

Supporting Information for

Low Cost and Environment-benign Crack-blocking Structure for Long Life and High Power Si Electrodes in Lithium Ion Batteries

*Min Ling^{a,b}, Hui Zhao^b, Xingcheng Xiao^c, Feifei Shi^b, Mingyan Wu^b, Jingxia Qiu^a, Sheng Li^a
Xiangyun Song^b, Gao Liu^{b*} and Shanqing Zhang^{a*}*

^a Centre for Clean Environment and Energy, Environmental Futures Research Institute and
Griffith School of Environment, Gold Coast Campus, Griffith University QLD 4222, Australia.

E-mail: s.zhang@griffith.edu.au

^b Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory,
Berkeley, California 94720, USA. E-mail: gliu@lbl.gov

^c General Motor Global R&D Center, 30500 Mound Road, Warren, MI 48090

Experimental

Electrode preparation

The silicon anode material is from the Umicore Inc. The gum arabic (GA) (51198-250 g) and polyacrylic acid (PAA) (416002-250 ml) are obtained from Sigma-Aldrich.

To prepare the GA-PAA (1:1 w/w) composite based electrode, the GA and PAA polymer was first dissolved in deionized water to 40 mg/mL as binder. An aqueous slurry was prepared by mixing the Umicore Si, super C₆₅ conductive additive and binder at a weight ratio of 2:1:1 (Si/C₆₅/binder). The slurry was coated onto the copper foil using doctor blade technique and dried at 150 °C under high vacuum for 2 hours to initiate the crosslinking structure via the esterification reaction and the complete removal of water. The GA/PAA mixture is prepared under the same condition above except the heat treatment at 150 °C. The areal loading is 0.3 mg/cm² for the 1000 cycles long term performance. The C-rate calculation of the Si based electrode is assuming the Si has the theoretical capacity of 4200 mAh/g.

Electrochemical evaluation

The electrochemical behaviour of Umicore Si electrodes were tested in coin cells in terms of galvanostatic discharge-charge cycling tests at ambient temperature using Maccor Instrument Testing System. All current density and specific capacity calculations are based on the active mass of Si. The volumetric capacity is based on the laminate volume before lithiation. The cell was assembled using a lithium foil as a counter electrode and 1.0 M LiPF₆ in ethylene carbonate (EC) and diethylene carbonate (DEC) (3/7, w/w), and 30 wt% fluorinated ethylene carbonate (FEC) as the liquid electrolyte. (Novolyte, now part of BASF). All the above reported procedures were performed in the inert atmosphere of an Ar-filled dry glove box (MBraun Labstar, O₂ and

H₂O content $\leq$ 0.1 ppm).

Materials Characterisation

The morphologies were observed with field-emission scanning electron microscopy (JEOL 7001F) scanning coupled with an energy-dispersive X-ray. The transmission electron microscopy (TEM) images were obtained on a Philips CM200 field emission microscopy operated at 200 kV at the National Center for Electron Microscopy (NCEN) at Lawrence Berkeley National Laboratory (LBNL).

Adhesion measurements of Si electrode were performed on a Chatillon® TCD225 series force measurement system. The Cu side of graphite electrode (1 cm $\times$ 1 cm) was fixed vertically to the bottom sample holder. The adhesive side of a Scotch Magic® tape was firmly applied onto the electrode laminate side. The Scotch Magic® tape was peeled off using the top sample holder at the direction of 180° angle to the adhered tape and parallel to one side of the Si electrode, and at 10 inch min⁻¹ moving rate to the bottom sample holder. The first data point of each test, between 0 and 0.05 cm, corresponds to the beginning of the tape tension, with the forced offset to zero. When the tension is fully applied, the measured force value reaches a plateau, representing the adhesion force of the electrode laminates.

Thermogravimetric analysis was conducted in the nitrogen atmosphere with a temperature ramp of 5 °C/min in nitrogen with SiO₂ as weight reference using the TGA/SDT Q600 from TA Instruments Inc.

FTIR spectra were acquired in attenuated total reflection (ATR) mode with a spectrometer (Nicolet Nexus 670 Fourier) equipped with a broad mercury-cadmium-telluride detector. Spectra were acquired with a 4 cm⁻¹ resolution and summed over 512 scans.

