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Asymmetric supercapacitor for sensitive elastic-electrochemical stress sensor

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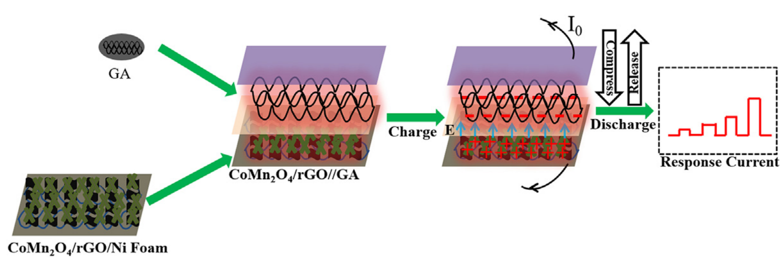
HIGHLIGHTS

- $CoMn_2O_4$/rGO electrode shows a high specific capacitance of 1783 F g^{-1}.
- The asymmetric device exhibits superior energy density of 53.33 Wh Kg^{-1}.
- A sensitive asymmetric elastic-electrochemical stress sensor is designed.
- The sensor exhibits stable and sensitive current responses to the applied stress.

GRAPHICAL ABSTRACT



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ABSTRACT

An asymmetrically elastic electrochemical supercapacitor is fabricated using $CoMn_2O_4$/rGO as positive electrode and ternary N, B, and S co-doped elastic graphene aerogel as negative electrode. The combination not only endows the device superior energy density of 53.33 Wh Kg^{-1} at a high density of 400.00 W kg^{-1}, but also offers a facile sensor application to feel external mechanical load with outstanding elasticity. Under the loading stress range from 0.1 to 10 N, the cell demonstrates sensitive current response towards the applied stress. It is observed that the elastic graphene aerogel offers important role by adjusting internal electric field, electric charge density and electrolyte contact in the device. Then, an elastic-electrochemical working mechanism is proposed. This declares that the elastic-electrochemical stress sensor can be a promising candidate for application in future wearable sensor electronics and system.

1. Introduction

As a promising electrochemical material, the spinel (AB_2O_4)-type binary oxide has been gained large interest and demonstrated to possess superior electrochemical properties because of their available multiple oxidation state and peculiar mixed spinel structure [1,2]. Nevertheless, due to their poor electrical conductivity, bad electrolyte wettability, and inefficient electrolyte transportation in practical electrochemical application, the electrochemical advantage of AB_2O_4-type oxides have not been sufficiently realized in the recent researches [3]. It is proposed that the combination of the oxides with conducting carbon materials is one of effective improving methods. With high mechanical strength,

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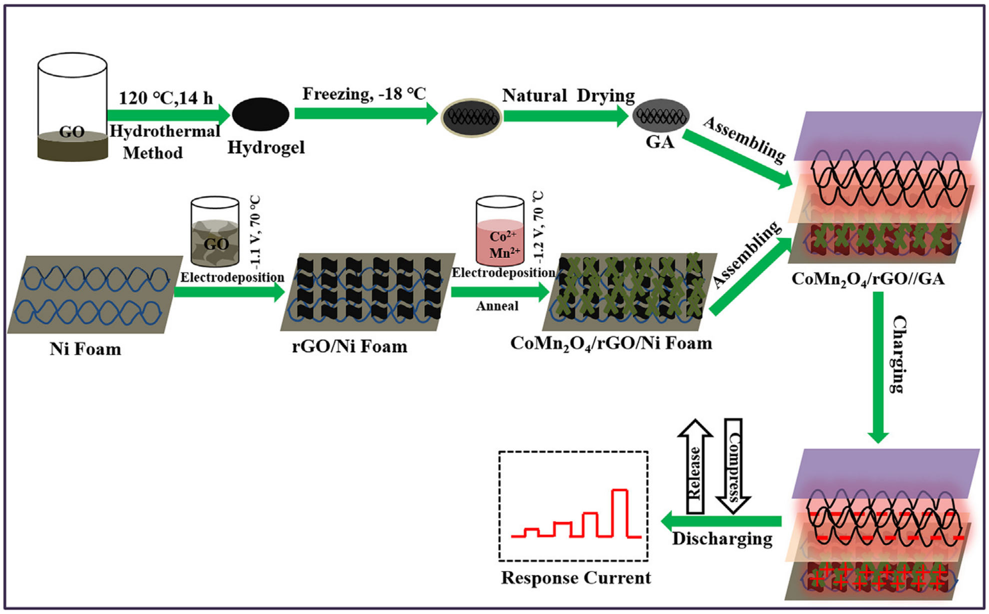

Fig. 1. A schematic illustration of assembling $CoMn_2O_4$/rGO//GA asymmetric supercapacitor and the application of the elastic-electrochemical stress sensor.

high chemical stability as well as excellent electronic conductivity, the graphene has been demonstrated as a good candidate among the myriad carbon materials [4]. The advantageous combination of graphene with transition metal oxides have been extensively applied in many fields, such as catalysis, electrochemical energy storage fields, sensor [5–7]. Nevertheless, it still suffers from narrow potential window, which can only operate in a maximum window of 1.0 V due to the limitation of the water decomposition [8].

