

Supporting information

Tea Polyphenol-Inspired Tannic Acid-Treated Polypropylene Membrane as A Stable Separator for Lithium-Oxygen Batteries

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Experiment section

Preparation of Poly-TA particles and TA coated PP separator

Poly-TA particles was prepared by adding tannic acid into bis-Tris buffer (100 mM buffer and 600 mM NaCl) aqueous solution at room temperature. In order to sufficient oxidation of TA, the solution was shaken for 24h at room temperature. The synthesized Poly-TA particles were dialyzed with distilled water several times and freeze-dried.

TA coated PP separator was prepared by immersing commercial microporous PP separators (Celgard 2400) in bis-Tris buffer (100 mM buffer and 600 mM NaCl) aqueous solution of tannic acid (1 mg mL^{-1} and pH 7.0) at room temperature for 24 h. After that, the separators were washed with deionized water several times to remove the residual tannic acid, and then dried at $60 \text{ }^\circ\text{C}$ for 24 h.

Superoxide radical scavenging test

To prepare the superoxide radical solution, 14.2 mg of potassium dioxide (KO_2) and 52.9 mg of 18-crown-6 were added to 2 mL of the electrolyte (1M LiTFSI-TEGDME). The solution was stirred for 4 h and centrifuged at 10000 rpm for 10 min to remove unreacted reactants, and the supernatant was used for tests. Nitroblue tetrazolium (NBT) was used for measuring the radical generation and its concentration. The degree of NBT reduction can be measured by ultraviolet-visible light (UV-vis) absorbance at 560 nm. 80 μL of 500 μM NBT solution was added to 200 mL of each radical solution

to investigate the relation of color change of NBT and radical concentration. As depicted in Figure S1 (a), the relation of radical concentration and absorbance intensity was linear. The different amounts of TA (1%, 5%, 8%) and poly-TA (0.75%) were added to the initial radical solution. After 10min mixing of samples, NBT was added. The solutions were centrifuged at 10000 rpm for 10 min to sink the TA or poly-TA particles. Then, the supernatants were collected and the absorbance values of the solutions were measured (see Figure S1 (b)). By using the equation in Figure S1 (a), the reduced radical concentrations were calculated. ^{S1}

Potassium superoxide (KO₂) screening method

Briefly, 85.2 mg of potassium dioxide (KO₂) and 317.4 mg of 18-crown-6 were added to 12 mL of the electrolyte (1M LiTFSI+TEGDME). After KO₂ dissolved completely, a piece of PP separators with and without coatings was soaked in this solution, respectively. The solution was thoroughly stirred after different times as 24h, 48h, 72h, 96h and 120h. After that, the separators were took out of the above mixture, washed with deionized water for three times, transferred into drying oven and dried at 80 °C for at least 24 hours to effective water removal. ^{S5}

Li-O₂ Battery Assembly and Electrochemical Tests

The air-electrode for the investigation of the electrochemical performance of Li-O₂ battery was prepared by casting slurry in which MWCNTs (80 wt%) and PVDF binder (20 wt%) were dissolved in NMP solvent on carbon paper. And the weight loading of MWCNT active material was about 1.0 mg cm⁻². Metallic lithium foil (1.56 cm diameter and 0.45 mm thick) as anode, and the original PP and TA coated PP

membranes as separator with 1.0 M LiTFSI in triethylene glycol dimethyl ether solution as electrolyte. The assembled Li-O₂ batteries were tested on Land CT2001A test system (Wuhan, China) at room temperature. The Li-O₂ cells were electrochemically tested under Autolab PGSTAT302 (Eco Chemie) electrochemical test system at room temperature inside a chamber. CV was carried out at a scan rate of 0.1 mV s⁻¹ in the range of 2.0-4.5 V vs Li/Li⁺.

Characterization

Attenuated total reflection-infrared spectra (ATR-IR) with an FT-IR spectrophotometer (Bruker, EQUINOX 55) and X-ray photoelectron spectroscopy (AXIS Ultra DLD system (Shimadzu-Kratos) measurements were used in our experiment. The morphology of membrane was analyzed by Scanning electron microscopy (SEM) analysis, carried out with a HITACHI S-4800 equipment. The tensile strength of membranes was measured with a universal test machine (Instron-4465, Instron, USA) at a crosshead speed of 20 mm min⁻¹.

