

Supporting Information

Multifunctional Polypyrene/Silica Hybrid Coatings with Stable Excimer Fluorescence and Robust Superhydrophobicity Derived from Electrodeposited Polypyrene Films

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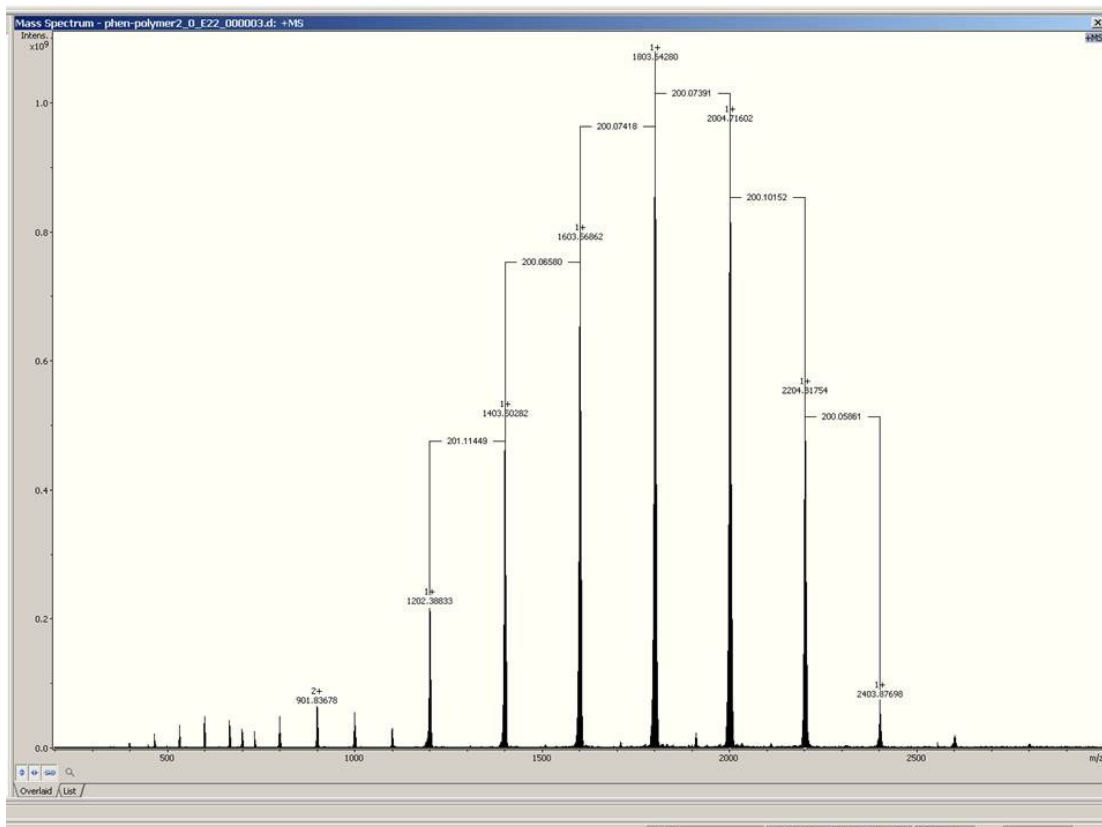


Figure S1. Polymerization degree measurement of the electrodeposited polypyrene film by using a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). As shown in the screenshots, the polypyrene was composed of about 6 ~ 11 pyrene units.

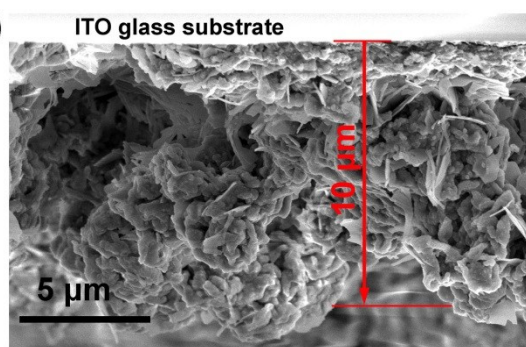


Figure S2. Cross-sectional SEM image of the FPSH film showing the inner porosity and a sheet-like structure. The film thickness was approximately equal to 10 μm .

