A Flexible and All-Solid-State Supercapacitor with Unique Self-Healing Property

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Abstract
This Research Highlight introduces a newly online-published research paper on the achievement of a novel mechanically and electrically self-healing supercapacitor. The fabrication strategy, self-healing mechanism, and key device performance are briefly presented. Finally the positive impact of this work on the ongoing research in advanced future energy storage devices is discussed.

Keywords: flexible, self-Healing, solid-state, supercapacitor

Nowadays, with the advances in semiconductors, integrated circuit and packaging, portable electronic devices are becoming smaller, thinner, more lightweight, and even flexible (El-Kady, 2012). In order to overcome the inevitable limitations of being boxy and rigid imposed by conventional energy storage devices based on liquid electrolyte encapsulated within a bulky packaging, a series of forwarding steps has been achieved to develop highly flexible and all-solid-state supercapacitors in various unique forms such as planar thin films (Meng, 2010), weaveable fibers or cables (Meng, 2013), and miniaturized micro-devices (Meng, 2013). In practice, most of these novel devices will be used in specific conditions where repeated bending or even folding is performed. Structure fractures and mechanical damages caused by deformation overtime or accidental cutting are inevitable (Huang, 2013). Therefore exploring robust energy storage devices with the capability for damage management is of scientific and technological importance.

To address the damage management issue of current state-of-the-art flexible and all-solid-state energy storage devices, in a recent article first online published on *Advanced Materials*, a research group led by Prof. Xiaodong Chen from Nanyang Technological University, for the first time, proposed and achieved a mechanically and electrically self-healing supercapacitor by uniquely constructing a sandwich-type device configuration (i.e., two carbon nanotube film electrodes separated by a gel polymer electrolyte layer) onto a self-healing TiO_2-supramolecular composite substrate (Wang, 2014).

The fabrication flow can be briefly described as follows. First, a self-healing composite with a low glass transition temperature below room temperature was obtained by uniformly incorporating the flower-like TiO_2 nanostructures (spheres with an average size of about 400 nm) into a supramolecular network that was thermally crosslinked via a large amount of hydrogen bond acceptors and donors. The composite was then thermally compressed and self-adhered on various hydrophilic plastic substrates to form a self-healing substrate. Next, a single-walled carbon nanotube (SWCNT) film with a thickness of approximately 20 μm (treated with concentrated nitric acid to graft a large amount of carboxylic and hydroxyl functional groups on the SWCNT surface) were uniformly coated onto the as-prepared self-healing substrate. Finally, an integrated supercapacitor device was achieved by assembling two such as-prepared SWCNT film electrodes (rectangular strips with a size of 1.5 × 3.5 cm^2) sandwiched by a polyvinyl pyrrolidone (PVP)-H_2SO_4 gel polymer electrolyte together.

Self-healing materials is referred to a class of artificial “smart” materials that is capable of repair its internal or external damages (Wong, 2011). In the past decade, various functional self-healing materials with capabilities of structural, mechanical and electrical restoration have been achieved (Tee, 2012; Li, 2012; Zheludkevich, 2007). However, there has been no report on realization of self-healing system on the device level with complicated working mechanism. In this work, the principle of the self-healing energy storage device works as follows. When the supercapacitor is subjected to mechanical damage like cutting, the lateral movement of the underlying self-healing composite on the substrate can bring the separated areas of the SWCNT film electrode into contact, enabling the restoration of the electrode’s conductivity. In addition, the PVP-based gel polymer electrolyte middle layer is a self-adhering material, enabling the self-healing of the electrolyte to some extent. These two key points together ensure the successful restoration of the whole device configuration. As a result, an ideal self-healing supercapacitor device is achieved.

A series of comprehensive characterization was carried out to evaluate performance including mechanical self-healing properties of the TiO_2-supramolecular composite substrate, and electrical conductivity of the SWCNT film electrode and electrochemical performance of the supercapacitor device before cutting and after self-healing. In detail, the mechanical strength and flexibility of the as-prepared TiO_2-supramolecular composite substrate could be restored by simply applying a gentle pressure and holding it constant for 5 min. In addition, an LED was observed to be extinguished when the as-prepared SWCNT electrode in-series connected in the circuit was cut, and lighted up again after the electrode was self-healed, indicating the restoration of the electrical conductivity. Moreover, observed from electrochemical measurement, the as-prepared supercapacitor device showed excellent self-healing performance. After the fifth self-healing upon cutting, the specific capacitance could be restored up to 85.7% of its original value, the equivalent series resistances slightly increased to 15.2 Ω, and the capacitance retention after 1000 charge/discharge cycles was almost 96.4%.

Prof. Xiaodong Chen’s pioneered work on the successful fabrication of this unique flexible and all-solid-state supercapacitor with merit of self-healing has great contributions in related field. First, this work remarkably prolongs the lifetime of future energy storage devices. The damage management of energy storage devices was for the first time well investigated, which opens a new research direction. In addition, the fabrication process of achieving self-healing devices presented in this work is a solution-based one utilizing drop-casting technique. Thus it is easy to be industrialized. Moreover, the developed fabrication strategy may be potentially extended to making other flexible electronic components, opening new opportunities for the design and fabrication of various next-generation self-healing electronic devices in the future. Numerous future research directions following this pioneered work could be done, i.e., enhance the mechanical strength by adding strong fillers, increase specific capacitance by adding pseudo-capacitive materials, and improve power density by using organic-based gel polymer electrolyte with higher working voltage.

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