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Short communication

Fully flexible, lightweight, high performance all-solid-state supercapacitor based on 3-Dimensional-graphene/graphite-paper

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HIGHLIGHTS

- A fully flexible supercapacitor based on 3D-graphene/graphite-paper was fabricated.
- The 3D-porous architecture provided space for easy migration of electrolyte ions.
- Our device exhibited excellent electrochemical performance and flexibility.
- The present approach is simple, fast, scalable, and highly efficient.

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ABSTRACT

Realization of a highly flexible, lightweight, and high performance flexible supercapacitor was achieved using three-dimensional graphene on flexible graphite-paper. A simple and fast self-assembly approach was utilized for the uniform deposition of chemical vapor deposition (CVD)-grown high quality 3D-graphene powders on a flexible graphite-paper substrate. The fabricated paper-based symmetric supercapacitor exhibited a maximum capacitance of 260 F g^{-1} (15.6 mF cm^{-2}) in a three electrode system, 80 F g^{-1} (11.1 mF cm^{-2}) in a full cell, high capacitance retention and a high energy density of 8.8 Wh kg^{-1} (1.24 μWh cm^{-2}) at a power density of 178.5 W kg^{-1} (24.5 μW cm^{-2}). The flexible supercapacitor maintained its supercapacitor performance well, even under bent, rolled, or twisted conditions, signifying the excellent flexibility of the fabricated device. Our straightforward approach to the fabrication of highly flexible and lightweight supercapacitors offers new design opportunities for flexible/wearable electronics and miniaturized device applications that require energy storage units that meet the demands of the multifarious applications.

1. Introduction

The tremendous demand for flexible/wearable electronic devices have stimulated the intense research on flexible energy storage devices for applications such as smart watches, bendable displays, smart cards, mobile phones, artificial electronic skin, and implantable medical devices, many of which call for aesthetic appeal and multi-functionality [1–3]. These applications require high-performance energy storage systems that are ultrathin, lightweight, portable, bendable, twistable, foldable, roll-able, stretchable or wearable [4–6]. Unfortunately, the conventional energy storage devices, including batteries and supercapacitors, cannot be directly used for those applications due to their major shortcomings such as heavy weight, rigidity, and bulkiness. Therefore, the rising demands for lightweight, flexible and ultra-thin forms of portable electronic devices require flexible batteries and supercapacitors [7,8].

Among the various types of energy storage systems, flexible supercapacitors (FSCs) have attracted much attention for their notable features, such as high-power density, fast charge/discharge

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rates, longer operating life span, low cost, and eco-friendliness [9–12]. To date, much progress has been made for the construction of FSCs using materials based on graphene, metal oxides and conductive polymers as active materials deposited on various flexible substrates, including plastics, metal sheets, textile fibers, and metal wires [9,13]. In spite of this progress, flexible supercapacitors still have a few drawbacks, such as limited mechanical durability, low energy density, and poor conductivity of the plastic substrate, which are all major challenges to commercializing this flexible device for real-time applications [14,15]. Therefore, it is critical to fabricate FSCs that are lightweight and have high mechanical durability with high electrochemical performance via inexpensive and facile methods.

Graphene has proved to be one of the most promising candidates for active materials for FSCs due to its peculiar characteristics, such as large specific surface area, excellent mechanical strength, high electrical conductivity, flexibility and good electrochemical properties [16–19]. However, graphene nanosheets have usually suffered from aggregation and/or restacking due to the strong π-π^* interactions, which significantly limits the accessible active surface area for ion adsorption/desorption processes, and thus leads to low electrochemical performance [16,18]. To overcome these limitations, several efforts have been devoted to fabricating high quality three-dimensional porous graphene nanostructures since they provide a large accessible surface area for the adsorption/desorption of ions, high porosity, and low density while keeping excellent electrical conductivity for fast electron transfer, and high mechanical stability [20–22].

In this study, we fabricated a thin, lightweight, mechanically stable yet flexible paper-based all-solid-state flexible supercapacitor (FSC) using CVD-grown high quality 3D-graphene coated on a graphite-paper current collector. The 3D-graphene powder suspended in an aqueous media was deposited onto the graphite-paper-based current collector by a lift-off method, which allowed a facile, cost-effective, scalable, lightweight, binder and conductive additive-free electrode. The resultant paper-based symmetric all-solid-state flexible supercapacitor delivered a high device capacitance of 80 F g^{-1} (11.1 mF cm^{-2}), excellent cycle stability (112% capacitance retention even after 10,000 cycles), and high power (178.5 W kg^{-1}; 24.5 μW cm^{-2}) and energy density (8.8 Wh kg^{-1}; 1.24 μWh cm^{-2}). More importantly, the as-fabricated device well retained its electrochemical performance even under harsh conditions such as bending, rolling and twisting. The good electrochemical performance and the ease of the fabrication approach demonstrate that our supercapacitor has a great potential for being embedded in flexible, bendable and wearable electronics.

