Supporting information:

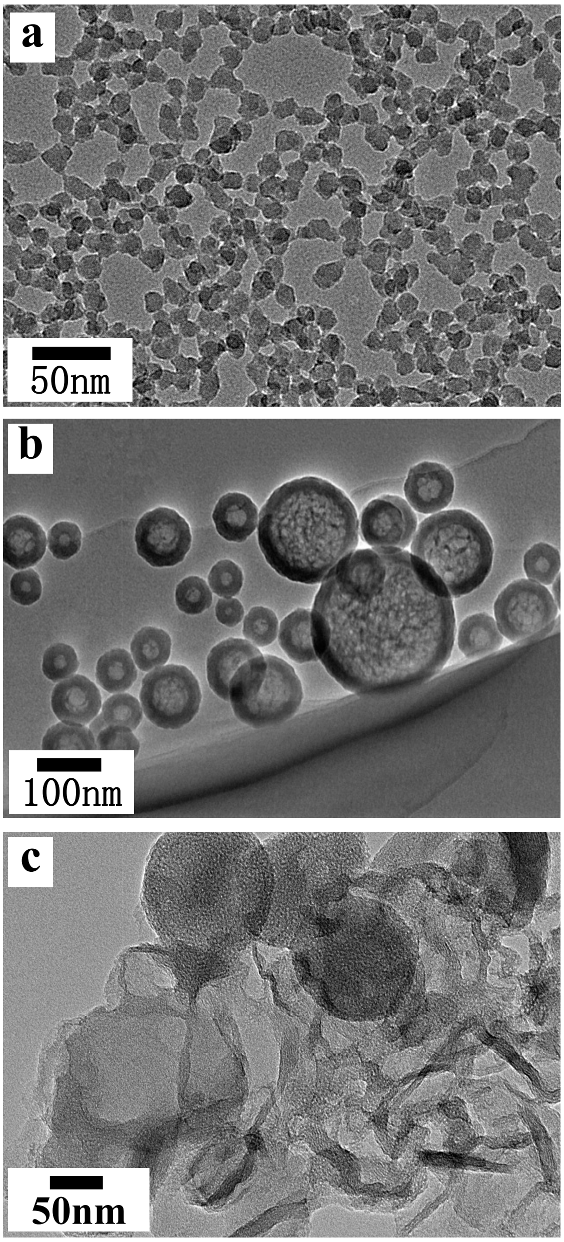

Figure S1 TEM images of 20 nm silica nanoparticles (a), 80 nm hollow silica nanospheres (b) and mesopore silica nanosheets (c).