For the Cyclic Voltammetry (CV) test, a ca. 20 μ m polymer film was coated on a stainless

steel electrode using the lithium metal as counter electrode. The potential sweeps between 1.0 V and 0.01 V at 0.2 mV/s.

The compatibility of the binder with the electrolyte solvent was examined by swelling test. Binder sheets were prepared by solution-cast samples and the solvents were removed under vacuum oven at 80 °C overnight. Binder sheets were then placed in ethylene carbonate (EC) and diethylene carbonate (DEC) (1/1 w/w) electrolyte at room temperature. The swelling ratio was defined as the weight ratio of the amount of solvent absorbed to the dry weight of the tested binder sheet.

The micro-scratch test was performed by scratching the electrode surface with a tip using a CETR Tribometer (Bruker Inc.). A conical diamond stylus with a tip radius of 1.5 μm and a cone angle of 60° was used. The micro-indenter tip was drawn over the electrode surface and a 2 mm long scratch track was made by translating the sample while linearly ramping up the normal load on the conical tip from 6 mN to 50 mN.

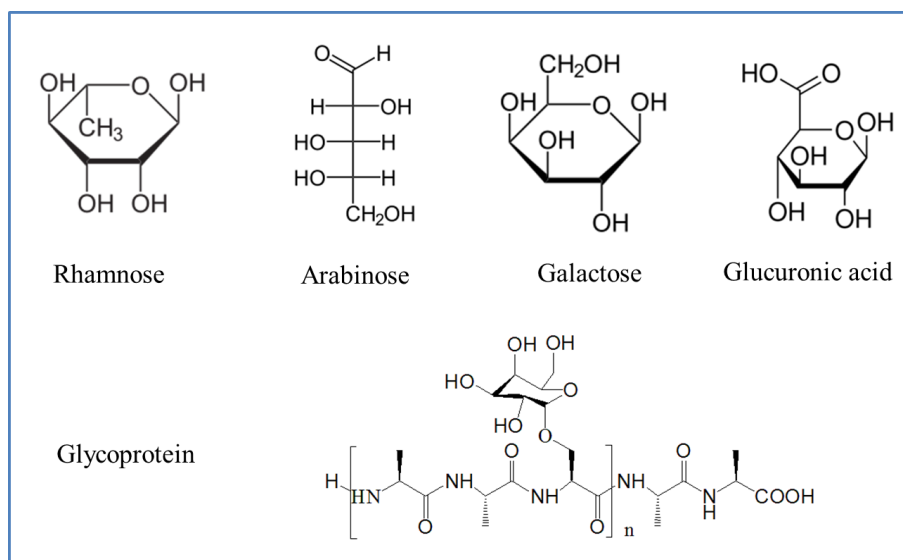


Figure S1. Chemical structure of gum arabic which composed of polysaccharides (*i.e.* rhamnose, arabinose, galactose and glucuronic acid) and glycoproteins.

