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Communication

Paper-based all-solid-state flexible asymmetric micro-supercapacitors fabricated by a simple pencil drawing methodology

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ABSTRACT

Flexible micro-scale energy storage devices as the key component to power the flexible miniaturized electronic devices are attracting extensive attention. In this study, interdigitated asymmetric all-solid-state flexible micro-supercapacitors (MSCs) were fabricated by a simple pencil drawing process followed by electrodepositing MnO_2 on one of the as-drawn graphite electrode as anode and the other as cathode. The as-prepared electrodes showed high areal specific capacitance of 220 $\mu F/cm^2$ at 2.5 $\mu A/cm^2$. The energy density and the corresponding power density of the resultant asymmetrical flexible MSCs were up to 110 $\mu Wh/cm^2$ and 1.2 $\mu W/cm^2$, respectively. Furthermore, excellent cycling performance (91% retention of capacity after 1000 cycles) was achieved. The resultant devices also exhibited good electrochemical stability under bending conditions, demonstrating superior flexibility. This study provides a simple yet efficient methodology for designing and fabricating flexible supercapacitors applicable for portable and wearable electronics.

Flexible/wearable electronic devices are hot topics in today's society due to the many advantages such as being flexible, thin and lightweight [1–5]. As the fundamental powering building blocks for electronic devices, efficient energy storage devices play an important role in the development of flexible/wearable electronics [6–9]. However, conventional energy storage devices, such as batteries [10,11] and electrolytic capacitors [12] are not suitable for use in flexible/wearable electronic devices because they fail to be lightweight, ultra-thin, and flexible [13,14]. In this regard, it is imperative to fabricate new energy storage devices with not only sufficient power and energy density but also good flexibility to meet the demands of the development of flexible electronics. Thin-film supercapacitors represent a new type of energy storage devices which bridge the gap between conventional electrolytic capacitors and batteries because of their larger energy density as compared with that of electrolytic capacitors and superior power density relative to that of batteries. Moreover, supercapacitors usually possess fast charging-discharging speed, long cyclic life time and comparatively excellent flexibility [15,16]. In this context, thin-film supercapacitors have been regarded as one of the most promising powering building blocks to facilitate the improvement of flexible/wearable electronics. Thin-film supercapacitors with sandwiched structure are currently the most commonly used flexible supercapacitors due to their simple fabrication process, low cost and ease of mass production. However, their large interface resistances and long ion diffusion paths lead to their relatively low energy densities, partly restricting their practical applications. Recently, flexible micro-supercapacitors (MSCs) with interdigitated configurations have attracted more and more attentions from both the academia and the industry because of their high energy density and excellent rate capability as a consequence of the short ion diffusion path, *etc.* [17–24].

Fabricating flexible MSCs is thus very significant but still challenging in flexible/wearable electronics. The key challenges in fabricating all-solid-state flexible MSCs not only lie in exploring excellent active electrode materials with high electrochemical performance and suitable substrate materials with low cost and high flexibility but also in developing simple methods for fabricating interdigitated patterns. Currently used active electrode materials are mainly classified into two kinds according to their working mechanism. Carbon based materials, also known as

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electric double-layer capacitors (EDLC), store energy by rapid ion adsorption/desorption at the interface between the electrode material and the electrolyte, showing long life time but with relatively low specific capacitance. By contrast, pseudocapacitive materials, such as conductive polymers and metal oxides, store energy by completely reversible faraday oxidation-reduction reaction, showing higher specific capacitance but lower cyclic stability. Combining the two kinds of electrodes can make full use of their advantages but overcome their weaknesses, providing a novel path to achieving high-performance supercapacitors [25]. As for substrate materials, paper provides a new paradigm for them due to its unique structural features (highly porous and hydrophilic) [13], which is quite different from conventional flexible substrates (*e.g.*, polyethylene terephthalate (PET) [26], polydimethylsiloxane (PDMS) [27]). Meanwhile, paper is cheap, low-cost, and environmentally friendly. Therefore, paper has been demonstrated as a promising substrate for the fabrication of light and flexible energy storage devices [28,29]. Of the many methods to fabricate interdigitated MSCs, pencil drawing is a promising approach which is simpler and cheaper than conventional photolithography, magnetron sputtering and vacuum vapor deposition [28]. The main composition of the pencil is graphite and clay (mainly SiO_2) and can be easily drawn on flexible paper substrates. The as-drawn pencil traces are mainly composed of percolated graphite particle networks with relatively high electrical conductivity ranging from 109 Ω/sq to 556 Ω/sq and moderate electrochemical energy storage capability, which manifests great promise in flexible paper-based storage devices [30]. M.P. Down *et al.* studied different types of pencil drawing interdigitated electrodes. They demonstrated that the pencil traces could be used as EDLC electrode materials but with a relatively low specific capacitance because of a certain amount of clay in them [30]. Thus, it is necessary to further improve the electrochemical performance to meet the demands of the practical applications. To this end, as mentioned above, asymmetric device configuration combining the two energy storage mechanism can be adopted by adding a different pseudocapacitive electrode material into the graphite. As a typical pseudocapacitive electrode material, manganese dioxide (MnO_2) is widely studied as electrode material for supercapacitors because of its abundance, high theoretical capacity, and environmental compatibility [31–33].