Silica layer thickness

Unfortunately, the covered silica layer on the polypyrene film could not be detected directly in the SEM image, and its thickness is not known. This may be due to the fact

that the silica layer created by CVD only had a nanoscale dimension in thickness, leading to a lower differentiation. Inhere, we provide evidence of the presence of the silica layer in the FPSH film via an indirect method, namely, annealing the FPSH film at 500 °C in air for 2 h. To remove the polypyrrole from the FPSH film and assess the thickness of the silica layer, the FPSH film was calcinated at 500 °C for 2 h in air. After calcination, a white silica coating was observed on the annealed FPSH film, while its original yellow color faded completely because of the polypyrrole combustion (Figure S3(a) (top)). For comparison with the FPSH film, the polypyrrole film was annealed also in the same conditions. The polypyrrole film on the ITO glass substrate disappeared after annealing (Figure S3(a) (bottom)). The cross-sectional SEM image of the silica coating shows several irregular holes that were initially filled with polypyrrole film (Figure S3(b)). The thickness of the silica layer was estimated to be ca. 30 ~ 40 nm. The Energy Dispersive Spectrometry (EDS) analysis shows the chemical composition of the resulting silica coating on ITO glass after annealing (Figure S3(c)).

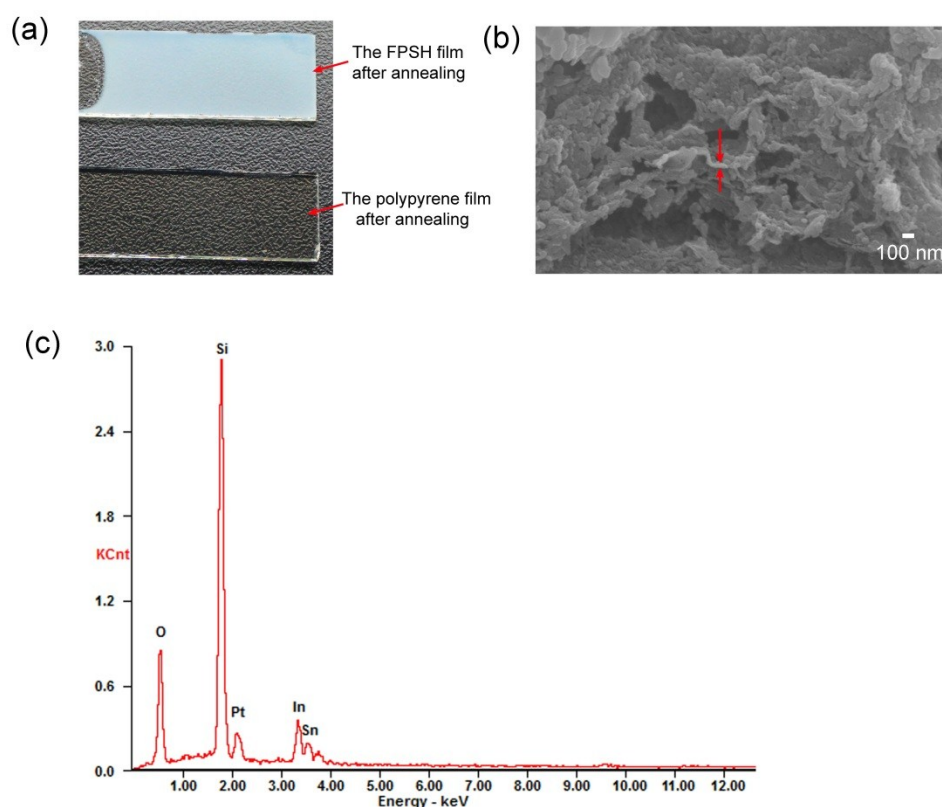


Figure S3. (a) Photographs of the FPSH film and the polypyrrene after annealing at 500 °C for 2 h in air. (b) Cross-sectional SEM image of the silica coating showing several irregular holes initially filled with polypyrrene film; the thickness of the silica layer is ca. 30 ~ 40 nm. (c) Energy Dispersive Spectrometry (EDS) of the resulting silica coating on ITO glass.

