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Hydrogel Electrolytes Surface Modified Eggshell Membrane Separators in All-Solid-State Supercapacitors with Thickness Dependent Performances

*Xinhua Liu, Chengyao Yin, Jie Yang, Meiying Liang, Junjie Wei, Ziyang Zhang, Huanlei Wang, and Qigang Wang**

Contents

1. Materials

N, N-Dimethylacrylamide (DMAA, 99%) was obtained from TCI Shanghai Development Co. Ltd. Ammonium persulfate was purchased from Reagent co., LTD. Bovine serum albumin (BSA) was purchased from Baoman Biological technology. N-Succinimidyl Acrylate (NAS, >98%) was obtained from TCI Shanghai Development Co. Ltd. Activated carbon (YP80F, 2100 m^2/g) was obtained from Kuraray Co. PTFE and acetylene black were purchased from Aladdin and Shanghai 3F New Material Co., Ltd.

2. Preparation of the composite gel electrolyte

Separation of eggshell membrane: the eggs firstly broken and emptied via the blunt end. Then the eggshells were washed in deionized water, and the inner membrane and outer shell were removed. Afterwards, the remaining eggshell membranes were immersed in 1 M HCl for 6 h to dissolve the residual $CaCO_3$ particles and obtain the organic outer eggshell membrane. Finally, the obtained eggshell membranes were washed twice with deionized water.

3. Pre-treatment and characterization

3.1 XRD analysis

The X-ray diffraction (XRD) analysis was tested by a D8 Advance testing machine (Bruker). In continuous scan mode between the 2θ range of 10–70° with a step size of 0.02 and Cu Kα radiation (λ = 0.15406 nm). The eggshell membranes without/with HCl treatment were sufficiently dried and kept in smooth membrane before test.

3.2 SEM measurement

The SEM images of the samples were monitored by the scanning electron microscope (Hitechi S-4800, JEOL, Japan). The pure eggshell membrane and the composite eggshell membrane-hydrogel applying various polymerization time were tested. The edges of the eggshell membrane and hydrogel are difficult to identify because the freeze-dried hydrogel possesses porous structures which are similar to the porous eggshell. Therefore, the as-prepared samples were simply dried out with towel and tested directly without further freeze drying treatment.

3.3 Mechanical tests

The tensile strengths of eggshell membrane, hydrogel, and their composite gels were performed by a tensile-compressive tester (FR-108B, Farui Co.). The tested samples were cut in the size of 1 cm $\times$1 cm with a thickness of 0.8 mm. The tensile tests were obtained at the speed of 10 mm min^{-1}. The compressive strength of the BSA-PDMAA-SiO_2 hydrogels were taken. The cylindrical gel samples with 13 mm in diameter and 8 mm in thickness were set on the lower plate and compressed by the upper plate. The compressive tests were taken at the speed of 1 mm min^{-1}. Every test was performed for three times.

4. Electrocheical tests

4.1 Preparation of electrodes

Titanium plating stainless steel (500 mesh) was used as current collector. The active material for the adsorption and diffusion of the electroactive species is activated carbon powder (YP 80F). The electrode was prepared with a mixture of activated charcoal powder, 60 wt% PTFE emulsion binder, and acetylene black conductor (with a w/w ratio of 80:10:10). The film was dried in vacuum at 120 °C for 24 h.

4.2 Fabrication of supercapacitors

Symmetrical cells of supercapacitors consist of a sandwiched structure of gel electrolyte membrane and two activated carbon electrodes

4.3 Electrochemical tests

The cyclic voltammetry, impedance measurements, and chronopotentiometry were measured by a Metrohm Autolab PGSTA302N potentiostats-galvanostats (The Netherlands).

5. Equations

To exhibit swellabilities of the eggshell membrane and composites, the swollen ratio was calculated as followed:

$$Ds = \frac{Vwet - Vdry}{Vdry} \times 100\% \qquad \text{[Equation S1]}$$

where V_{wet} is the volume of the wet sample, and V_{dry} is the volume of the dry membrane.

$$Da = \frac{Mwet - Mdry}{Mdry} \times 100\% \qquad \text{[Equation S2]}$$

where M_{wet} is the mass of the wet sample, and M_{dry} is the mass of the dry membrane.