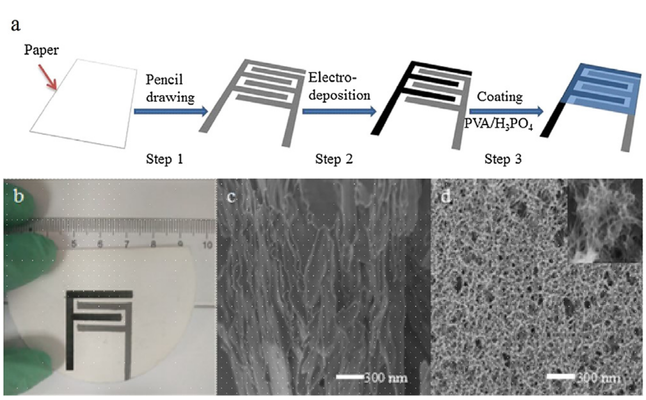

Fig. 1. (a) Schematic illustrations of the fabrication process of paper-based all-solid-state flexible MSCs. (b) Optical image of paper-based all-solid state flexible MSC. SEM images of (c) pencil trace and (d) pencil trace/MnO_2.

In this context, we present herein our successful development of a simple methodology to construct interdigitated all-solid-state asymmetric flexible MSCs based on paper substrates by using pencil drawing traces and electrodeposited MnO_2/pencil traces as the electrodes. The as-fabricated all-solid-state flexible MSCs could make full use of the two mechanism and thus exhibited comparatively high specific capacitance of 220 $\mu F/cm^2$ at 2.5 $\mu A/cm^2$, which is much higher than that of some excellent previously reported supercapacitors [30,34,35]. Besides excellent electrochemical performance, MSCs also showed superior flexibility. The resultant high-performance paper-based MSCs fabricated by the simple pencil drawing methodology pave the way to developing low-cost and efficient energy storage devices for flexible electronic devices.

The all-solid-state flexible MSCs were fabricated as follows: To begin with, electrodes with interdigitated patterns were drawn on a piece of filter paper using a 12 B pencil until a layer of thin graphite sheet was evenly deposited on the paper. Then, MnO_2 was selectively electrochemically deposited on one finger electrode in 0.3 mol/L $Mn(CH_3COO)_2$ solution. Three-electrode system was used in the electrodeposition process using $Hg/HgCl_2$ as the reference electrode, platinum wire as the counter electrode and the pencil trace as the working electrode. MnO_2 was electrodeposited by cyclic voltammetry (CV) in which the potential window from 2.0 V to 2.4 V, scanning rate of 10 mV/s and sweep segments of 2 were set, respectively. Then the sample was washed with deionized water and dried at room temperature. Then, 1 g polyvinyl alcohol (PVA), 10 mL deionized water and 1 g H_3PO_4 were mixed and stirred at 90 °C until the solution became a clear gel. After the PVA gel was cooled down to room temperature, the gel electrolyte was coated on the electrode surface to assemble the asymmetric all-solid-state flexible MSCs. Wherein, common experimental filter paper (medium-speed qualitative) was used as the substrate without extra pretreatment. PVA (Mw ≈ 150,000) was purchased from Aladdin reagent Co., Ltd. Manganese acetate ($Mn(CH_3COO)_2$, A.R.) and acetic acid (CH_3COOH, A.R.) purchased from Aladdin Industrial Corporation (Shanghai, China) were used without further purification. Commercial 12 B pencil (CHUNG HWA, China) was used to draw the interdigitated traces.

Materials characterization were conducted by scanning electron microscopy (SEM) (Hitachi S-4800), optical microscopy, X-ray diffraction (XRD, D8 ADVANCE), X-ray photoelectron spectroscopy (XPS, Axis Supra) and electrochemical workstation (CHI 660E).

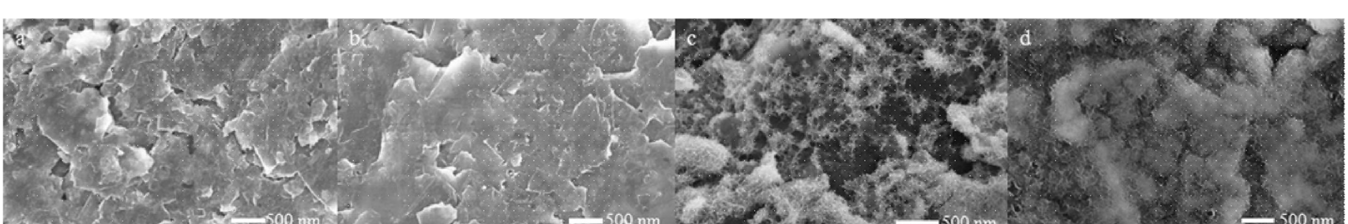

Fig. 2. SEM images of pencil traces before (a) and after (b) being bent. SEM images of pencil traces/MnO_2 before (c) and after (d) being bent.

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