Transparent superhydrophobic hollow films (TSHFs) with superior thermal stability and moisture resistance

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Experimental section

Materials

Ammonia solution (28%) was purchased from Shanghai Chemical Reagent Co., Ltd., China. Methyltrimethoxysilane (MTMS) was purchased from Ark (FoGang) Chemicals Industry Co., Ltd., China. Milli-Q water was kindly supplied by Nanjing Profem chemical (Jiangsu) Co., Ltd., China. All chemicals were used as received without any further purification.

Preparation of transparent superhydrophobic hollow films (TSHFs)

Candle soot exhibits a particle chain structure, which is made up of 42±5 nm spherical carbon balls. Thus, in this paper, we used candle soot to achieve initial sub-100 nm roughness. Additionally, MTMS based material exhibits highly thermal stability. It has been reported that MTMS based superhydrophobic material retains its superhydrophobicity after calcining up to 500 °C. So MTMS was adopted as precursor to form shell network on candle soot, which is expected to maintain its shell structure and superhydrophobicity after removing template by calcination.

The preparation of transparent superhydrophobic hollow films: holding the glass substrate on a candle flame for a few seconds, then dark transparent glass substrate with a thin candle soot film can be obtained. The soot coated glass was moved into a closed desiccator with two open glass beakers containing 10 g MTMS and 10 g ammonia solution. The chemical vapor deposition (CVD) of MTMS on candle soot was carried out for 2, 4, 6, 8, 10, 12, 16, 20, 24 hours, respectively, at 25 °C.
Taking out the soot coated glasses after CVD process, calcining the obtained glasses at 450 °C in air to remove the template and immersing the glasses in Milli-Q water for 3 seconds to eliminate surface stain from calcining procedure, transparent superhydrophobic hollow films can be obtained after drying the substrates at 150 °C overnight. The prepared transparent superhydrophobic hollow films were denoted as TSHF-a, where a is the chemical vapor deposition (CVD) time of MTMS.

Characterizations

Fourier-transform infrared (FT-IR) spectra of films (scratched from the substrates) were carried on Nicoletis10. Water contact angle (CA) and the sliding angle (SA) of transparent superhydrophobic hollow films were measured with a SL200B automatic contact angle detector. The transparency of coated substrates was determined by PerkinElmer lambda 950 ultraviolet spectrometer. Only one film sample was chosen for further $^{29}$Si CP (cross-polarization) MAS NMR, XPS, thermogravimetric (TGA), AFM and TEM analysis. $^{29}$Si CP (cross-polarization) MAS NMR, XPS, thermogravimetric (TGA) and TEM analysis of film sample were conducted by scratching the sample from the glass substrates. AFM analysis was carried out by directly depositing the film sample on silicon wafer. $^{29}$Si CP (cross-polarization) MAS NMR spectrum of the film was conducted on Bruker advance 400D. The surface chemical composition of film was detected on X-ray photoelectron spectroscopy (XPS) (PHI5000 VersaProbe). A Shimadzu DTG 60H was employed to study the thermogravimetric (TGA) of film with a heating-rate of 20 °C/min from 25 to 1000 °C under nitrogen atmosphere. Bruker Autoprobe CP-Reaserch (AFM) was employed to get the information of surface roughness of hollow film. The surface morphology of film was observed by JEM-2100 (TEM) (JEOL. Ltd) (operating at 120 kV).
Fig. S1. The FT-IR spectra of TSHF samples from different CVD time (8, 10, 12, 16, 20 and 24 h)

**Table S1.** The transmittance of bare glass and TSHF coated glasses in three visible wavelengths

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of CVD (h)</th>
<th>Relative transmission (%)</th>
<th>400 (nm)</th>
<th>550 (nm)</th>
<th>700 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare glass</td>
<td></td>
<td></td>
<td>91.26</td>
<td>91.64</td>
<td>91.27</td>
</tr>
<tr>
<td>TSHF-2</td>
<td>2</td>
<td></td>
<td>91.69</td>
<td>91.64</td>
<td>91.47</td>
</tr>
<tr>
<td>TSHF-4</td>
<td>4</td>
<td></td>
<td>90.75</td>
<td>91.14</td>
<td>91.00</td>
</tr>
<tr>
<td>TSHF-6</td>
<td>6</td>
<td></td>
<td>90.51</td>
<td>90.99</td>
<td>90.99</td>
</tr>
<tr>
<td>TSHF-8</td>
<td>8</td>
<td></td>
<td>90.87</td>
<td>91.61</td>
<td>91.57</td>
</tr>
</tbody>
</table>
Fig. S2. $^{29}$Si NMR spectrum of TSHF-24 sample.
Fig. S3. XPS spectra of TSHF-24 sample: the full spectrum and the O 1s, C 1s, Si 2p spectrum.

Table S2. The chemical shift $\delta_{\text{Si}}$ and the anchoring structures of MTMS

<table>
<thead>
<tr>
<th>Structure</th>
<th>Siloxane (Q4)</th>
<th>Free silanols (Q3)</th>
<th>Tridental structure (T3)</th>
<th>Bidental structure (T2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{\text{Si}}$ in ppm</td>
<td>-110.8</td>
<td>-103.4</td>
<td>-65.9</td>
<td>-56.7</td>
</tr>
</tbody>
</table>

Note: R represents $-\text{CH}_3$ groups in this paper