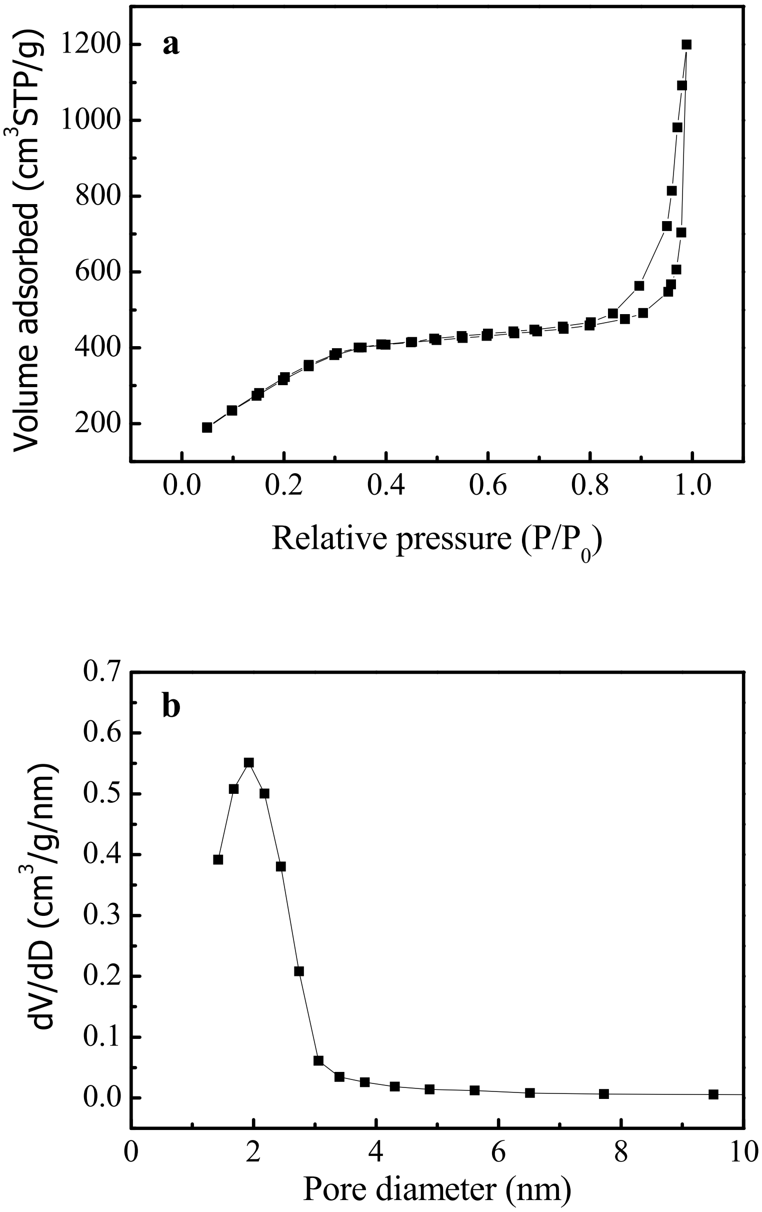

Figure S2 (a) Nitrogen adsorption-desorption isotherms of S’’ and (b) corresponding pore size distribution obtained from the adsorption branch.

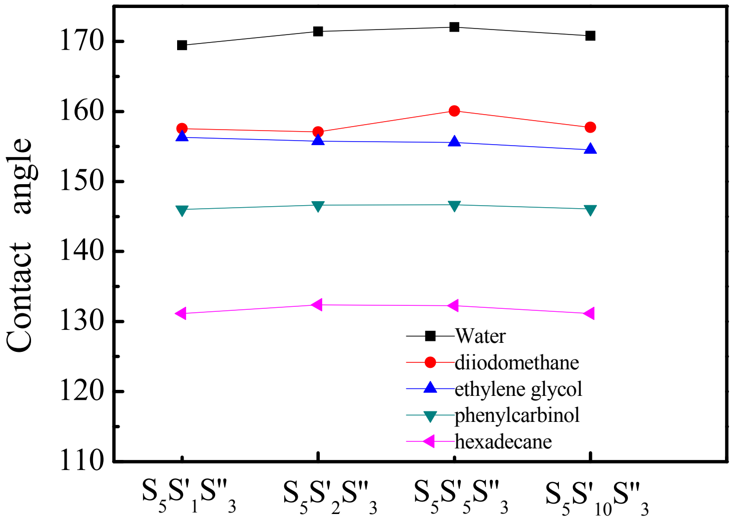

Figure S3 Contact angles of different liquids on different coatings.