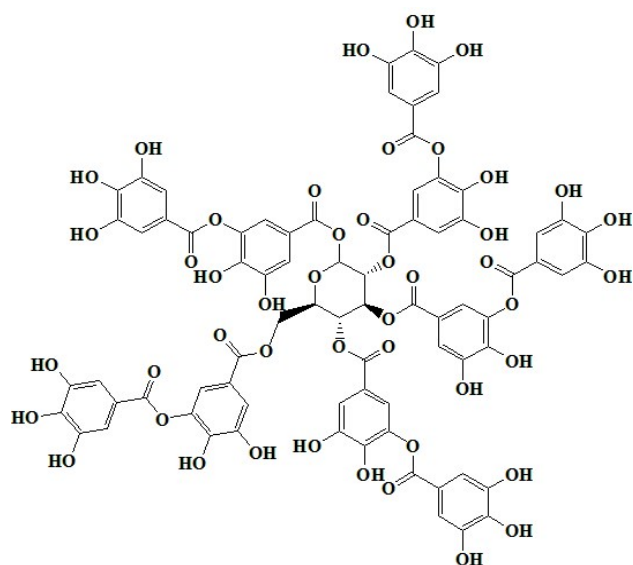


Figure S1 Chemical structure of tannic acid.

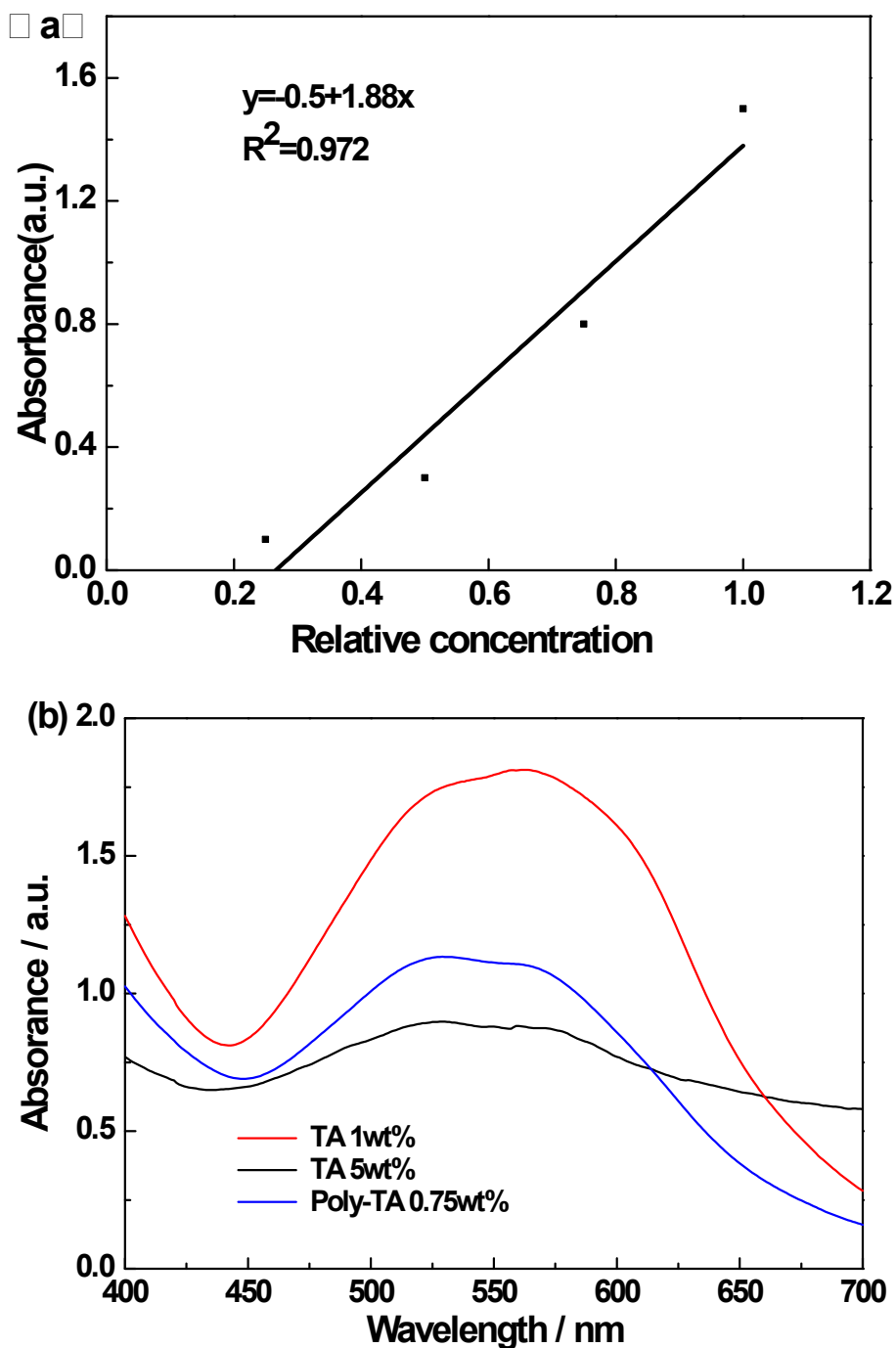


Figure S2. (a) The relation between the concentration of the radical solution and the absorbance of NBT. The UV-Vis absorbance at 560 nm increases with the increasment of the radical concentration. (b). UV-Vis spectra of the NBT solution at different TA concentrations (1 wt% and 5 wt%) and Poly-TA (0.75 wt%).

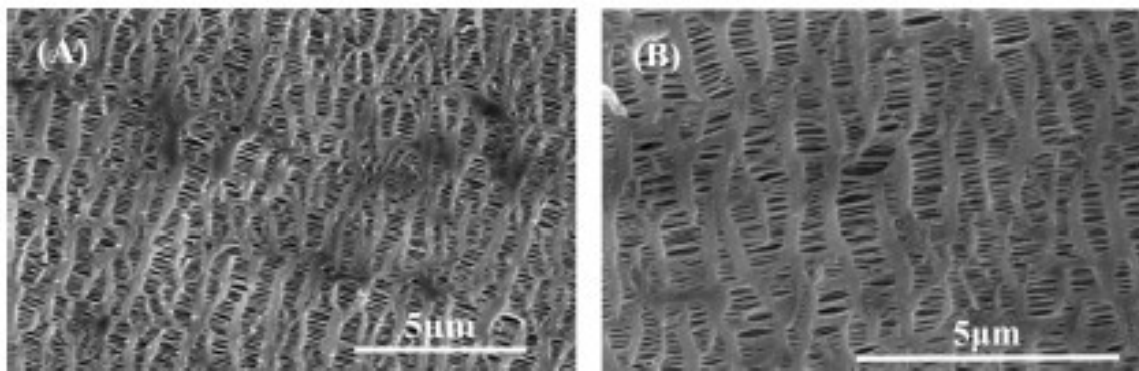


Figure S3. SEM images of PP separators without (A) and with (B) tannic acid coating.

