. Limited, China, diameter 10-20 nm and length ~1 μm. Perfluorinated ion exchange resin (Nafion) was procured by Sigma Aldrich. Sodium sulphosuccinate (AOT) was used as surfactant (supplied by Alfa Aesar).

2.1. Synthesis of Graphene oxide nanoribbon GONR

Graphene oxide nanoribbon (GONR) was synthesized by longitudinal unzipping of carbon nanotubes [29]. Briefly, MWCNT (3 g) was added in a mixture of 400 ml of conc. H_2SO_4 (98%) and conc. H_3PO_4 under stirring for 15 minutes. Then, $KMnO_4$ (18 g) was added gradually to the H_2SO_4/H_3PO_4 dispersed MWCNT. The solution was heated for 4 hr at 70 °C and allowed to cool naturally. For extracting GONR from the reaction mixture, 400 ml ice containing 30% H_2O_2 solution was added and dark brown solid precipitate settled at the bottom. This was repeatedly washed with ethanol and deionized water. The product was filtered through

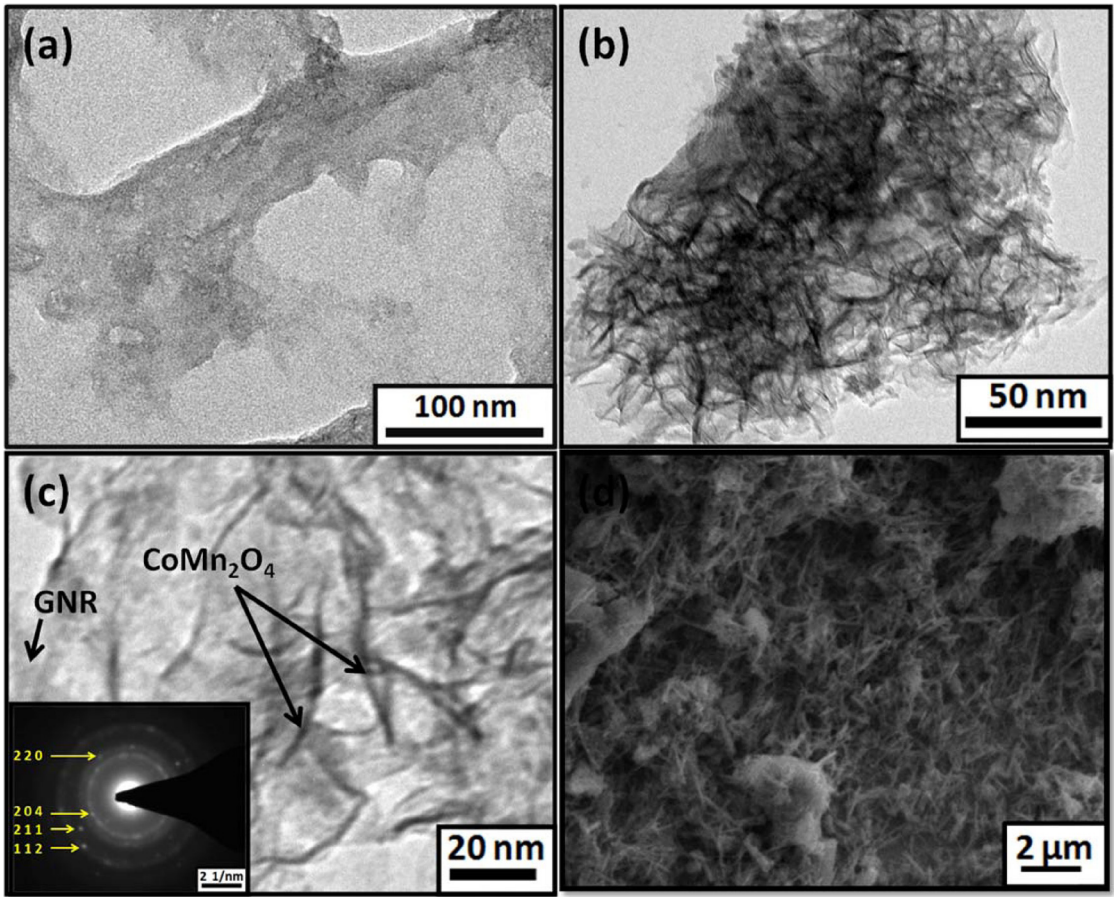

Fig. 1. (a and b) TEM of GNR and $CoMn_2O_4$/GNR respectively (c) HRTEM revealing uniform distribution of $CoMn_2O_4$ nanofibers dispersed over GNR. Inset shows SAED pattern and (d) SEM micrograph of $CoMn_2O_4$/GNR.