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Supporting Information

A Facile *Immersion-Curing* Approach to Surface-Tailored Poly(vinyl alcohol)/Silica Underwater Superoleophobic Coatings with Improved Transparency and Robustness

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Table S1 Weight loss percentages of PVA/SiO_2/35-GA(*bc*) and PVA/SiO_2/35-GA(*ic*) after immersion in water.

	W_{before} [*mg*]	W_{after} [*mg*]	W_{loss} [%][a]
PVA/SiO_2/35-GA(*bc*)	30.13	29.48	2.16
PVA/SiO_2/35-GA(*ic*)	7.02	6.92	1.45

[a] W_{loss} (%)= (W_{before}-W_{after})/W_{before} ×100%

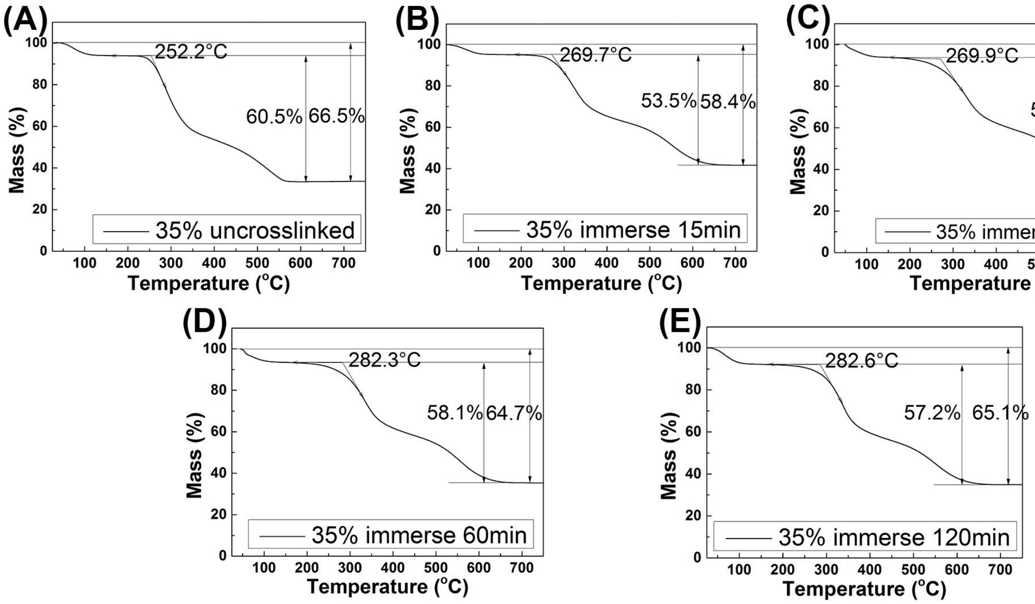

Fig. S1 TGA curves of (A) uncrosslinked PVA/SiO_2/35, and PVA/SiO_2/35-GA(*ic*) with an immersion time-period of (B) 15 min, (C) 30 min, (D) 1 h, (E) 2 h.

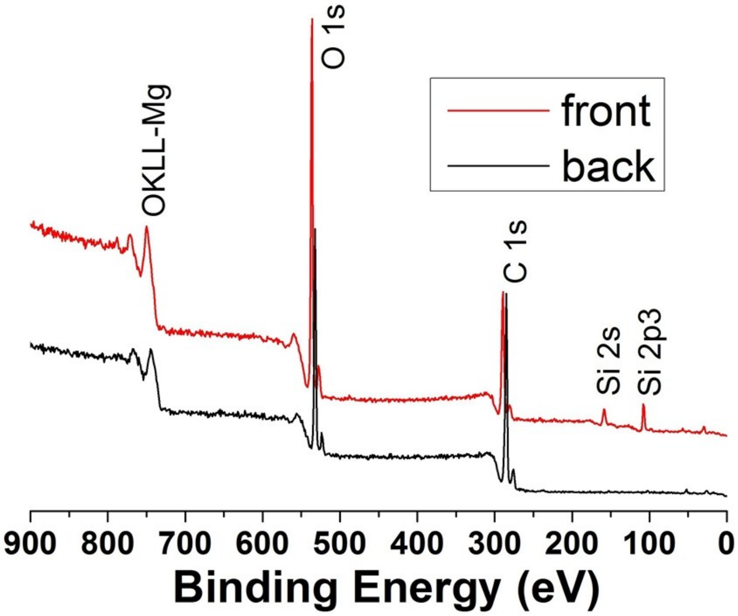

Fig. S2 XPS spectra of the surface and interface of PVA/SiO_2/35-GA(*ic*) film (peeled off from the substrate).

Table S2 XPS atomic percentages of the corresponding two surfaces in Fig. S2.