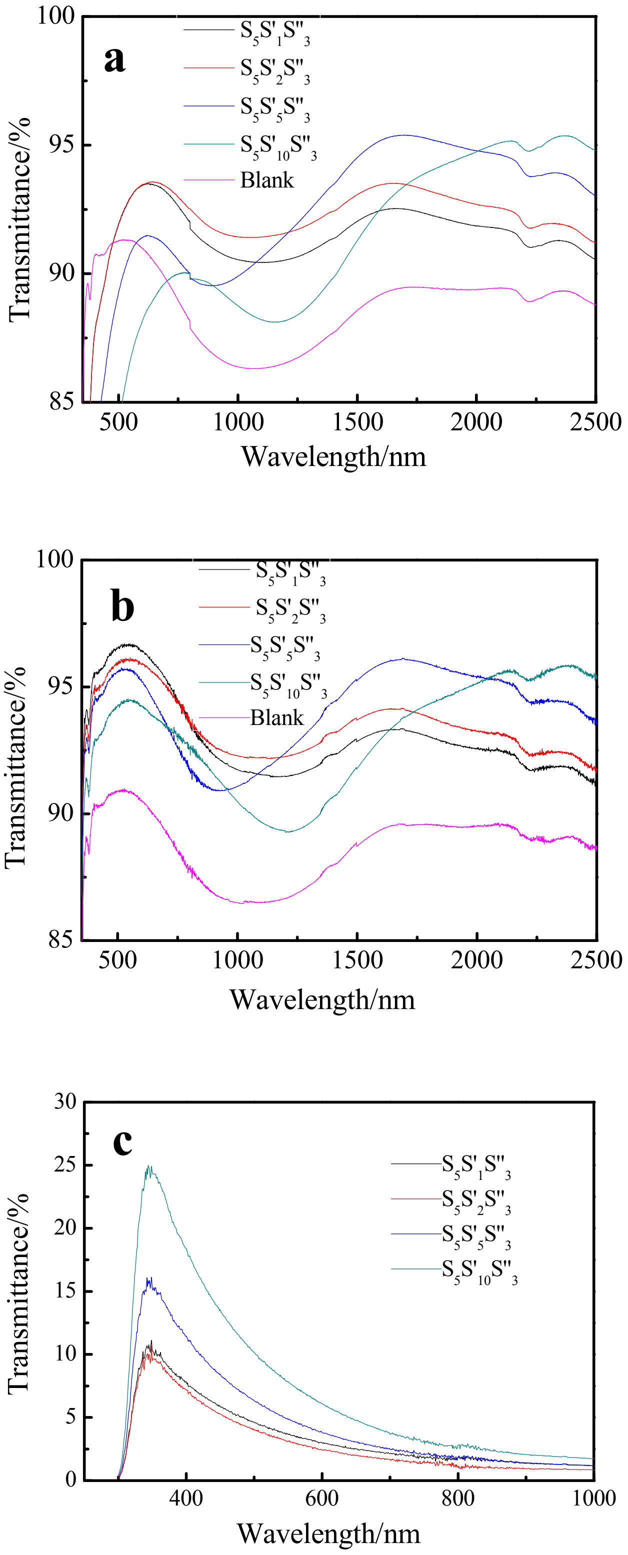

Figure S4 UV-Vis-NIR transmission spectra of different coatings recorded by (a) the conventional mode and (b) the integrating-sphere mode, respectively. (c) is the scattered transmission spectra of different coatings.