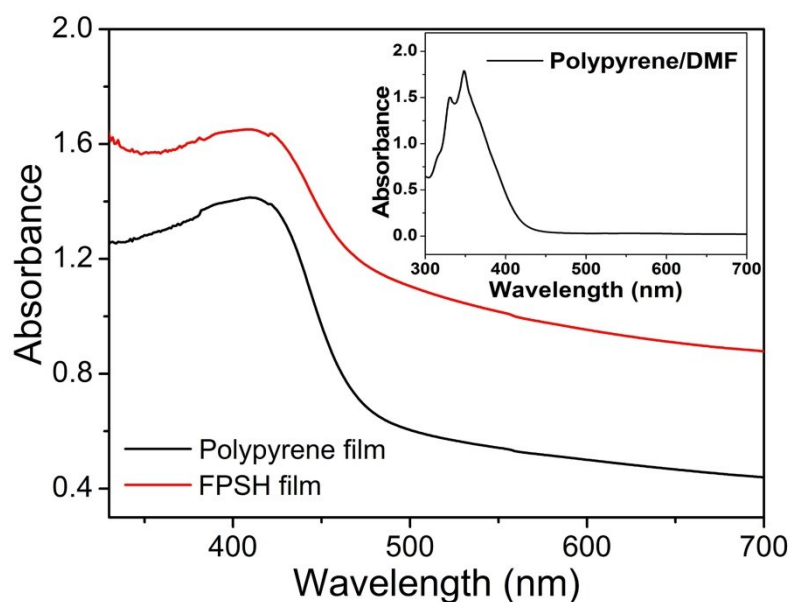


Figure S4. UV-vis measurements of the polypyrrene film (black line) and the FPSH film (red line). Inset: UV-vis spectrum of polypyrrene dissolved in DMF.

The excimer emission

The excimer emission originated from the solid polypyrrene film was evidenced by the fact that the significant red-shift of the excitation and emission spectra of the solid polypyrrene film can be observed when compared with that of polypyrrene/DMF solution (see Figure 3a and b). The shape and maximum position of the excimer emission band of the polypyrrene film were not affected significantly by changing the electrodeposition charge of the polypyrrene films from 105.3 to 406.7 mC cm⁻² which correspond to the film thickness (Figure S5). However, the lower electrodeposition charge of the polypyrrene film (such as 15.8 mC cm⁻²) showed a slight blue-shift with a wavelength of about 482 nm. Conversely, the fluorescence could be quenched obviously if the polypyrrene film was prepared with greater electrodeposition potential

(such as constant potential of +2.0 V) which could lead to greater polymerization degree of pyrene (Figure S6).

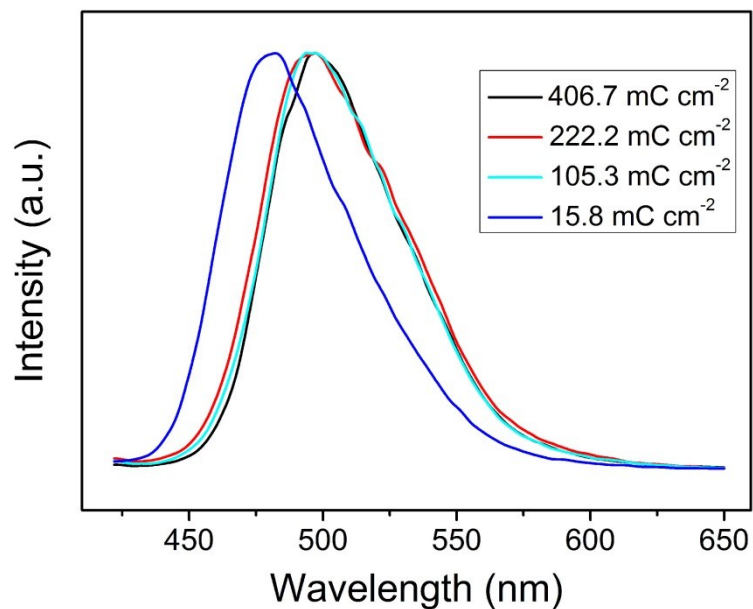
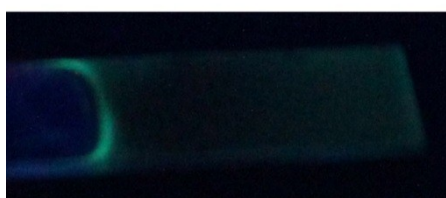


Figure S5. The fluorescence spectra of the polypyrene films prepared with the electrodeposition charge of the 15.8, 105.3, 222.2, and 406.7 mC cm⁻², respectively. When the electrodeposition charge is above 105.3 mC cm⁻², there are no obvious changes in the maximum position of the emission with the increase of the electrodeposition charge.



