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A facile prestrain-stick-release assembly of stretchable supercapacitors based on highly stretchable and sticky hydrogel electrolyte

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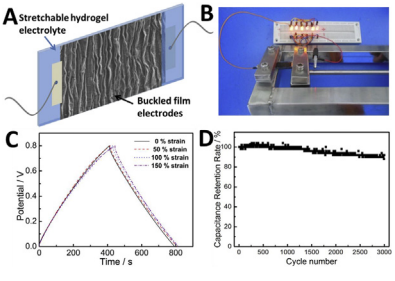
HIGHLIGHTS

- A facile prestrain-stick-release assembly is developed for a highly stretchable supercapacitor.
- A novel Na_2SO_4-*a*PUA/PAAM hydrogel electrolyte with high stretchability, electrical conductivity and stickiness is developed.
- The stickiness of the hydrogel electrolyte ensures its close interface contact with film electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile prestrain-stick-release assembly strategy for the stretchable supercapacitor device is developed based on a novel Na_2SO_4-*a*PUA/PAAM hydrogel electrolyte, saving the stretchable rubber base conventionally used. The Na_2SO_4-*a*PUA/PAAM hydrogel electrolyte exhibits high stretchability (>1000%), electrical conductivity (0.036 S cm^{-1}) and stickiness. Due to the unique features of the hydrogel electrolyte, the carbon nanotube@MnO_2 film electrodes can be firmly stuck to two sides of the prestrained hydrogel electrolyte. Then, by releasing the hydrogel electrolyte, homogenous buckles are formed for the film electrodes to get a full stretchable supercapacitor device. Besides, the high stickiness of the hydrogel electrolyte ensures its strong adhesion with the film electrodes, facilitating ion and electronic transfer of the supercapacitor. As a result, excellent electrochemical performance is achieved with the specific capacitance of 478.6 mF cm^{-2} at 0.5 mA cm^{-2} (corresponding to 201.1 F g^{-1}) and capacitance retention of 91.5% after 3000 charging–discharging cycles under 150% strain, which is the best for the stretchable supercapacitors.

1. Introduction

Research on stretchable electronics has been accelerated by the emerging applications of wearable electronics, deformable displays and biocompatible systems [1–3]. Up to now, various types of stretchable devices such as stretchable LEDs [4,5], logic devices [6], photodetectors [7] have been studied. However, most of these

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devices need external power supply wire physical wiring [8]. Therefore, to realize an independent stretchable electronic, it is necessary to integrate a stretchable energy storage system, which could be in the form of batteries [9–11], solar cells [12], supercapacitors [13–18] and so on. Among them, supercapacitors exhibit many advantages such as fast charging/discharging ability, safety and long cycling life, showing great potential for practical application [19]. However, compared with more researched bendable [20–28] or compressible [29,30] supercapacitors, it is more challenging to fabricate stretchable ones since stretching typically induces much larger arbitrary deformation (>>1%), which includes not only bending, but also compressing, stretching, twisting and others [31].

A full stretchable supercapacitor device is commonly made up of a stretchable solid electrolyte (functioning as both the electrolyte and separator) sandwiched by two electrodes. However, to our knowledge, research on stretchable energy storage systems is mainly concentrated on the electrodes components [32–37], and systematic research on stretchable solid electrolyte [15,38] is quite scarce and immature up to now. For example, common H_3PO_4 (or H_2SO_4)-poly(vinyl alcohol) (PVA) hydrogel electrolytes [14] which are applied in flexible storage-energy devices generally functions under quasi-solid-state since their mechanical performance dramatically decrease after adsorbing too much aqueous electrolyte. In such cases, their conductivity, stretchable and resilient properties are restricted. Thus, it is critical to develop a highly stretchable and resilient hydrogel electrolyte with excellent conductivity.

Another critical issue arises from the assembly of a full stretchable supercapcitor device. In previous literatures, it often relies on stretchable rubber base such as polydimethylsiloxane (PDMS) [13] to provide stretchability, which involves a complicated process to prepare buckled film electrodes. Another case is to deposit electrochemically active materials such as polypyrrole on the stretchable electrolyte which was preplated with conductive base of gold [39], which is also complex for fabrication. Besides, in above situations, the specific capacitance of the electrodes is restricted to less than 110 F g^{-1} by the small electrical double-layer capacitance of single carbon nanotubes films or the deposited active materials. Therefore, to fabricate a high-performance stretchable supercapacitor, assembly process should also be simplified and the capacitance of the electrodes be enhanced.