	C 1s	**O 1s**	**Si 1s**
surface	46.71%	44.44%	8.84%
interface	69.99%	29.27%	0.74%

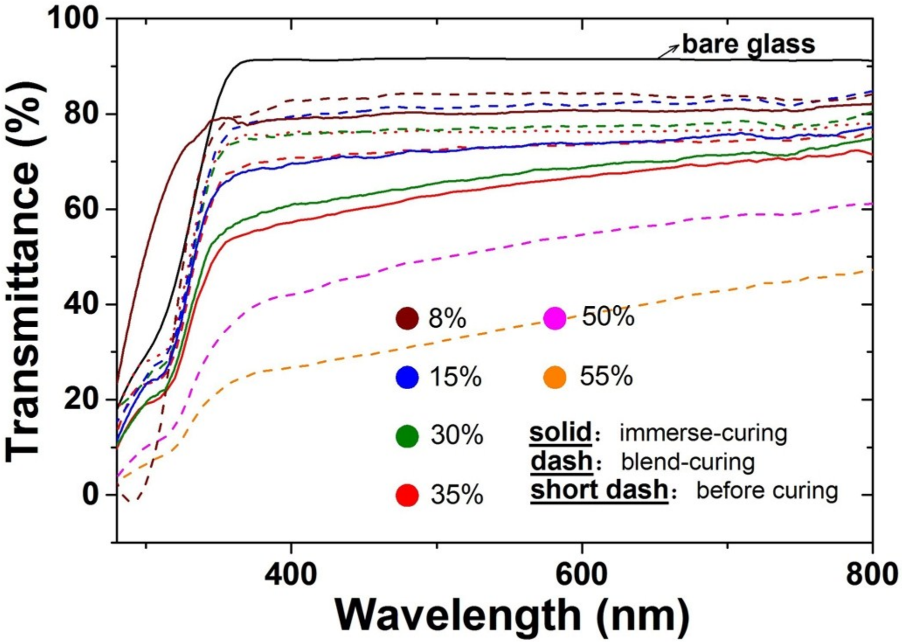

Fig. S3 Transmission spectra of different PVA/SiO_2-coated glasses.

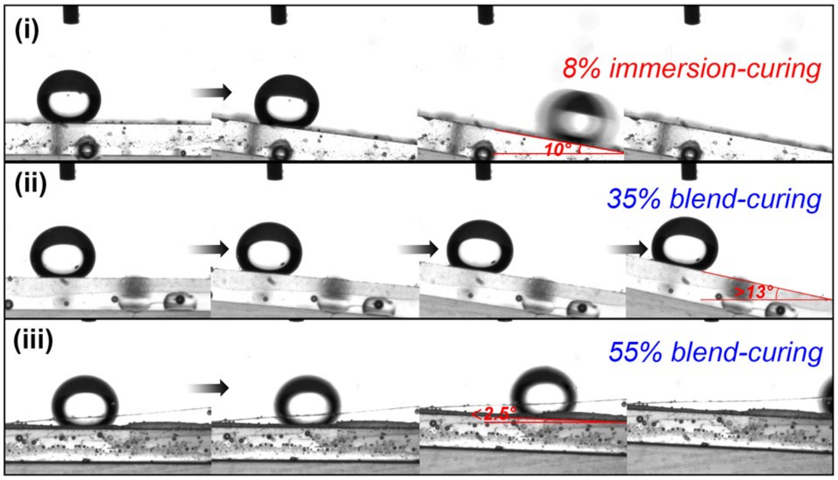

Fig. S4 Underwater sliding angles of CCl_4 droplets on (i) PVA/SiO_2/8-GA(*ic*) (from Movie S7), (ii) PVA/SiO_2/35-GA(*bc*) (from Movie S8), and (iii) PVA/SiO_2/55-GA(*bc*) (from Movie S9) coatings.