The polypyrene film prepared with constant potential of 2.0 V



The prepared polypyrene film under UV of 365 nm

Figure S6. The polypyrene film was prepared with constant potential of +2.0 V (top) which could lead to greater polymerization degree of pyrene, and such polypyrene film presents the very weak

fluorescence.

Microcrystalline oligopyrene

As shown in a few previous reports,^[22,24] the electrodeposited polypyrene film usually has a low polymerization degree. In our case, the oligopyrene film contains several microcrystalline structures, as verified by a good progression of diffraction peaks appearing at 2θ angles of 5.7° , 11.4° , and 16.6° in the wide angle X-ray diffraction (XRD) pattern (Figure S7(a) (bottom)). The transmission electron microscopy (TEM) image illustrates a smooth sheet-like morphology (Figure S7(b)). The microscopic electron diffraction (ED) pattern presents a series of bright diffraction rings and spots (inset in Figure S7(b)), further confirming the multicrystalline nature of the oligopyrene.^[22,24,27]

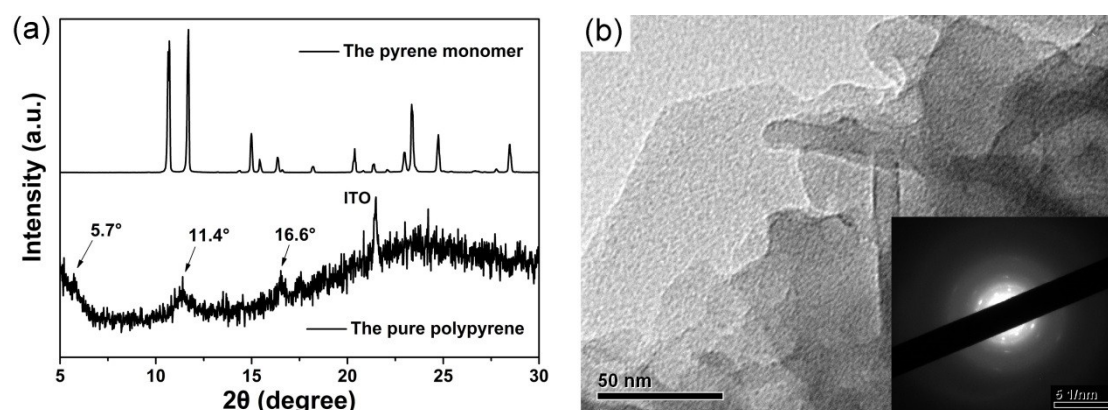


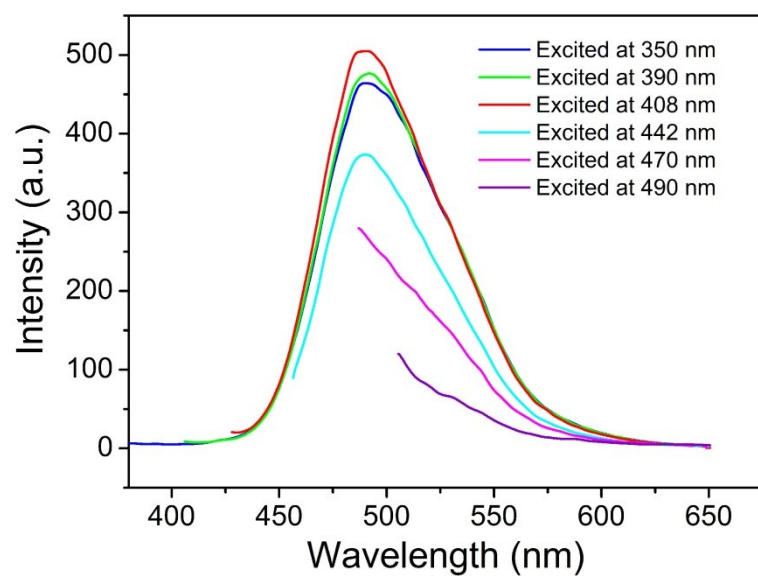
Figure S7. Microcrystalline oligopyrene. (a) X-ray diffraction (XRD) patterns of the pyrene monomer (top), and the pure polypyrene film (bottom) showing a good progression of diffraction peaks at 2θ angles of 5.7° , 11.4° , and 16.6° . (b) Transmission electron microscopy (TEM) image of the pure polypyrene film showing a smooth sheet-like morphology. Inset: microscopic electron diffraction (ED) pattern of the polypyrene showing a series of bright diffraction rings and spots.