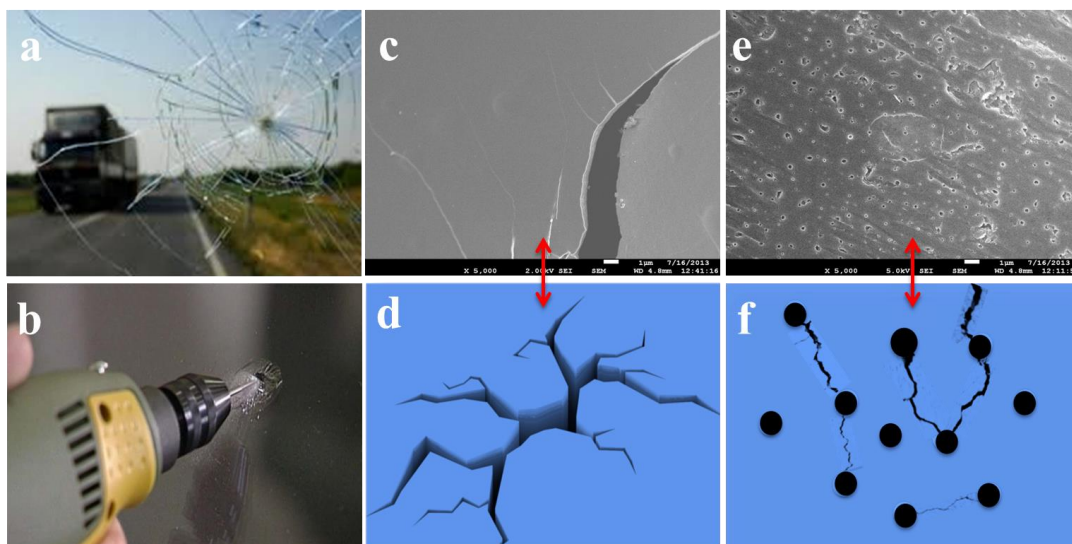


Figure S2. Design concept of the crack-blocking polymer binder. (a, b), Hole-drill into glass to stop glass from cracking. (c, d) The crack-propagation in the electrode based on GA binder in the absence of the micro pores. (e, f) The crack-blocking functions of the GA-PAA composite binder in the presence of the micro pores.

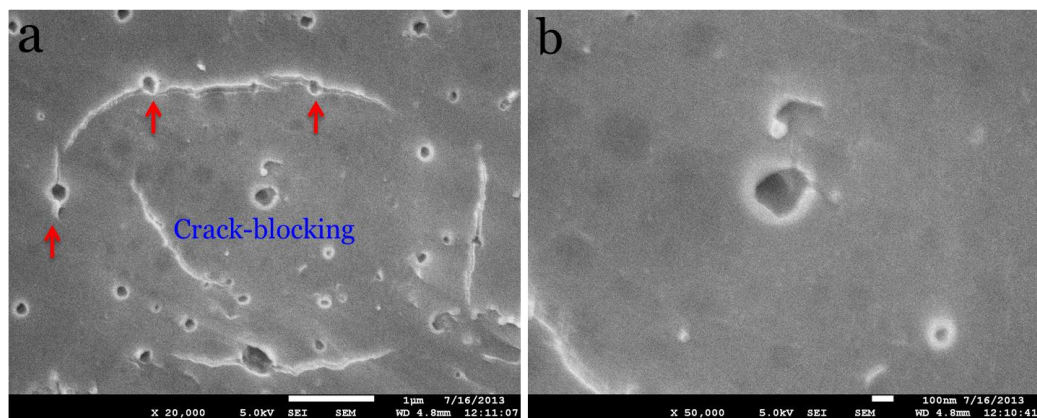


Figure S3. SEM images of the stress-releasing micro pores generated by the polymerization between GA and PAA.