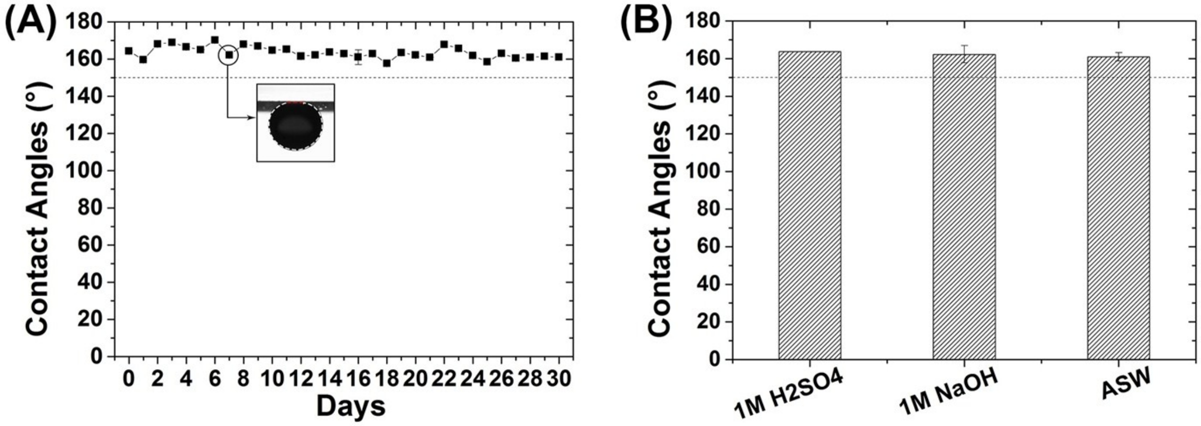

Fig. S5 Underwater crude oil CAs of the PVA/SiO_2/35-GA(*ic*) coatings immersed in (A) DI water (30 days), and (B) 1 M H_2SO_4 (1 h), 1 M NaOH (1 h), artificial sea water (ASW) (5 days).

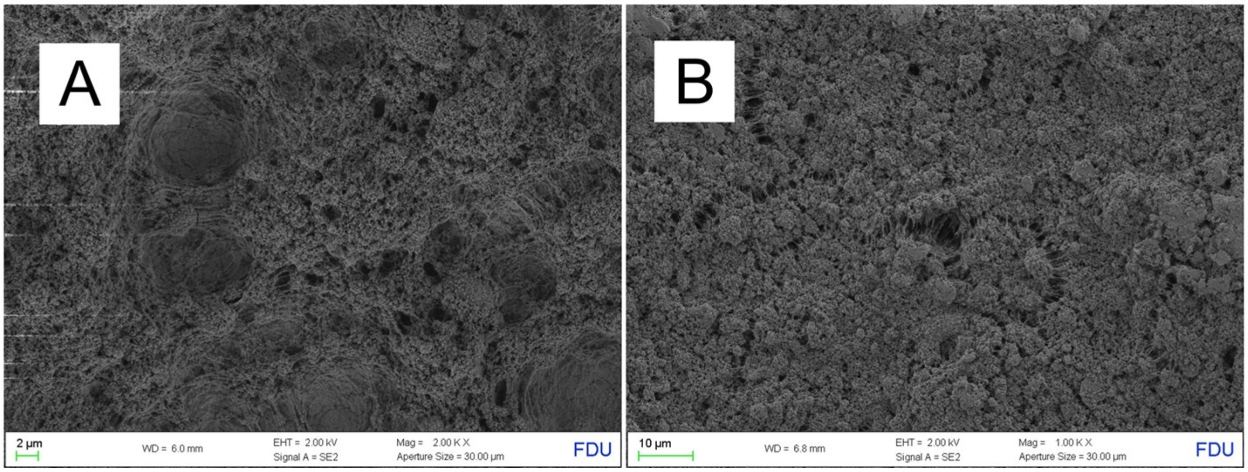

Fig. S6 SEM images of uncrosslinked PVA/SiO_2 coatings with the silica content of (A) 55%; (B) 60%.