The fluorescence emission and the excitation wavelengths

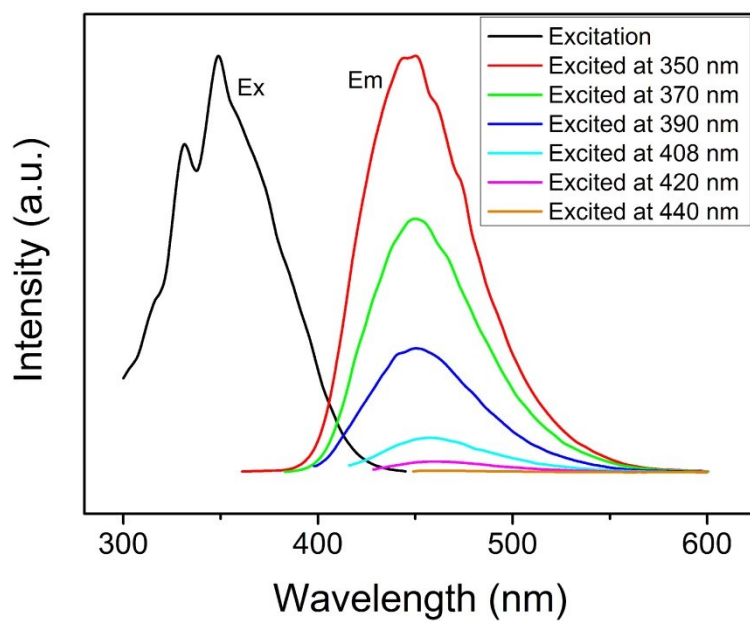
The emission spectra of the FPSH film excited at different excitation wavelengths (350, 390, 408, 442, 470 and 490 nm, respectively) was also measured. As shown in Figure S8, when exciting the FPSH film at the wavelength of 350, 390, 408 and 442

nm, the broad excimer emissions centered at about 491 nm can be observed. Notably, the shape and the maximum position of the excimer emission band were not obviously affected by the excitation wavelengths. When excited at wavelength of 470 and 490 nm, the film still presents the fluorescence emission (the emission bands were from 490 to 625 nm and from 505 to 625 nm, respectively) within the excimer emission range. This means the different fluorescence color can be observed when excited the film with different excitation wavelength. This result could be attributed to the wide-range UV/vis absorption in solid polypyrene (see Figure S4).

The polypyrene presents the different UV/vis absorption in its solid and in its solution. The excitation spectrum of the solid polypyrene ($\lambda_{em} = 498.5$ nm) is also different from that of polypyrene/DMF solution ($\lambda_{em} = 451.5$ nm), as shown in Figure 3a and b. The fluorescence spectra of the polypyrene in DMF solution were also measured by exciting the sample at various wavelengths of 350, 370, 390, 408, 420 and 440 nm, respectively (Figure S9). The fluorescence intensity has a significant decrease with the increase of the excitation wavelength, but the shape and the maximum emission peaks position are not obviously affected, apart from that the maximum emission peaks excited at about 450 to 454 nm have a slight red-shift. This result corresponds to the great decrease in the UV/vis absorption of the polypyrene dissolved in DMF above the wavelength of 350 nm. Therefore, the fluorescent emission spectra of the FPSH film are different from that of polypyrene/DMF solution when exciting them with the same excitation wavelength, such as 350 and 408 nm. Their maximum emission wavelength could be determined by either the polypyrene emission or the excimer emission. There was no obvious effect of different excitation wavelengths on their emission bands.



Figurer S8. The fluorescence spectra of the FPSH film excited at the wavelength of 350, 390, 408, 442, 470 and 490 nm, respectively.



Figurer S9. The fluorescence spectra of the polypyrrene dissolved in DMF excited at the wavelength of 350, 370, 490, 408, 420 and 440 nm, respectively.