Every sample was immersed in 0.6 M Na_2SO_4 aqueous solution for 2 h before measurement.

6. Figures

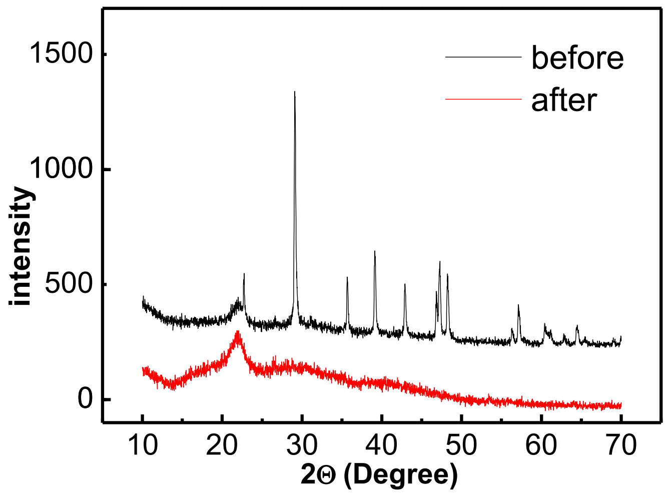

Figure S1. XRD spectra of outer eggshell membranes before and after HCl treatment.

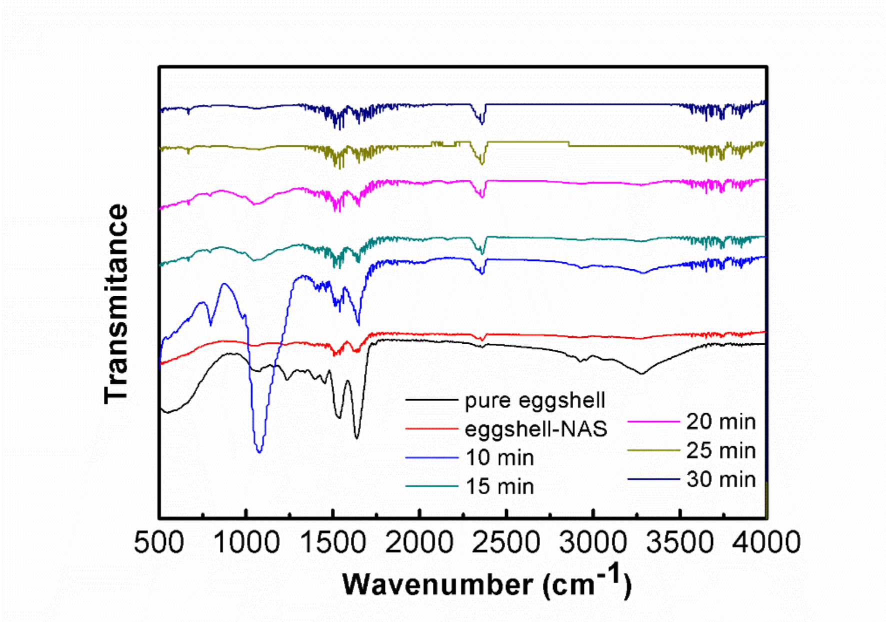

Figure S2. FT-IR investigations of eggshell membrane, modified eggshell, and eggshell-hydrogel composites with different polymerization time.