As shown in the Figure S3A and Figure S3B, the microporous structure of the PP separators with and without the TA coating remained almost the same, even the TA was coated on the PP membrane. Plus, the porosity of the separators with and without the TA coating were also not changed. These results indicate that the TA coating did not destroy the microporous structure of the PP separator.

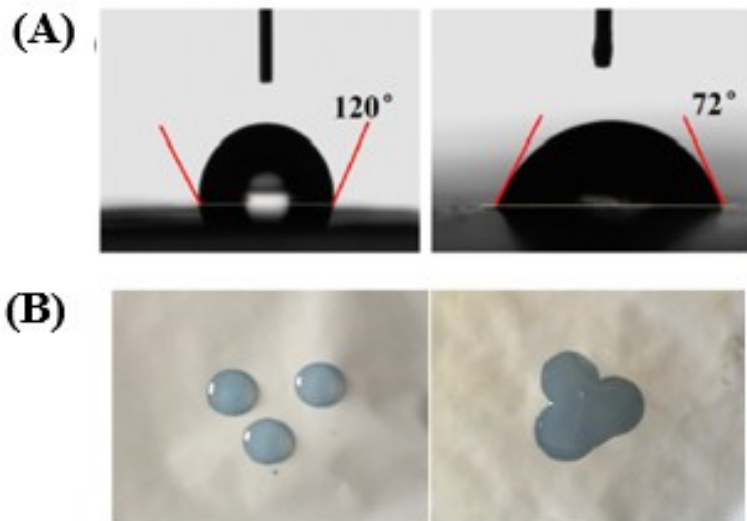


Figure S4. (A) Contact angle images of PP separators without (left) and with (right) tannic acid coating. (B) A wetting test of PP separators without (left) and with (right) tannic acid coating. 1 M LiTFSI in 3G liquid electrolyte was poured on the separator surfaces.