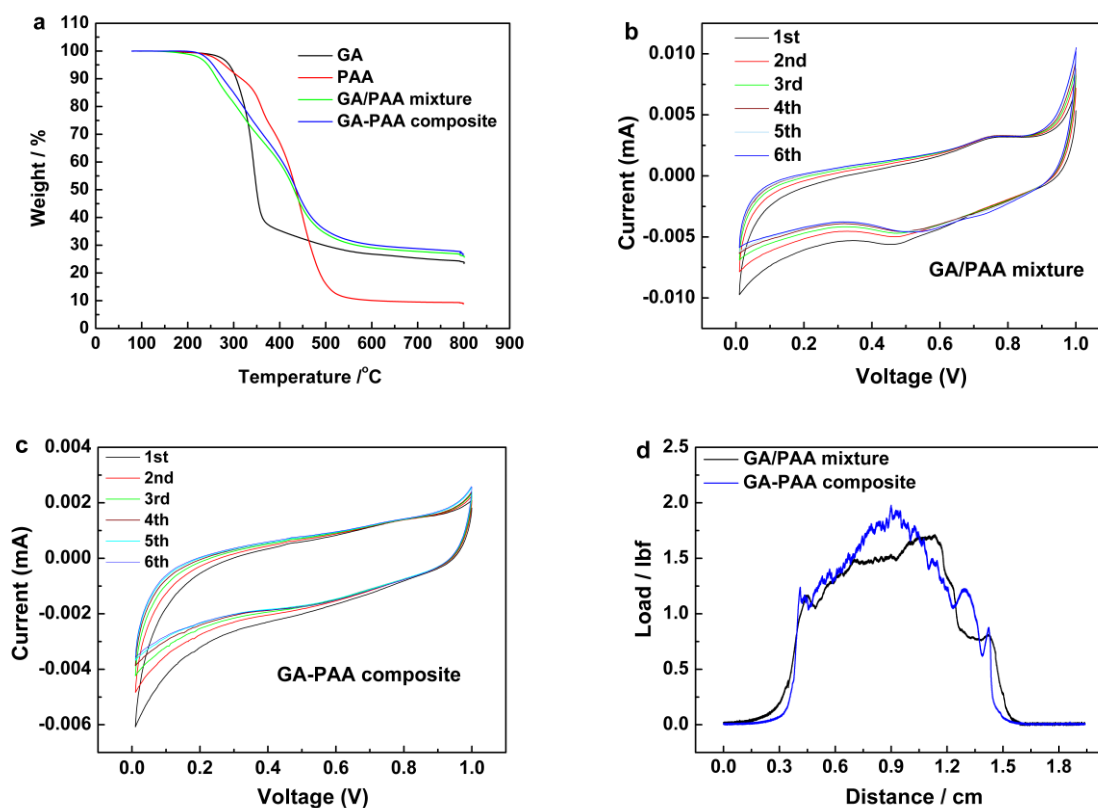


Figure S4. (a) TGA plots of GA, PAA and GA-PAA composite binders in the nitrogen atmosphere. Cyclic voltammograms of (b) the GA/PAA mixture and (c) the GA-PAA composite. (d) Peel tests of the Si laminates made from GA-PAA composite and GA/PAA mixture on copper foils.

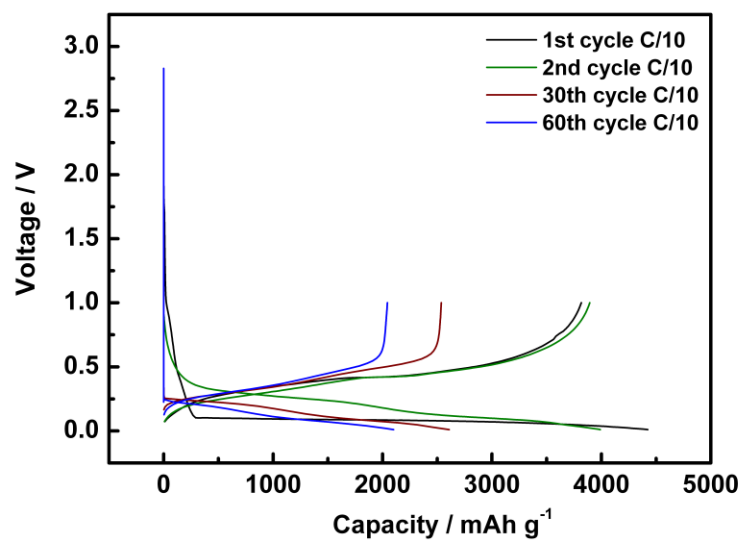


Figure S5. Galvanostatic charge-discharge voltage profiles of the Si anode based on the GA-PAA composite as binder at C/10 rate (420 mA/g) over the potential window of 0.01-1.00 V (versus Li/Li⁺).