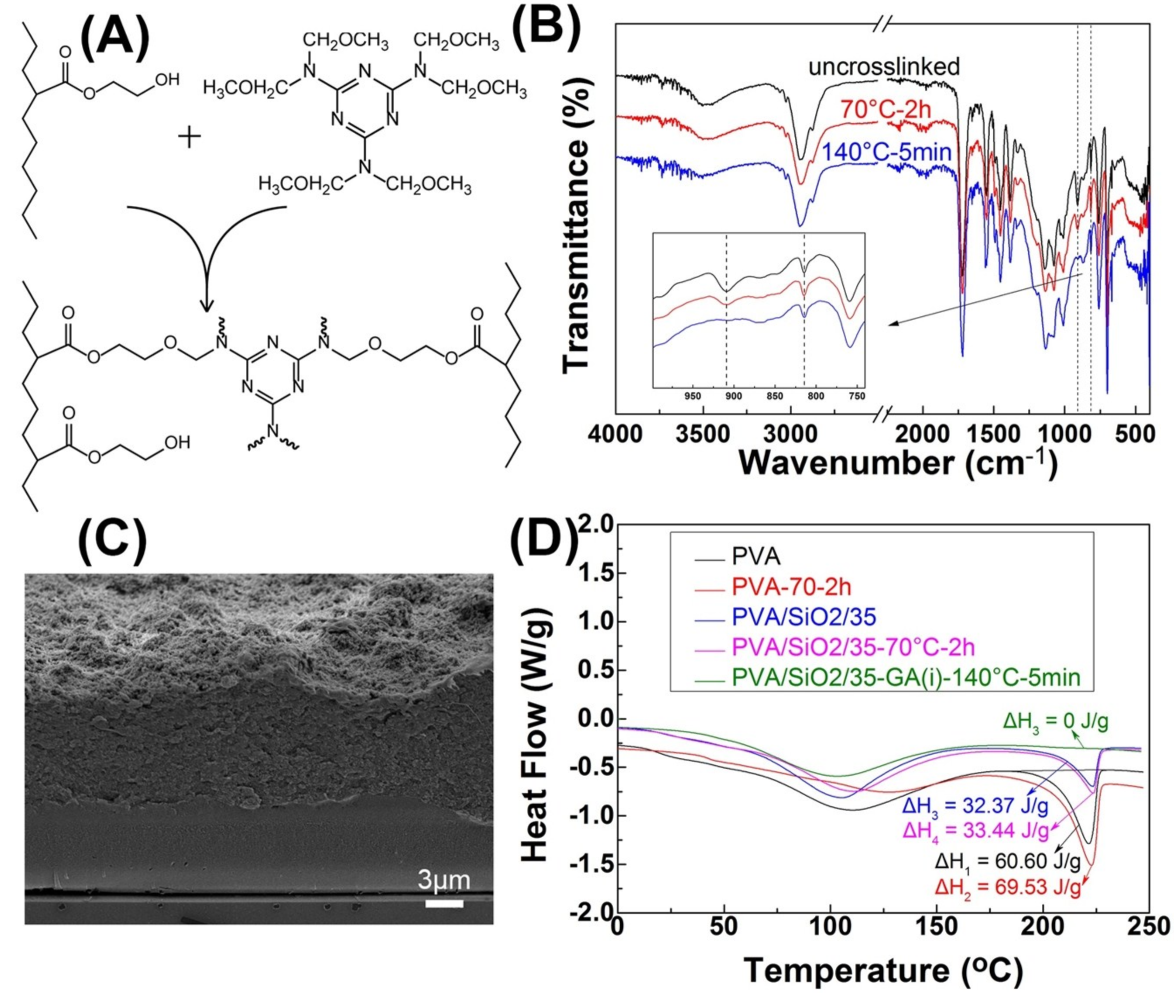

Fig. S7 Characterizations of the acrylic/melamine base-coat. (A) Schematic reaction of the acrylic/melamine coatings. (B) FTIR spectra of the base coats after undergoing different thermal treatments. (C) SEM cross-section image of the double-layer structure with the PVA/SiO_2/35-GA(*ic*) coating on top. (D) DSC curves of five coatings, i.e. pure PVA before, and after thermal treatment under 70 °C 2h, uncrosslinked PVA/SiO_2/35 films before, and after thermal treatment under 70 °C 2 h, and PVA/SiO_2/35-GA(*ic*) after 140 °C for 5 min, during the 1st heating cycle.

The obvious decrease in intensity of -OH oscillations at around 3500 cm^{-1} (Fig. S7B) elucidated the increasing extent of crosslinking degree with the increasing temperatures at the two curing stages. Indicative of the degree of crosslinking, the intensity of the 910 cm^{-1} band (the CH_3-O normal deformation vibrations of the melamine molecules) decreased with the increase in temperatures, after being normalized to that at 815 cm^{-1} due to the unchanging triazine ring vibrations (inset of Fig. S7B),[1] and the treatment under 140 °C for merely 5 min witnessed a complete depletion of this peak.

Note that the hydroxyl acrylic resins were intentionally over-dosed, as is evidenced by the weak yet visible band at 3500 cm^{-1} after complete crosslinking. This was done on purpose to avoid severe shrinkage induced by high crosslinking density on one hand, and on the other to ensure the spread of aqueous solution of the top coat.

The relaxation in the temperature range of 175–240 °C (Fig. S7D) is caused by the melting of the crystalline domains of PVA, whose enthalpy is characteristic to the degree of crystallinity (Xc) of the entire top layers. The Xc of a pure PVA film changed from 37.6% to 43.2% while that of PVA/SiO_2/35 film remained stable from 20.1% to 20.8%, according to Equation S1, where ΔHn is the melting enthalpy of the specimens from Fig. S7D and 161 J g^{-1} is the standard enthalpy when PVA is 100% crystalized. This results indicates that such mild heating environment did not take much effect in the silica-containing PVA films, even though 2 h treatment under 70 °C did promote the crystallinity of the pure uncrosslinked PVA dry films.[2-4]

$$X_c = \frac{\Delta H_n}{161\, J/g} \times 100\% \qquad \text{(S1)}$$

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