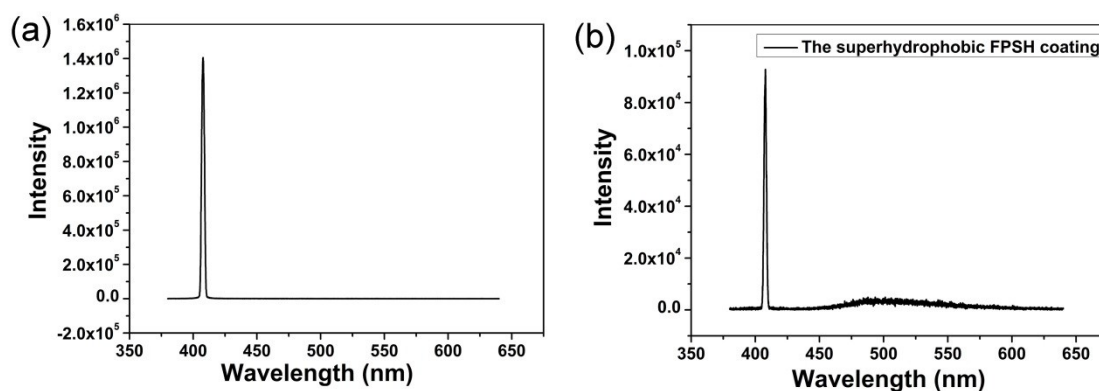


Figure S10. Absolute fluorescence quantum yield measurement of the superhydrophobic FPSH film. The emission spectra of (a) the blank sample and (b) the superhydrophobic FPSH coating under 408 nm excitation light.

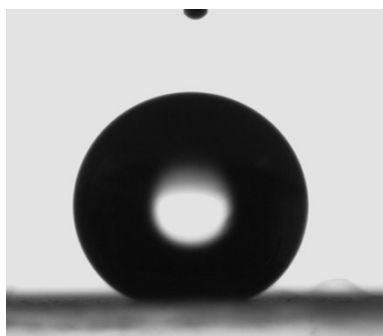


Figure S11. WCA measurement of the FPSH film after water drop impact (radius of 2.1 mm) from a height of 6 cm at a dropping rate of one droplet per second for more than 12 h. The WCA is ca. $153.9^\circ \pm 1^\circ$.

Hydraulic Pressure Resistance

Critical transition pressure (P_c) is an important parameter to measure the stability of superhydrophobic coatings under hydraulic pressure. If a static hydraulic pressure (P) applied to a superhydrophobic coating exceeds its inherent P_c , the cavities of the rough structure of the coating will be impregnated by water,^[28] which can cause a wetting transition of the coating surface from a Cassie state to a Wenzel state, eventually leading to the disappearance of its self-cleaning properties. To investigate the superhydrophobic stability, the FPSH film was immersed in water ca. 20 cm below the surface (Figure S12). The magnified photograph shows that the FPSH film under water can form a mirror-like reflective interface. This means that under

hydraulic pressure (P_1), the rough structure of the FPSH film can easily trap air to prevent the penetration of water into its cavities. According to the equation $P = \rho gh$ (where P is the water pressure, ρ is the density of water, g is the acceleration of gravity, and h is the water depth from the surface), the value of P_1 can be estimated to be approximately 1.96 kPa. Therefore, the P_c of the FPSH superhydrophobic coating must have a value > 1.96 kPa. In addition, the FPSH coating under water still exhibits a strong fluorescence when exposed to 365 nm UV light. These results demonstrate that the superhydrophobic FPSH film can withstand a significant hydraulic pressure while maintaining its superhydrophobic and fluorescent properties.

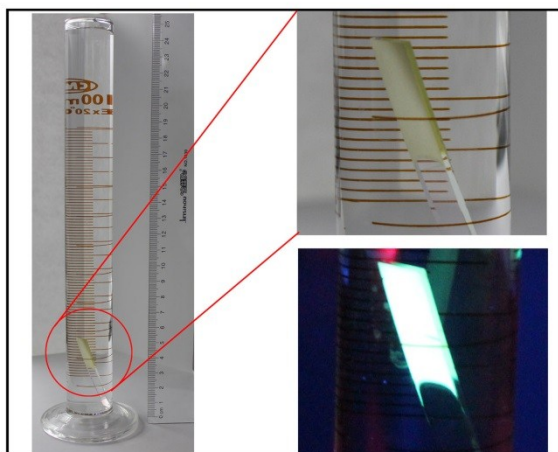


Figure S12. Photograph of a 100-mL measuring cylinder filled with water and a FPSH film on the ITO glass substrate immersed in water ca. 20 cm below the water surface (left). Insets: magnified photograph of the FPSH film under water (top right corner) forming a mirror-like reflective interface; fluorescence photograph in water when exposed to 365 nm UV light (bottom right corner).