One of effective strategies to apply higher window voltage is to employ asymmetric device structure, which consists of different active materials on positive and negative electrodes. In supercapacitor application, the electric double-layer capacitance (EDLC) material is generally served as the negative electrode because they store charge electrostatically through fast and reversible adsorption/desorption of electrolyte ions on the surface of active materials. Many researchers select the porous carbonaceous materials widely due to their high surface area and well-controlled pore characteristics. It has been found graphene aerogel (GA) with interconnected pores represent a new class of porous, large specific surface area and ultralight materials which can provide multidimensional electron transport pathways, easy access to the electrolyte, and minimized transport distances between bulk electrode and electrolyte [9–12]. These excellent properties qualify aerogels as promising candidates for applications in assembling asymmetric supercapacitor device. Recently, Anindita et al. have designed flexible asymmetric supercapacitor based on functionalized reduced graphene oxide aerogels with wide working potential window [13]. Zhang et al. have reported a high-performance asymmetrical supercapacitor composed of rGO-enveloped nickel phosphite hollow spheres and N/S co-doped rGO aerogel [14]. Cao et al. have applied $CoNi_2S_4$ nanoparticle/narbon nanotube sponge cathode with ultrahigh capacitance for highly compressible asymmetric supercapacitor, demonstrating excellent compressibility and high energy density [15]. While those works or the vast majority of the researches devote themselves to improve the power and energy density, self-healing, stretchable, compressive, and shape-memory property to explore other novel domains [16–21], which still limit the development of asymmetric supercapacitor from the point of the energy conversion for expanding new practical function. In addition, as far as we know, the compressible graphene aerogel is just applied as traditional sensor with variable resistor effect in the past. However, the incorporation of excellent elasticity with electrochemistry for compressible graphene aerogel in asymmetric supercapacitor is rarely reported.

In this work, we report a facile, low-cost approach to assemble the asymmetric supercapacitor. The positive electrode $CoMn_2O_4$/rGO is synthesized simply via electrodeposition approach and exhibits a high specific capacitance of 1783 F g^{-1} at 1 A g^{-1}, and the negative electrode N, B and S co-doped graphene aerogel is prepared via the natural drying post-process. The superior pseudocapacitance electrochemical properties of $CoMn_2O_4$/rGO and the excellent double-layer capacitance of graphene aerogel endows the asymmetric supercapacitor with the high energy density of 53.33 Wh Kg^{-1} at a power density of 400.00 W kg^{-1}. The cell exhibits stable and sensitive current responses towards the applied stress. This elastic-electrochemical stress sensor provides a new understanding on the mechanism of interaction between force and electrochemistry.

2. Experiments

2.1. Reagents and materials

Ethanol (AR, 99.7%), acetone (AR, 99.5%), kalium chloratum (KCl) (AR, 99.5%), potassium hydroxide (KOH) (AR, 85.0%), Manganese chloride ($MnCl_2·4H_2O$) (AR, 99.0%), cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$) (AR, 98.5%), lithium perchlorate trihydrate ($LiClO_4·3H_2O$) (AR, 99.0%), boric acid (AR, 99.5%), thiourea (AR, 99.0%) and ammonia (AR, 25.0–28.0%) solution are purchased from Sinopharm Chemical Reagent Co., Ltd. All of chemical reagents are used without further purification. The Ni foam (99.8% purity, 1.0 mm thickness, 97.2% porosity, 110 PPI pore size) is used as the current collector.

2.2. Electrode synthesis

Fig. 1 shows a schematic illustration of assembling the asymmetric supercapacitor $CoMn_2O_4$/rGO//GA and the application for the elastic-electrochemical stress sensor. To prepare the negative electrode graphene aerogel, 2 mL graphene oxide (5 mg mL^{-1} GO) aqueous dispersion mixed with 50 μL of ammonia solution, 12 μL of boric acid solution (6 mg mL^{-1}), and 20 μL thiourea (6 mg mL^{-1}) is treated by sonication for 60 min. The resulted solution is sealed in a Telfon-lined autoclave at 120 °C for 14 h. Then, we take out the formed hydrogel and dialyze with 100 mL of solvent containing deionized water and ethanol (V_{water}:V