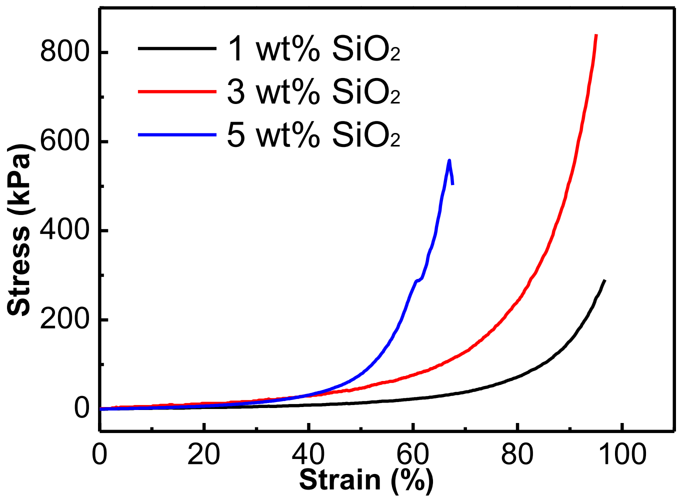

Figure S3. Compressive stress-strain curves of the nanocomposite hydrogels with various SiO_2 content.

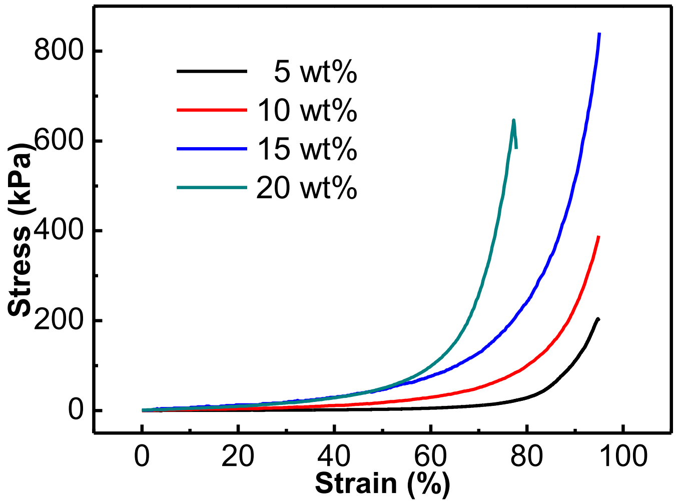

Figure S4. Compressive stress-strain curves of the nanocomposite hydrogels with various monomer content.

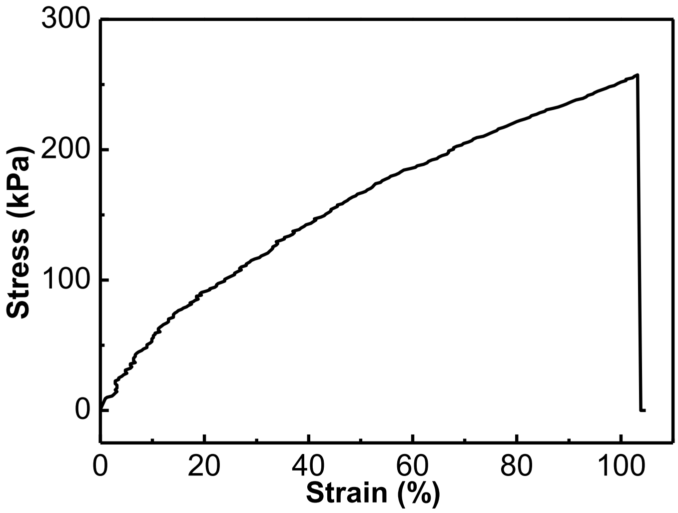

Figure S5. Tensile strength of the BSA-PDMAA-SiO_2 nanocomposite hydrogel.