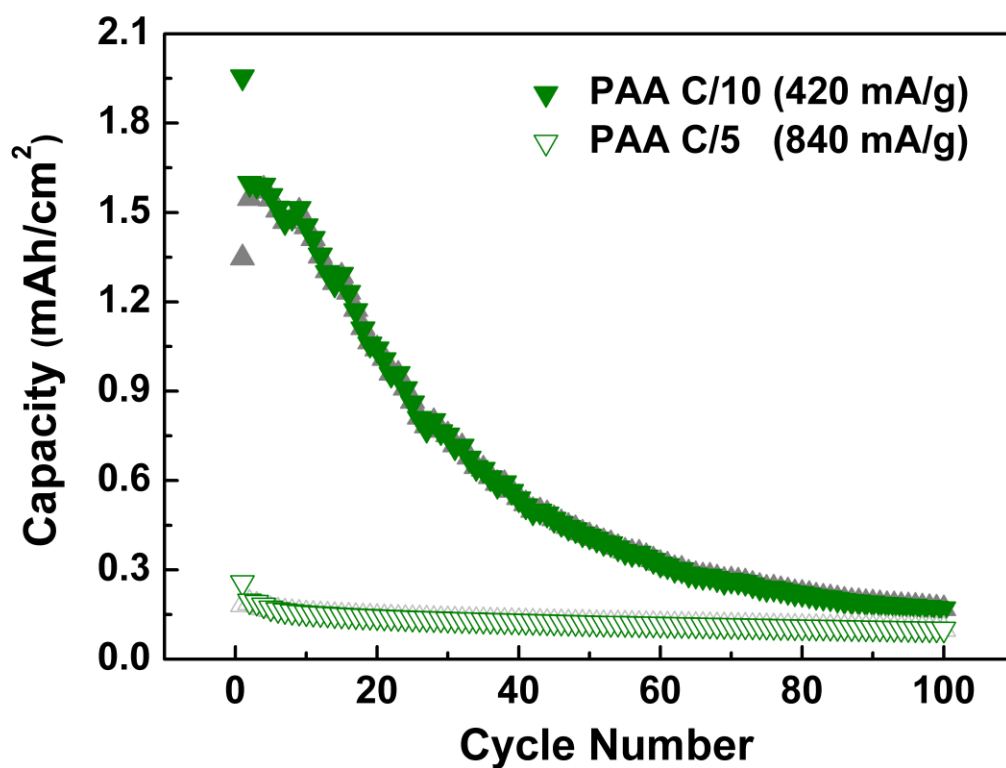


Figure S6. Reversible Li-extraction capacity of the Si electrodes based on PAA binder collected at the C/10 (420 mA/g) and C/5 rate (840 mA/g) over the potential window of 0.01-1 V (versus Li/Li⁺).⁺ (Si:C:binder = 2:1:1, wt%).

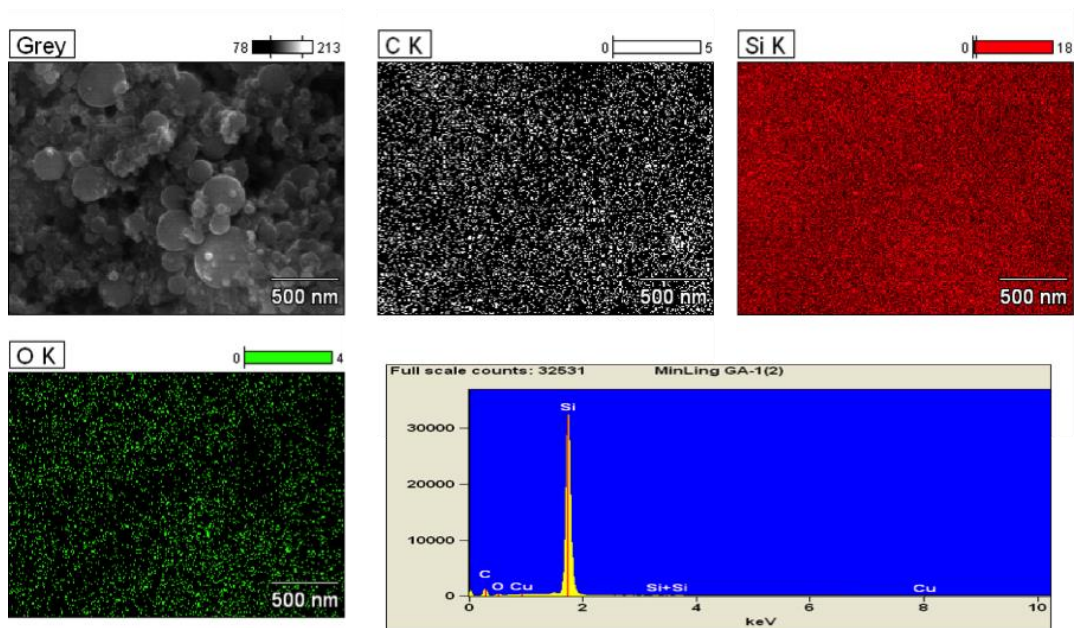


Figure S7. The EDS analysis of the Si anode based on the GA-PAA composite as binder.