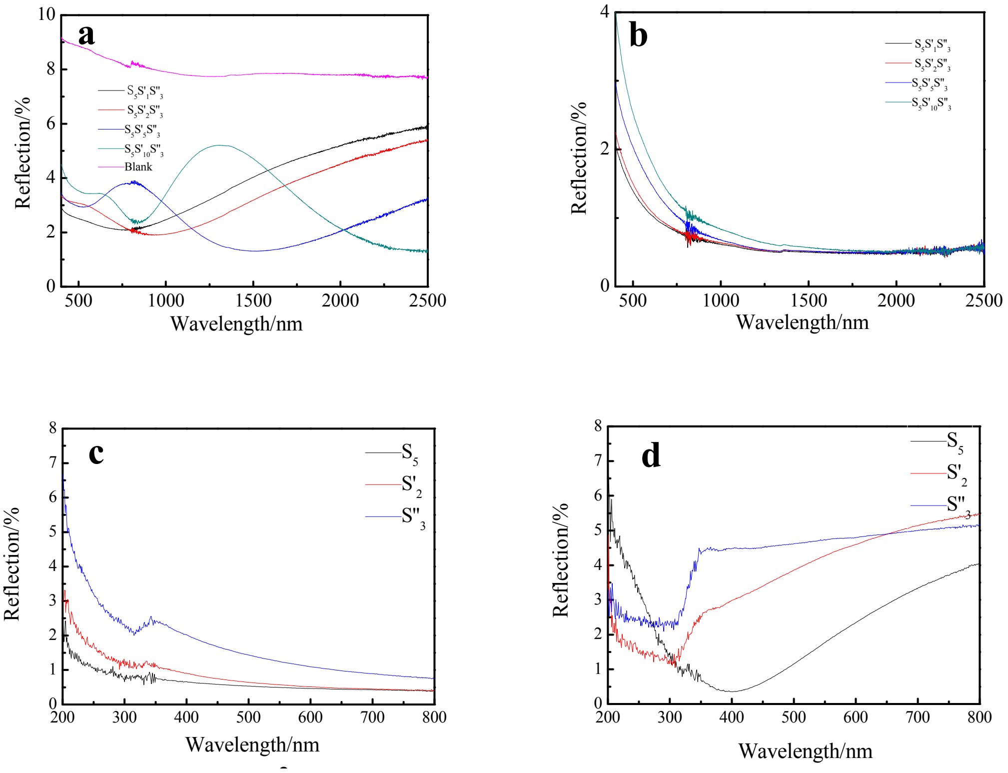

Figure S5 Total reflection (a) and scattered reflection (b) spectra of different coatings, scattered (c) and mirror (d) reflection spectra of S_5, S'_2, and S''_3 coatings.

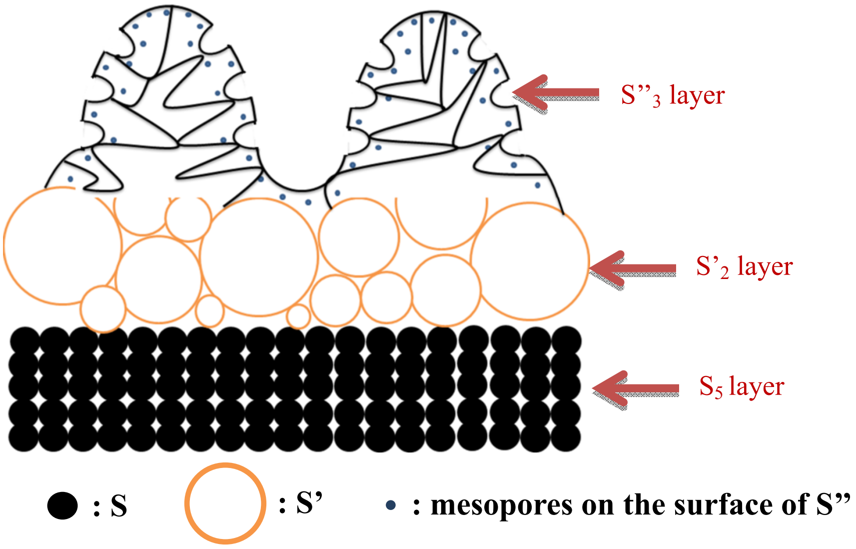

Figure S6 Schematic drawing of the $S_5S'_2S''_3$ coating.