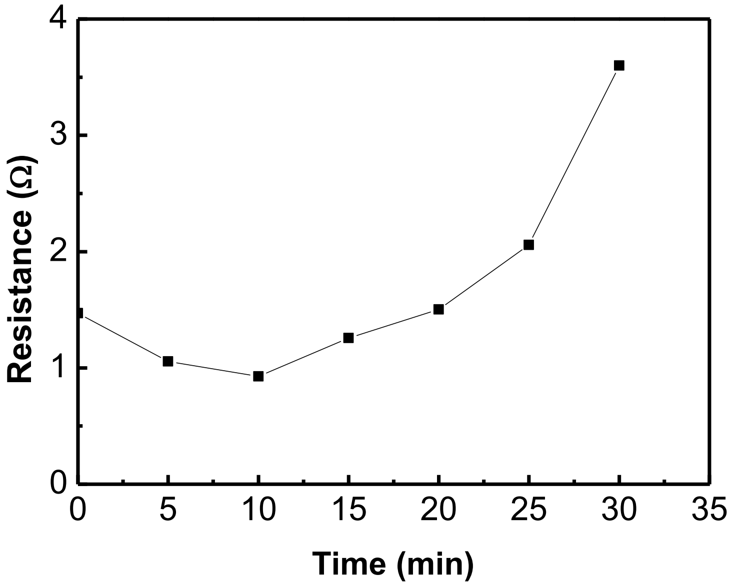

Figure S6. The resistance of the eggshell membrane with hydrogel coating applying various polymerization time after absorbing enough electrolyte.

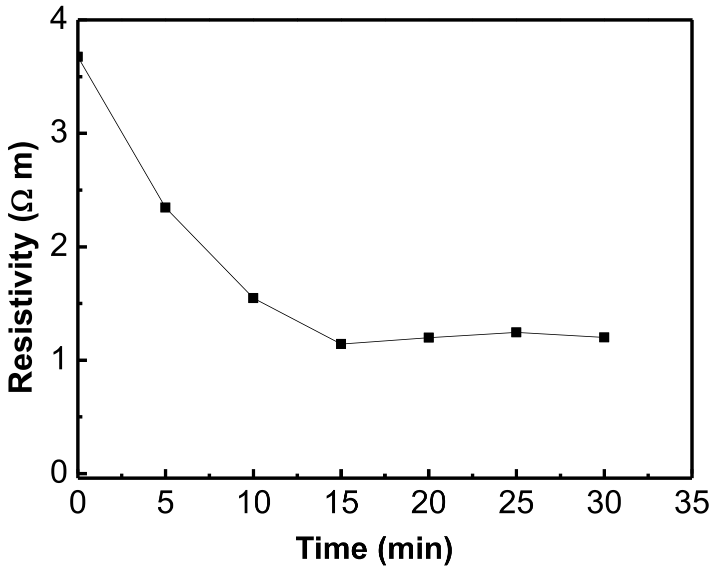

Figure S7. The resistivity of the eggshell membrane with hydrogel coating applying various polymerization time after absorbing enough electrolyte.

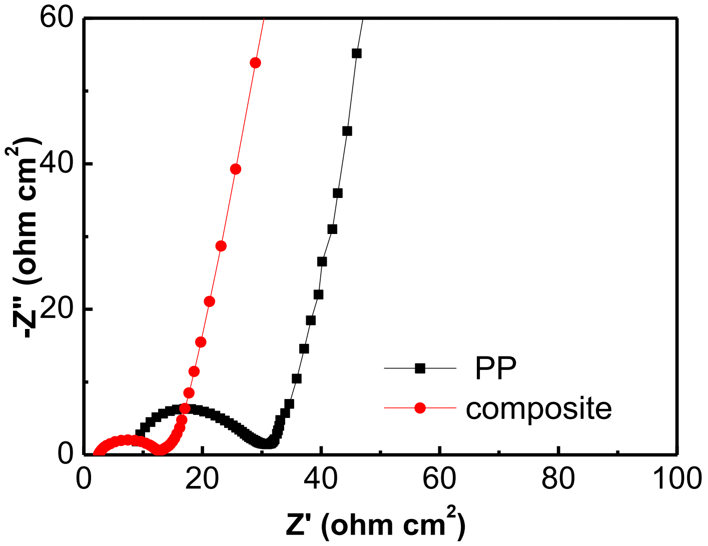

Figure S8. Impedance plots (Nyquist plots) of supercapacitors employing ESM and PP separators (with an AC perturbation of 10 mV).