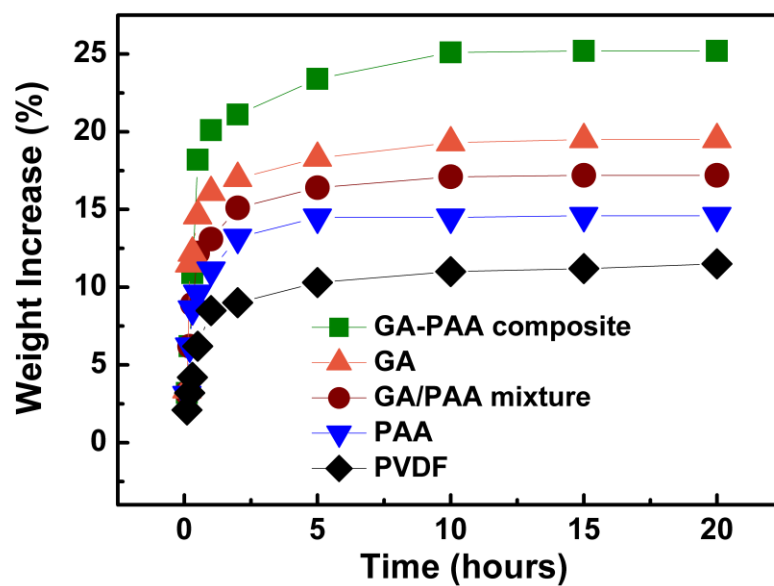


Figure S8. The swelling tests of PVDF, GA, PAA, GA/PAA mixture and GA-PAA composite binder film in ethylene carbonate (EC) and diethylene carbonate (DEC) (1/1 w/w) electrolyte at room temperature.

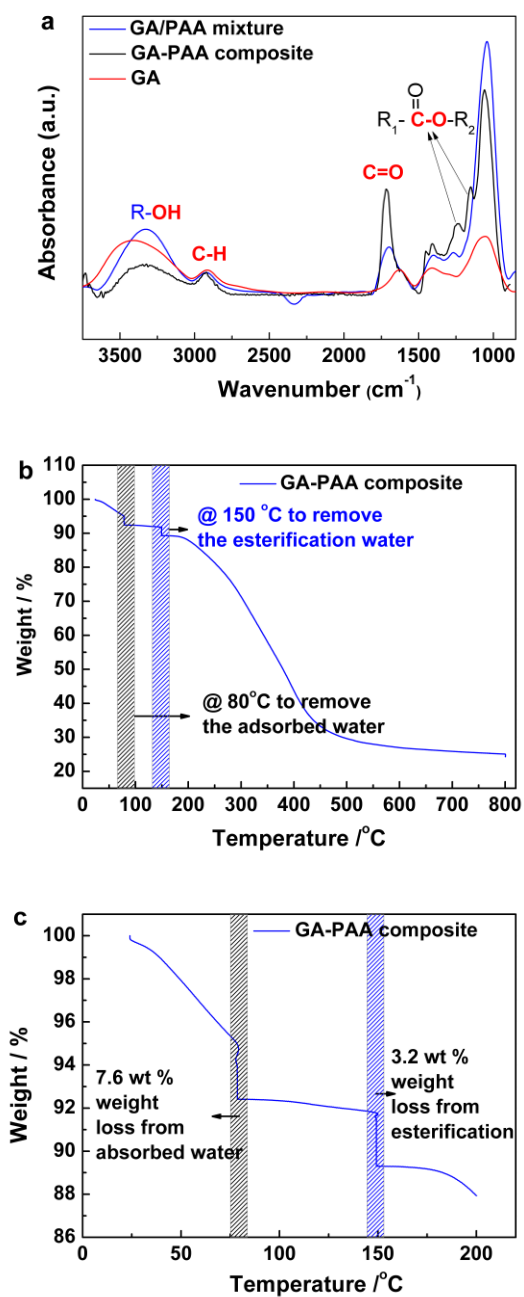


Figure S9. (a) Attenuated Total Reflectance (ATR) mode FTIR of the GA polymer binder and GA-PAA composite polymer binder. (b, c) Thermal gravimetric analysis (TGA) plots of GA-PAA composite polymer binder for *in situ* curing in the nitrogen atmosphere.

