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Compact graphene/MoS_2 composite films for highly flexible and stretchable all-solid-state supercapacitors†

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Two-dimensional layered nanomaterials, such as graphene and metal sulfides, exhibit great potential to be used as efficient electrode materials for high-performance energy storage devices. However, it remains a great challenge to achieve highly stretchable devices based on the above mentioned nanomaterials because their layered structures are easily damaged even under very little tensile strength. In this paper, compact graphene and its composite films were fabricated by a facile pressing method and showed high flexibility and stretchability (100%). By using the compact graphene/MoS_2 composites as electrodes, flexible all-solid-state supercapacitors with a volumetric capacitance of 19.44 F cm^{-3} (70.00 mF cm^{-2}) were developed. These newly-developed graphene-based supercapacitors can bear a high tensile strain of 60% with slight performance degradation and can retain 87% of their original capacitance after 300 stretching cycles to 30% strain, exhibiting much higher stretchability and stability than most of the graphene-based stretchable supercapacitors reported previously. These compact graphene-based materials may prove to be a promising candidate to be used as electrodes for other stretchable electronics.

Introduction

Flexible and stretchable electronics can sustain their electronic performance even under large deformation strain[1–4] and exhibit great potential to be widely used in various fields, such as wearable equipment,[5] wireless sensors,[6] bioimplantable systems,[7] and so on. Currently, various flexible and stretchable electronics have been designed and developed, including field effect transistors,[8] light-emitting diodes[9] and artificial skin sensors.[10] As an important component in such stretchable electronics, highly flexible and stretchable energy devices with high performance are required to be used as power supplies for a fully stretchable system.[1–3,11–15] So far, intense attention has been paid to develop stretchable energy conversion and storage devices, such as solar cells,[16] lithium batteries,[17] supercapacitors[18] and their integrated devices.[19] Among these energy devices, supercapacitors (also called electrochemical capacitors or ultracapacitors) are considered as one of the most promising candidates because of their high power density, fast charge/discharge rate, long cycling stability and high safety.[20,21] Stretchable supercapacitors can be easily realized by sandwiching two electrodes with a gel electrolyte in between, whose stretchability greatly depends on the stretchable properties of the used electrodes.[22–24] Until now, various stretchable electrodes for supercapacitors have been developed by fabricating conducting materials (*e.g.*, carbon nanotubes, conducting polymers and graphene) on elastic polymeric substrates (*e.g.*, polydimethylsiloxane, PDMS).[25–28] Previously reported results showed that the stretchabilities of stretchable electrodes mainly depend on the conducting materials used. For instance, the stretchability of supercapacitors based on carbon nanotube electrodes can reach more than 100%,[29] but this is a great challenge for graphene-based supercapacitors because of the layered structure of graphene.

Due to their large specific surface area, excellent electrochemical performance and high mechanical properties, two-dimensional layered nanomaterials (*e.g.*, graphene and transition-metal sulphide) have been widely investigated to be used as efficient electrode materials for high-performance supercapacitors, and great achievements have been obtained in the last ten years.[30–34] However, it remains a great challenge to achieve highly stretchable supercapacitors based on graphene or metal sulphide materials because their layered structures are very easily damaged under even relatively low tensile strain (*e.g.*, 30%).[35] The previously reported stretchable all-solid-state supercapacitors based on graphene electrodes typically exhibited rather low stretchability (30–40%) and stretching stability,[36–43] which are much lower than those of devices using carbon nanotube or conducting polymer electrodes. To enhance the stretchability of graphene-based supercapacitors, herein, we first developed highly stretchable (up to 100%) graphene films

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Ag-Doped PEDOT:PSS/CNT composites for thin-film all-solid-state supercapacitors with a stretchability of 480%†

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Currently, it remains a great challenge to achieve all-solid-state supercapacitors with both high electrochemical performance and excellent stretchability because of the limitations of stretchable electrodes and solid-state electrolytes. Here, we developed all-solid-state supercapacitors by using aligned carbon nanotube/conducting polymer (Ag-doped poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate)) composites as electrodes and polyvinyl alcohol-based electrolytes. The obtained all-solid-state supercapacitors not only exhibited a high specific capacitance of 64 mF cm^{-2} (corresponding to 85.3 F g^{-1}), but could also maintain 98% of their original capacitance even under a tensile strain as high as 480%, which represents the highest value for thin-film all-solid-state supercapacitors using the same electrolyte to date, to the best of our knowledge. The newly developed thin-film supercapacitor maintained 90% of its original capacitance after 100 stretching cycles to a tensile strain of 400% and maintained 93% after stretching to 200% for 2000 cycles, indicating excellent stretching stability. The present work provides an efficient strategy to achieve highly stretchable energy storage devices with high performance.

Introduction

Stretchable electronics that can maintain their intrinsic performance under unpredictable tensile conditions have attracted increasing attention in the last ten years and are promising for use in the fields of sensors,[1,2] wearable electronics,[3–5] implantable systems,[6,7] and so on. Currently, various stretchable electronics have been developed, such as transistors,[8] light-emitting diodes,[9] photodetectors,[10–12] and strain and press sensors.[13] To power these stretchable electronics, it is necessary to develop highly stretchable energy conversion and/or storage devices (such as solar cells,[14,15] nanogenerators,[16] batteries,[17,18] and supercapacitors[19]). Due to their high power density, rapid charging characteristics and long cycling life, supercapacitors (also called electrochemical capacitors or ultracapacitors) have attracted great attention, and can be easily fabricated on elastic polymer substrates, resulting in stretchable devices.[20,21] So far, stretchable all-solid-state supercapacitors in fibrous and thin-film formats have been reported,[22,23] in which nanocarbon-based materials (*e.g.*, carbon nanotubes and graphene) are often used as both active electrodes and current collectors and polymer gel electrolyte are used as separators. For instance, fibrous all-solid-state supercapacitors with stretchability as high as 600% have been developed by using coiled CNT composite fibers as electrodes.[19] However, the stretchable thin-film supercapacitors often exhibited stretchabilities lower than 400% (most ranging from 30% to 240%),[24–27] which can be ascribed to the larger area of loading tensile force compared with that in fibrous devices, making them more easily damaged under a large tensile strain. Therefore, much effort should be made to enhance the stretchability of thin-film all-solid-state supercapacitors with high electrochemical performance through designing high electrical conductive active electrodes with high stretchability.

As one of the most important nanocarbon materials, carbon nanotubes (CNTs) exhibit large surface area, high aspect ratio, and excellent electrochemical and mechanical properties and are widely used as electrodes for stretchable all-solid-state supercapacitors. However, serious aggregation of CNTs caused by strong π–π stacking effect among them often results in low energy storage performance of supercapacitors. In addition, double-layer capacitance generated by bare CNT electrodes is also relatively low, but can be enhanced by introducing pseudocapacitive materials, such as conducting polymers,[28,29] metal oxides,[30,31] metal sulfides,[32,33] and so on. Herein, we developed highly stretchable thin-film electrodes by compositing aligned compact CNTs and silver (Ag)-doped poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS), in

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