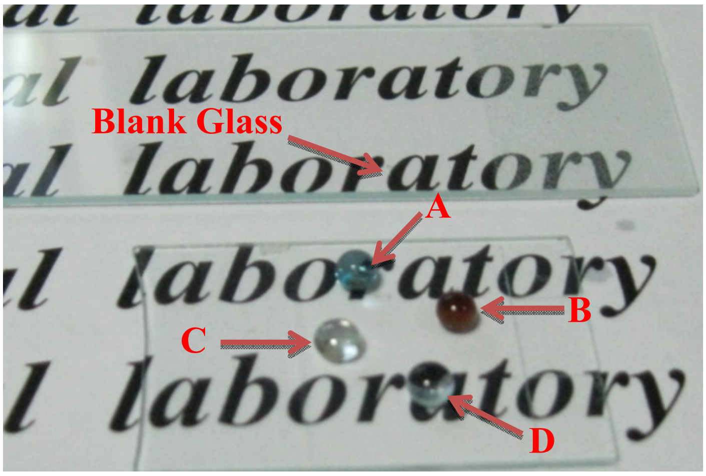

Figure S7 Digital image of the $S_5S'_2S''_3$ coating with water (A), ethylene glycol (B), diiodomethane (C) and hexadecane (D) droplets on its surface.

S I :

Experimental

Materials.

Tetraethyl orthosilicate (TEOS, 99+ %), sodium poly(4-styrenesulfonate) (PSS, Mw=70000) and 1H,1H,2H,2H-perfluorooctyltrichlorosilane ($CF_3(CF_2)_5CH_2CH_2SiCl_3$, PFTS) were obtained from Alfa Aesar. Poly(diallyldimethylammonium chloride) (PDDA, Mw=200000–350000, 20wt%) was purchased from Aldrich. Cetyltrimethylammonium bromide (CTAB, ≥ 99%), aqueous ammonia (25%), absolute ethanol (99.5%) and ethyl ether (≥99.5%) were purchased from Beihua Fine Chemicals. Poly(acrylic acid) (PAA, 30wt% in water, Mw=5000) was purchased from Shandong Heli water treatment company. Ultrapure water with a resistivity higher than 18.2 MΩ·cm was used in all experiments and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

Preparation of Varied Silica Nanoparticles.

Synthesis of 20 nm silica nanoparticles: 100 mL absolute ethanol (99.5%) and 5 mL aqueous ammonia (25%) were mixed in a round-bottomed flask with stirring. Then the flask was placed in a 60^{o}C water bath. 3 mL TEOS was added in the mixture when the temperature became stable. After stirring for additional 12 h, silica nanoparticles of ca. 20 nm were obtained, which are denoted as S.

Synthesis of 80 nm hollow silica nanoparticles: 0.98 g PAA dissolved in 4.5 mL aqueous ammonia was mixed with 90 mL absolute ethanol, followed by injection of 5 aliquots of TEOS totaling 2.25 mL over a time interval of 50 min under vigorous magnetic stirring at room temperature. After 10 h, 80 nm hollow silica nanoparticles formed, which are denoted as S'.

Synthesis of mesoporous silica nanosheets: 0.5 g CTAB was dissolved in a mixture composed of 70 mL water, 0.8 mL aqueous ammonia, and 20 mL ethyl ether. After the emulsion system was vigorously stirred at room temperature for 0.5 h, 2.5 mL of TEOS was quickly dripped into the mixture. The resulting mixture was vigorously stirred at room temperature for 4 h, and a white precipitate was obtained, filtered, washed with pure water, and dried in air at 60° C for 24 h. After calcination of the as-obtained product in air at 550°C for 5 h to remove CTAB and other organic components in the product, mesoporous silica nanosheets were eventually obtained, which are denoted as S''.

Thin Film Assembly.

Slide glass was used as substrate. First, the substrate was washed with ultrapure water and cleaned by oxygen plasma for 5 min. Second, the cleaned substrate was alternately dipped in PDDA and PSS solutions for 5 min, and redundant polyelectrolytes were removed by shaking in pure water for 2 min and rinsing for 1 min, followed by drying with N_2 flow. The concentrations of PDDA and PSS aqueous solutions were 2 mg mL^{-1}. A multilayers thin film of $(PDDA/PSS)_5/PDDA$ was prepared, and was used as a primer in all experiments. Third, the $(PDDA/PSS)_5$/PDDA-covered substrate was alternately dipped in varied silica nanoparticles (S, S', and S") suspensions (0.4wt%) and a PDDA solution (2 mg mL^{-1}) by the same procedure for an appropriate number of cycles. Finally, the as-prepared coatings were calcinated (heating rate: 1 K min^{-1}) at 550°C for 3 h to remove the polyelectrolytes and other organic components.

