Supporting Information

An efficient strategy for preparation of super-hydrophobic silane fluorinated polystyrene films with monomethoxypolyethyleneglycol -graft-polyethoxydisiloxane gel

Experimental Materials

Tetraethylorthosilicate (TEOS, AR), hydrofluoric acid (HF, purity > 39.5 wt% of aqueous solution), anhydrous ethanol (AR), anhydrous toluene (AR), anhydrous dimethylbenzene (AR) and hexane (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd (China) and used directly. Deionized water was produced from Millipore Elix®, USA. Perfluoroalkyltriethoxysilane ($CF_3(CF_2)_5(CH_2)_2Si(OC_2H_5)_3$, FTEOS, purity>98%) was obtained from Jessica Chemicals Co., Ltd (Hangzhou, China). General purpose polystyrene (GPPS, Polystyrol®143E) was purchased from Yangzi-BASF styrenics Co., Ltd (Nanjing, China). Monomethoxypolyethylene glycol (MPEG, Pluriol® A 1020E) was purchased from BASF.

Characterization

The surface morphology and element distribution of films and MPEG-g-PEDS were characterized by scanning electron microscopy (SEM) and accessorial electron energy disperse spectroscopy (EDS) (JSM-5900, JEOL Ltd, Japan) respectively. The water contact angles (CAs) of film were measured by the contact angle measurement apparatus (K100, Krüss Ltd, Germany), using a 4μl water droplet as the indicator. If those droplets that could not be adsorbed from the needle tip onto the surface due to too hydrophobic, a pair of tweezers with acuate tip was used with a certain force to transmit them onto the surface. The reported results were the average of five different positions of the same sample.

The number-average molecular weight and distribution of molecular weight of the PEDS were

measured by gel permeation chromatography (GPC) with 18 angle laser light scattering detector (Dawn Eos, Wyatt Ltd, USA). The MPEG-g-PEDS gel substituted for MPEG-g-PEDS precursor was studied by Fourier transform infrared (FT-IR) because it is difficult to remove the unreacted MPEG from the MPEG-g-PEDS precursor. The MPEG-g-PEDS gel was extracted using dimethylbenzene for 6 hours, then dried at 80□ for 12 hours, and so do the PEDS gel compared the MPEG-g-PEDS gel. After the surfaces modified with FTEOS were washed by hexane, the fluorinated modification was studied by the accessorial attenuated total reflection infrared (ATR) spectroscopy (Nexus 670, Nicolet Ltd, USA). All measurements were carried out at the room temperature.

Preparation of the PEDS

TEOS, ethanol, water and HF as catalyst were added to a stirred tank with a molar ratio of 1:6:1.2:0.05. The reaction solution had been kept in 4~5□and for 5 days, then the ethanol was removed from the solution at 70□ under the pressure of 2 kPa. The number-average molecular weight of the PEDS about 1.2□103 g/mol (The degree of polymerization is approximately 8-10) was synthesized and the distribution of molecular weight of the PEDS is shown in Fig.S1.

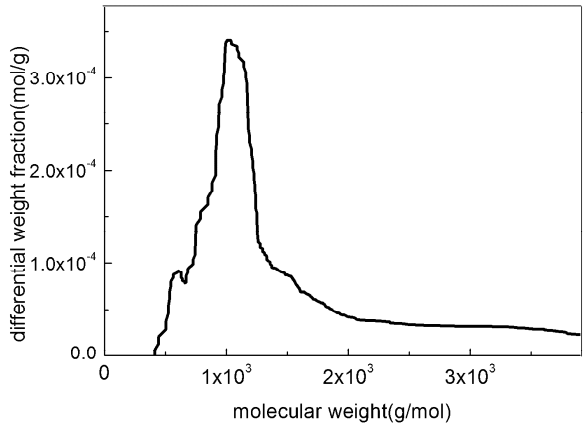


Fig. S1 Distribution of molecular weight of PEDS

ATR of the MPEG-g-PEDS gel /polystyrene film

The blending vibrations of Si-OH near 1637 cm^{-1}(a) and 952 cm^{-1}(c) and the asymmetric stretching vibrations for Si-O-Si around 1085 cm^{-1}(b).

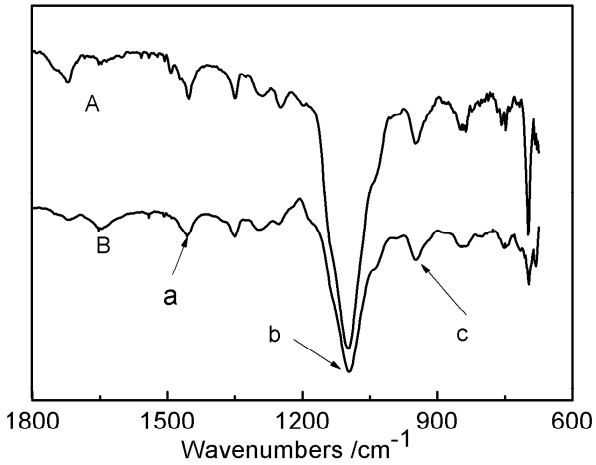


Fig. S2 ATR of untreated composite films under RH=15% (A) and RH=50% (B), respectively.