Herein, we report a novel Na_2SO_4-anionic polyurethane acrylates/polyacrylamide (Na_2SO_4-*a*PUA/PAAM) hydrogel electrolyte with ultrahigh extensibility (>1000%) and conductivity (0.036 S cm^{-1}). The *a*PUA acts as a multi-functional cross-linking agent, which endows the hydrogel with high extensibility even after adsorbing 500% water. Taking advantages of its high stickiness, the carbon nanotube film-supported MnO_2 nanoarray (CNT@MnO_2) electrodes can be closely attached to the prestretched hydrogel electrolyte to obtain highly stretchable supercapacitors, greatly simplifying the fabrication process by saving the stretchable

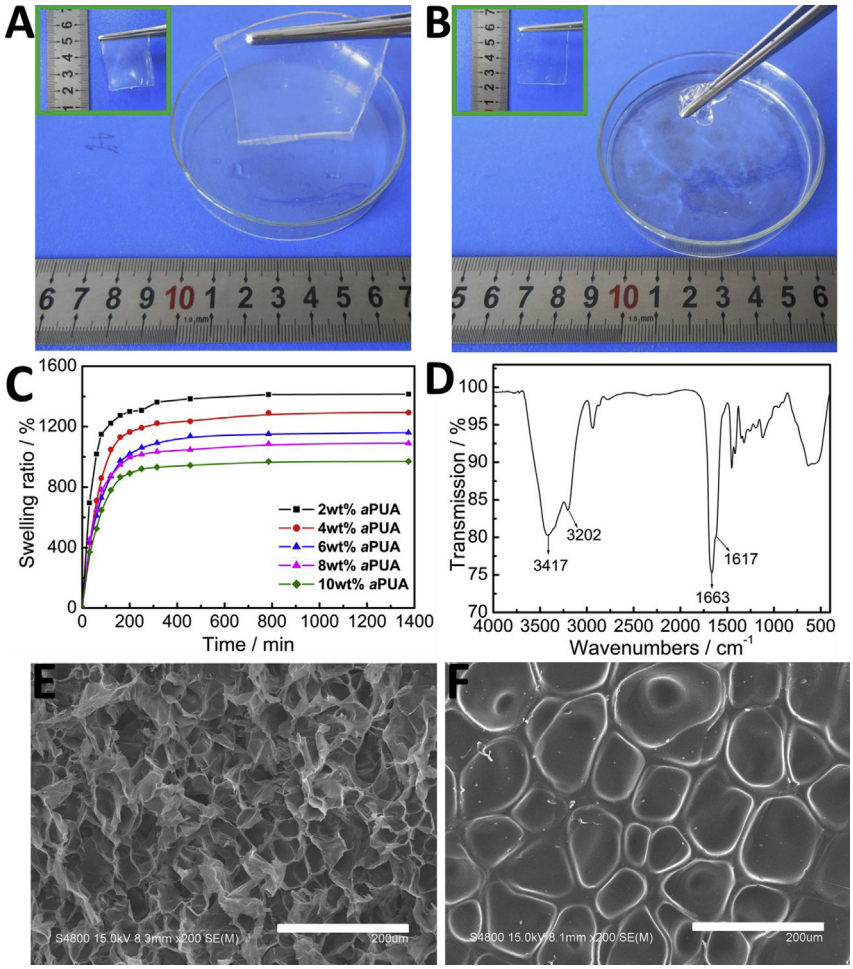

Fig. 1. Digital photos of (A) *a*PUA(4)/PAAM and (B) PAAM hydrogel after immersing in deionized water at 50 °C for 12 h (the inserted photos showing the samples before immersing), (C) swelling ratios at various immersing time for *a*PUA/PAAM with different *a*PUA content, (D) FT-IR spectrum of *a*PUA(4)/PAAM, (E) cross-sectional and (F) superficial FE-SEM images of freezing-dried *a*PUA(4)/PAAM hydrogel after swelling equilibrium (scale bar = 200 μm).