The surface properties of the PP separators before and after the TA coating are shown in Figure S4. As shown in Figure S4A, the contact angle of water decreased from $120^\circ \pm 2.5^\circ$ for the original PP separator to $72^\circ \pm 1.3^\circ$ for the TA-coated PP separator, indicating the more hydrophilic property of PP separator with TA coating than the original PP separator. The wetting test of the liquid electrolyte on the separators was carried out by pouring 1 LiTFSI in triethylene glycol dimethyl ether liquid electrolyte onto the surfaces of the PP separators with and without the TA coating. As shown in Figure S4B, the original PP separator showed poor compatibility with the liquid electrolyte, and only liquid drops was observed on the separator surfaces. After the TA coating, the PP separator exhibited better compatibility with the liquid electrolyte and completely wetted the surfaces. Furthermore, the liquid electrolyte uptake increased from $60 \text{ wt } \% \pm 2.1 \text{ wt } \%$ of the original PP separator to $85 \text{ wt } \% \pm 2.1 \text{ wt } \%$ of the TA-

coated PP separator. In general, ionic conductivities are expected to depend mainly on the uptake amount of liquid electrolyte in the separators.^{S2, S3}

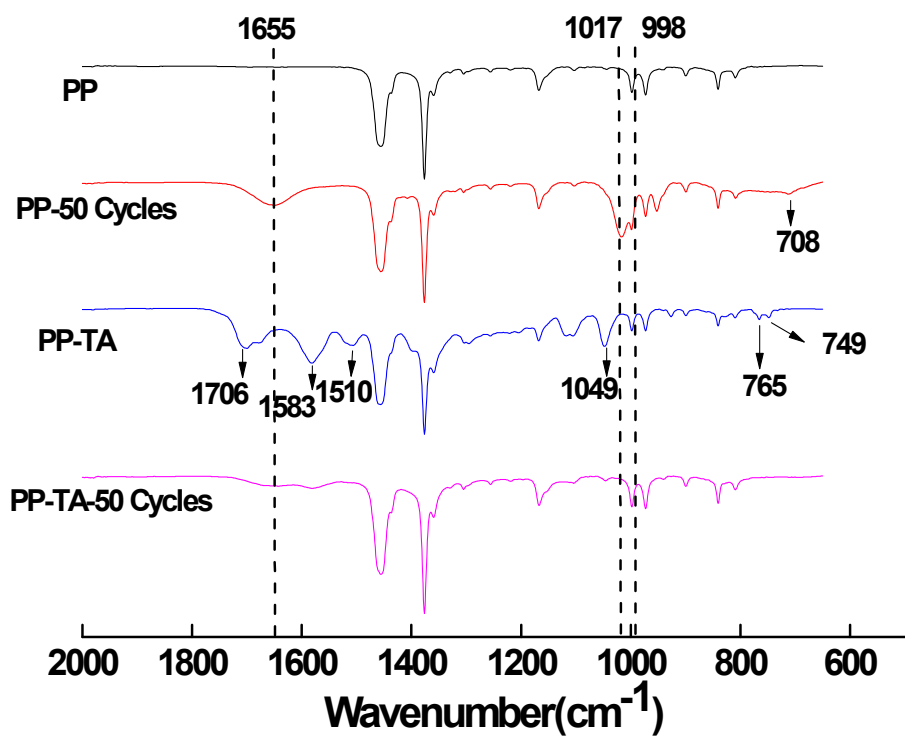


Figure S5 ATR-IR spectra of the PP and PP-TA separator before and after the 50 and 100 cycles, respectively.

Proposed mechanism of tannic acid scavenging superoxide radicals

According to the research work about the scavenging ability of polydopamine^{S1} and tannic acid^{S4}, we provided a proposed mechanism of tannic acid scavenging superoxide radicals as mentioned below.