SEM of the MPEG-g-PEDS gel /polystyrene film

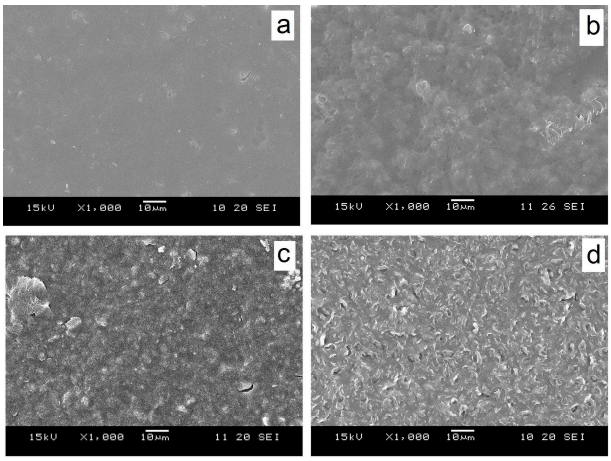


Fig. S3 SEM of the MPEG-g-PEDS gel /polystyrene film dried under dry air (RH =15%), at 30 wt%(a), 50 wt% (b), 70 wt% (c) and 100 wt% (d).

The surfaces of untreated films become rougher under dry air (RH =15%) with the weight content of MPEG-g-PEDS gel increasing from 30 to 100 wt%, but the micro-conformation of wet gel particle isn't appeared obviously because of the MPEG-g-PEDS gel particles embedded into the untreated composite film.

SEM of the treated film

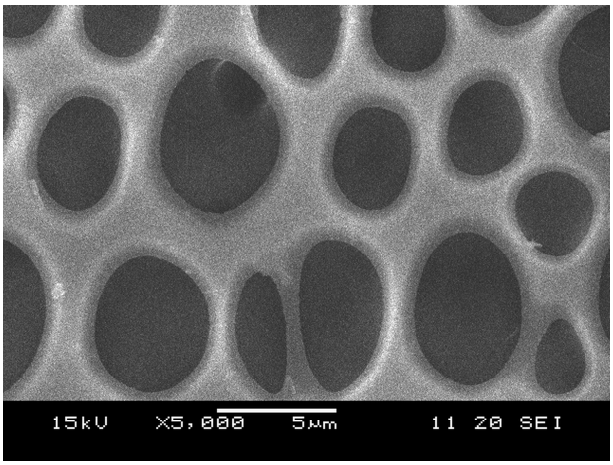


Fig. S4 SEM of the treated film (RH =50%) at 70 wt% of the MPEG-g-PEDS gel.

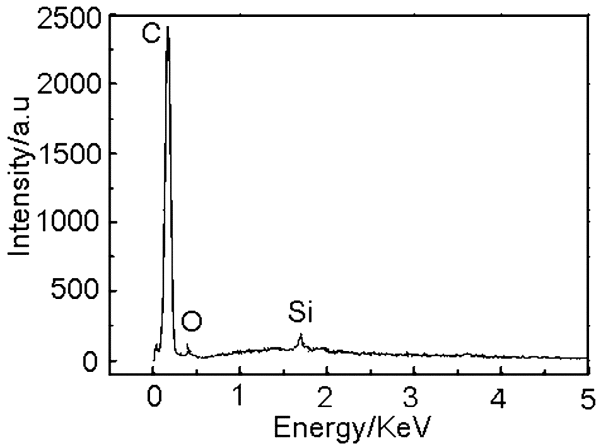
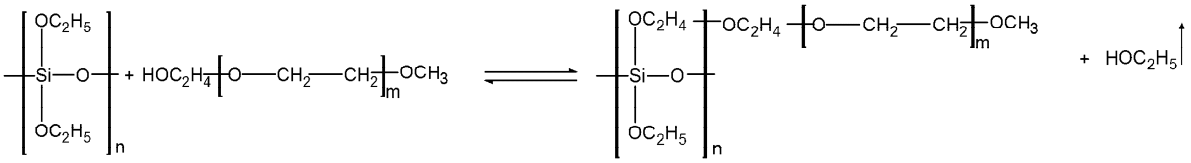


Fig. S5 EDS of the surface of the treated film (RH =50%) at 70 wt% of the MPEG-g-PEDS gel.

However, the treated film (RH=50%) displays the porous conformation. The SEM image magnified 5000 times of treated film clearly shows nothing in honeycomb-patterned porous surface, and the wall is comprised of main carbon by EDS. It indicates that the porous wall is composed of polystyrene and the gel particles as nucleating agent in these holes were dissolved into the FTEOS/water/ethanol aqueous solution.

Reaction of MPEG with PEDS



Formula. S1 Reaction of MPEG grafted PEDS.

CA of the treated films

Table.S1 The CA of films under different humidity conditions and content

Content of MPEG-g-PEDS gel	RH =15%		RH=50%	
(wt%)	Untreated	Treated	Untreated	Treated
0	90.4°	95.3°	97.1°	105.5°
30	100.2°	154.7°	74.8°	119.3°
50	81.4°	161.0°	69.3°	122.7°
70	73.5°	150.3°	57.3°	123.0°

'Treated' means that the films had been soaked in the FTEOS/H_2O/ethanol solution for 24 hours, and 'untreated' by contraries.

In Table.S1, the water CA of untreated films decreases with the weight content of hydrophilic MPEG-g-PEDS gel increasing, and the CA of untreated films under RH=50% is less than that under RH=15%. The CA of untreated pure polystyrene film (RH=50%) is 97.1° larger than 90.4° of that under RH=15%. As for the treated pure polystyrene films, the CA is raised to 105.5° and 95.3° respectively owing to a few hydrolysates of FTEOS depositing on the films. The treated films have a high CA of larger than 150°.