2. Results and discussion

The entire fabrication process of the flexible and lightweight 3D-graphene on graphite-paper electrode was as follows: First, 3D-graphene powder (with a surface area of 1661 m^2/g and conductivity of 4.39 S/cm as shown in Figs. S2–S3) was synthesized in a gram scale by a precursor-assisted CVD method [23]. The Raman spectrum of the 3D-graphene (Fig. 1a) displays three prominent peaks at 1331, 1579, and 2718 cm^{-1}, corresponding to the D, G and 2D bands, respectively, with an I_D/I_G ratio of 0.97 and I_{2D}/I_G ratio of 0.63, which specified the formation of high quality of a few layer of graphene powder [24] (The Raman spectrum of 3D-graphene/graphite-paper electrode is shown in Fig. S1.). Deconvoluted C1s spectra (Fig. 1b) show a prominent peak associated with C–C and relative weak peaks attributed to C–O, C–O–C, C=O, and O=C–O, respectively [23]. The atomic percentages for C–C, C–O, C–O–C, C=O, and O=C–O are 70.00, 12.9, 3.46, 3.08, and 10.53%, respectively. The lower content of oxygen-containing functional group compared to C–C groups in 3D-graphene confirms the high quality of the bulk-scale-fabricated 3D-graphene powder via the precursor-assisted CVD process. The conductivity of 3D-graphene measured by a powder conductivity measurement kit is 4.38 S/cm as shown in Fig. S2.

Finding a suitable flexible substrate with a high mechanical durability is one of the crucial factors for the fabrication of flexible supercapacitors. The flexible yet mechanically stable graphite-paper current collector was simply created by placing a piece of transparent tape over the graphite sheet, applying pressure by hand, and then pulling it off. The as-prepared graphite-paper substrate was more highly flexible (bendable, roll-able and twistable), highly conductive, cost-effective, rough, and easy to fabricate than other commercially existing flexible substrates, such as polyethylene terephthalate, metal sheets, and metal wires. In particular, the high electrical conductivity and rough surface of the graphite-paper current collector facilitated a fast electron transfer and better attachment of electroactive material.

Second, the interfacial self-assembly of 3D-graphene powder, created by the precursor assisted CVD method was triggered within two minutes at room temperature by adding EA (ethyl acetate) into a 3D-graphene suspension in a water-NMP (N-Methyl-2-pyrrolidone) mixture (Fig. 1c).

Finally, the self-assembled 3D-graphene was transferred onto the flexible graphite-paper electrode using a simple lift-off technique, dried at 75 °C for 12 h, and directly used as an active material for supercapacitors without the use of any conductive addictive or binders. The FE-SEM and digital camera images of the fabricated 3D-graphene/graphite-paper electrodes are shown in Fig. 1d–g. It is clear that the 3D-graphene was uniformly and firmly anchored on the surface of the graphite-paper as can be seen in Fig. 1e. Further, the 3D-porous graphene consisted of large pores in numerous interconnected three-dimensional networks, displaying continuous interspaces in the form of pore walls (Fig. 1d). The as-fabricated 3D-graphene with a large active surface area (Fig. S3) and thus more electroactive sites due to the highly porous nature facilitated the diffusion of the electrolyte ions into to the inner region of the electrode and more adsorption of the electrolyte ions for enhanced electrochemical energy storage in the supercapacitors. Digital photographs of bent and rolled 3D-graphene/graphite-paper electrodes safely sitting on the green foxtail (Fig. 1e–g) confirmed the excellent flexibility (excellent mechanical strength) and ultra-low density of our fabricated electrodes. These results inspired us to fabricate an extremely flexible and lightweight all-solid-state symmetric supercapacitor.

3. Flexible symmetric supercapacitors

To investigate the electrochemical performance of the as-fabricated flexible electrodes, cyclic voltammetry and galvanostatic charge/discharge tests were performed using the three-electrode configuration in a 1 M H_2SO_4 electrolyte as shown in Fig. S4. The CV and galvanostatic charge/discharge profiles of the fabricated electrodes exhibited rectangular and triangle shapes, respectively, which indicated an ideal capacitive behavior. The calculated gravimetric and areal capacitance values of 3D-graphene/graphite-paper electrode were 260 F g^{-1} and 15.6 mF cm^{-2} at a scan rate of 5 mV s^{-1}, and retained 79.5% of initial capacitance even with an increasing scan rate to 100 mV s^{-1}, which indicated the excellent rate capability of the as-prepared electrodes. The electrochemical impedance spectroscopy (EIS) data in Fig. S5 clearly demonstrate excellent electrochemical performance of the 3D-graphene/graphite electrode in a three-cell electrode system.

An all-solid-sate flexible symmetric supercapacitor was assembled using two pieces of 3D-graphene/graphite electrodes