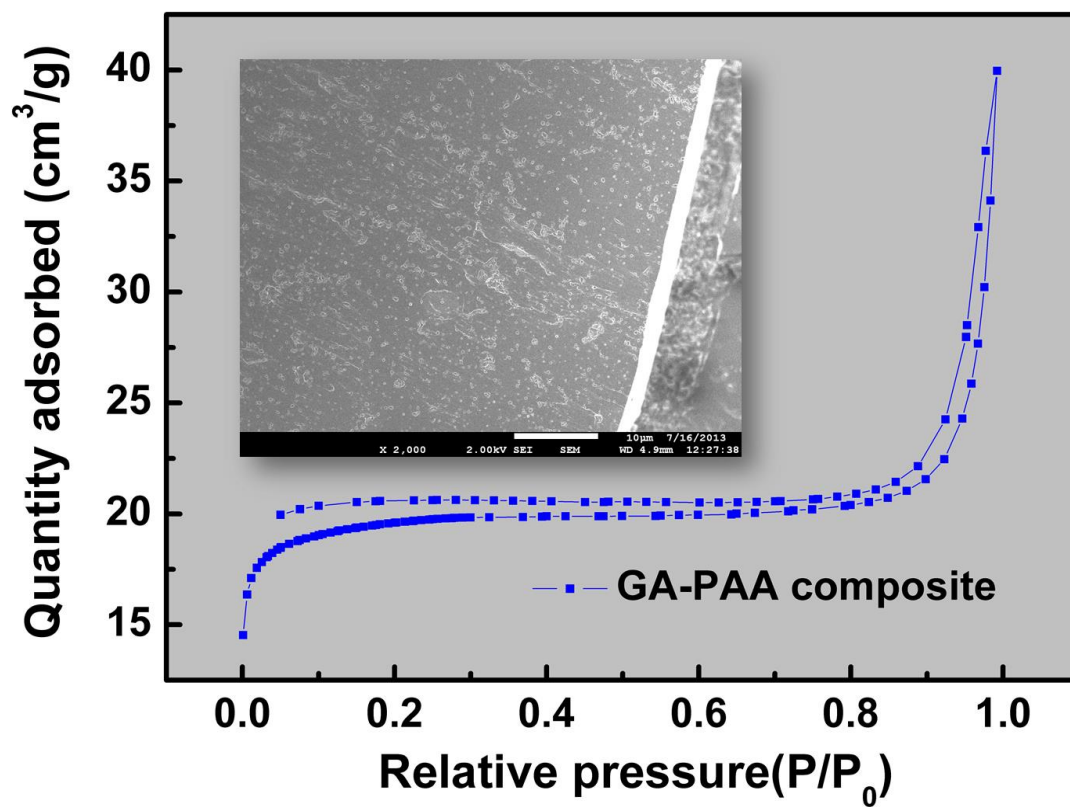


Figure S10. N_2 isotherms adsorption of GA-PAA composite sample.

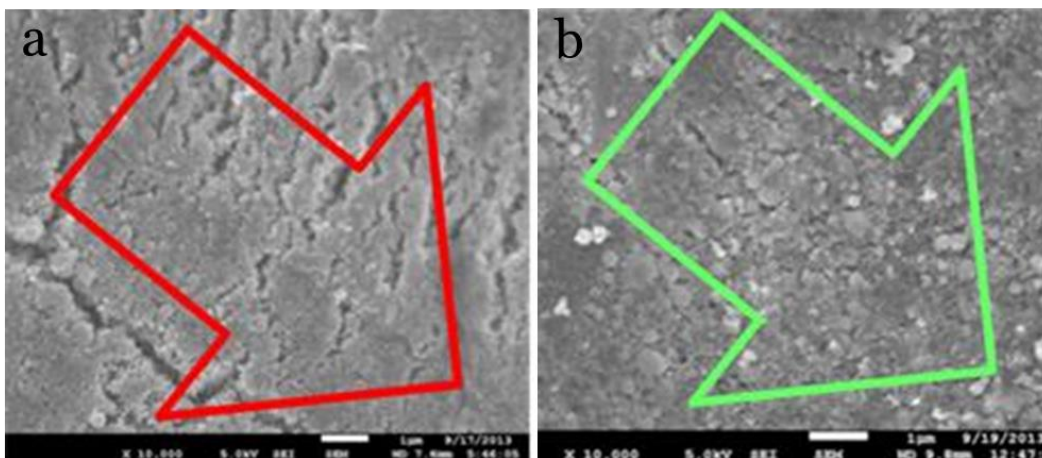


Figure S11. The scratch tests of the (a) GA/PAA mixture and (b) GA-PAA composite binders. The arrows indicate the direction of the scratches.