Amphiphobic Modification of Coatings.

Amphiphobic modification of the coatings surface was carried out by a simple chemical vapor deposition (CVD) of PFTS. The glass substrate with assembled silica nanoparticles coatings on both sides was treated by oxygen plasma for 10 min, placed in a Teflon container, on the bottom of which was dispensed a few droplets of PFTS, and sealed by stainless steel autoclave. There was no direct contact between the substrate and the PFTS droplets. The autoclave was put in an oven at 120°C for 2 h to enable the vapor of PFTS to react with the hydroxyl groups on the coating surface. Finally, the autoclave was opened and placed in an oven at 150°C for an additional 1.5 h to volatilize unreacted PFTS molecules on the coating.

Characterization.

For transmission electron microscopy (TEM) observations, powder samples were added on carbon-coated copper grids and observed on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. Freshly fabricated coatings were examined by scanning electron microscopy (SEM) on a Hitachi S-4300 scanning electron microscope operated at 10 kV. Nitrogen adsorption-desorption measurements were carried out on a QuadraSorb SI automated surface area and pore size analyzer. Contact angles of different liquids on fabricated coatings were measured at ambient temperature on a Kino SL200B3 automatic contact angle meter. Transmission spectra in the wavelength range of 300–2500 nm were recorded using a Varian Cary 5000 UV/Vis-NIR spectrophotometer. Transmission and reflection spectra in the wavelength range of 300–2500 nm were also recorded using an integrating-sphere attachment on Varian Cary 5000 UV/Vis-NIR spectrophotometer.

SⅡ: Estimation of refractive index and porosity for S_5, S'_2 and S''_3 coatings.

The method to estimate the refractive index of coatings is based on the formula $n_{coating} = \sqrt{n_{bulk} \times n_{substrate}}$ and $n_{bulk} = \frac{1+\sqrt{R_{min}}}{1-\sqrt{R_{min}}}$, in which $n_{coating}$ is the refractive index of coating only, n_{bulk} represents the refractive index of coating and substrate, $n_{substrate}$ is the refractive index of substrate and the R_{min} stands for the minimum mirror reflection of coating.[1]

Thus, the minimum mirror reflection of coating should be measured to estimate the refractive index. The total reflection and scattered reflection of S_5, S'_2, S''_3 coatings were measured using an integrating-sphere attachment, and the total reflection minus the scattered reflection gave the mirror reflection of coating (Figure S5d). The minimum mirror reflection is 0.35% at 401 nm for the S_5 coating, 1.11% at 304 nm for the S'_2 coating, and 2.09% at 290 nm for the S''_3 coating, respectively. Thus, the refractive index was estimated to be 1.30 for the S_5 coating, 1.36 for the S'_2 coating and 1.41 for the S''_3 coating, respectively.

The formula $n = 1.49(1 - x) + x$ was used to estimate the porosity of these coatings, where n is the refractive index of coating, and x is the porosity of coating.

For the S'$_2$ coating, a modified formula $n = 1.49(1-x)(1-\frac{D_1}{D_2})^3 + (1-x)(\frac{D_1}{D_2})^3 + x$ was derived and used, where D$_1$ represents the mean inner diameter and D$_2$ represents the mean sphere diameter. Based on Figure S1b, D$_1$ was measured to be 44.79 nm, and D$_2$ was measured to be 80.17 nm. As a result, the porosity was estimated to be 39% for the S$_5$ coating, 10% for the S'$_2$ coating and also 10% for the S''$_3$ coating, respectively.

Reference

1. L. Xu, L. Gao and J. He, *RSC Adv*., 2012, **2**, 12764