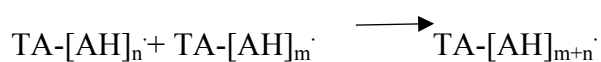
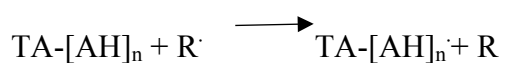
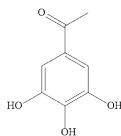


Figure S6. Proposed mechanism of TA scavenging superoxide radicals.

AH represents the chemical structure of



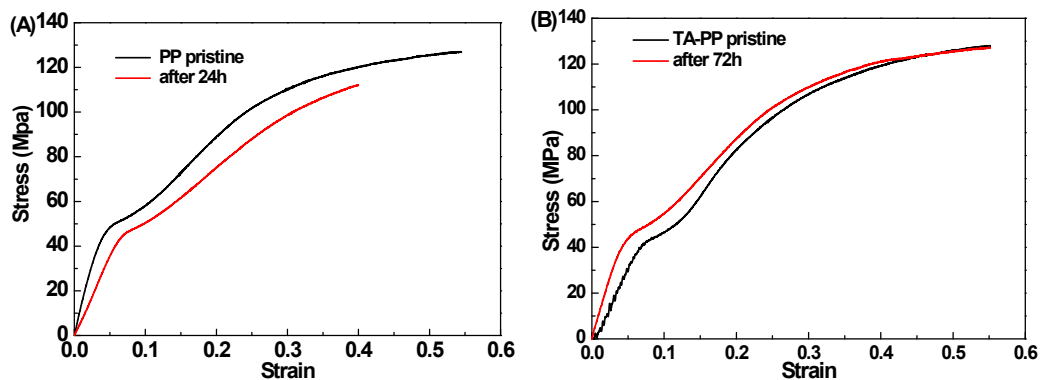


Figure S7. The mechanical strength of PP membrane (A) and TA coated PP membrane (B) before and after immersed in superoxide radicals solution.

Table S1 The mechanical strength of PP membrane and TA coated PP membrane before and after immersed in superoxide radicals solution.

	PP before	PP after 24h	TA-PP before	TA-PP after 72h
Tensile strength (MPa)	127	112	128	127

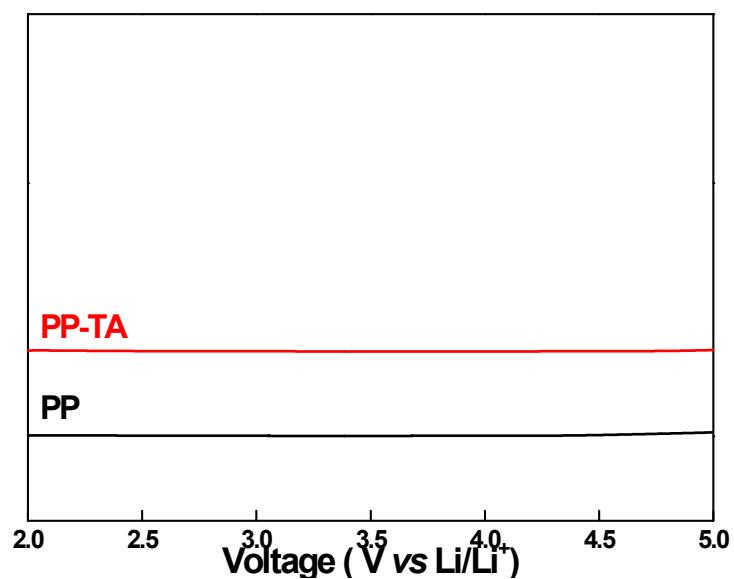


Figure S8. Linear sweep voltammetry curves of PP separators with and without tannic acid coating with stainless steel as the working electrode, Li foil as the reference, and counter electrodes at room temperature. Scan rate: 10 mV sec⁻¹.

As shown in Figure S8, it can be observed that there is no decomposition in either of the PP separators between 2 to 5 V versus Li/Li⁺. Thus, PP separator with and without TA coating are both stable in the working voltage of Li-O₂ battery.

Table S2 Intensity comparison of TA functional groups before and after the battery cycling in XPS spectrum.

Functional groups	PP-TA Intensity (Area)	PP-TA-Cycle Intensity (Area)	Decreased Intensity (%)
O-C=O	3340	2240	33±0.1
C-O	2790	1870	33±0.1
C-OH	6000	4020	33±0.1

References

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