Chemical sensing for 4-nitrobenzene chloride

The as-prepared FPSH film is composed of the underlying polypyrrole film and the overlying silica layer. Although the existence of the self-cleaning superhydrophobic silica layers can lead to the separation of the underlying fluorescent polypyrrole layer from the other species in aqueous solutions, the FPSH film can still be used as sensor for the 4-nitrobenzene chloride in the ethanol solution, as shown in the following

Figure S13. It well known that the organic solvents, such as ethanol, have the lower surface-energy than that of water. This means that the other species in organic solutions might get through the superhydrophobic silica layers and contact with the underlying fluorescent layer. As can be seen in the phenomenon in the Figure S13b, the 0.01 M 4-nitrobenzene chloride/ethanol solution (about 20 ~ 30 μL) dripped on the FPSH film prepared on the stainless steel woven wire mesh (100 mesh) can cause the fluorescence quenching (the FPSH film was exposed under ultraviolet light of 365 nm).

However, when the pure polypyrene film without the overlying superhydrophobic silica layers was immersed into the CuSO_4 aqueous solution (many studies reported that the derivants of pyrene displayed the sensing on Cu^{2+}), it still exhibited the strong fluorescence (under UV of 365 nm), as shown in the Figure S14. This result also indicated that the fluorescence of the as-prepared FPSH film possessed a good stability in the water.

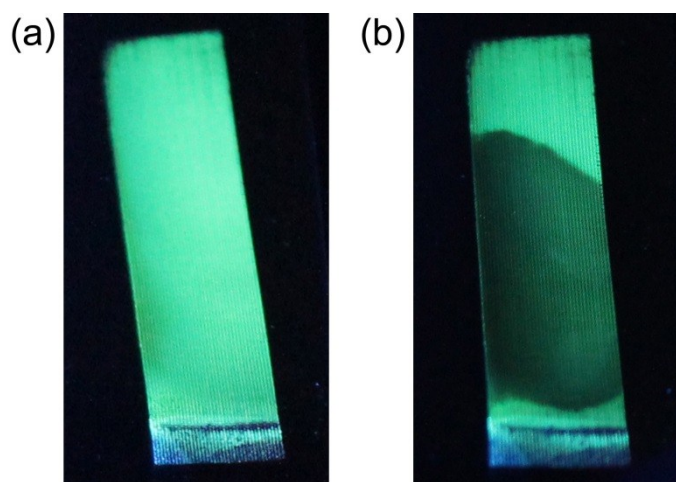


Figure S13. (a) The FPSH film was prepared on the stainless steel woven wire mesh (100 mesh), and it emitted the bright blue-green fluorescence light when exposed under ultraviolet light of 365 nm. (b) After dripping a drop of about 20 ~ 30 μL ethanol solution containing 0.01 M 4-nitrobenzene chloride on the luminous FPSH film, its fluorescence can be quenched obviously.

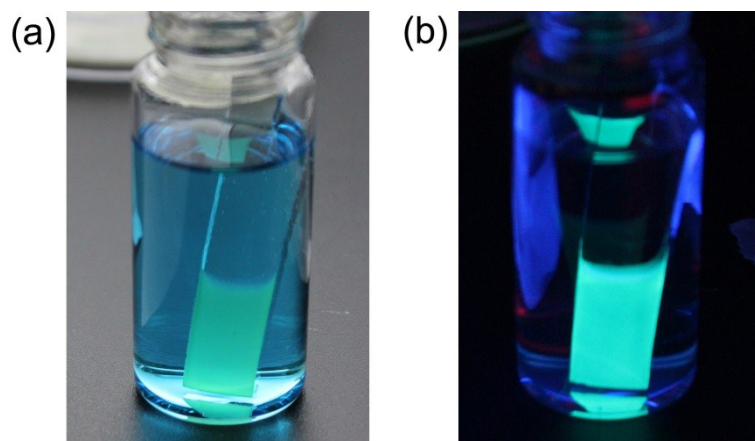


Figure S14. (a) The pure polypyrrole film on the ITO glass substrate was immersed into the CuSO_4 aqueous solution. (b) The polypyrrole film emitted the bright blue-green fluorescence under ultraviolet light of 365 nm.

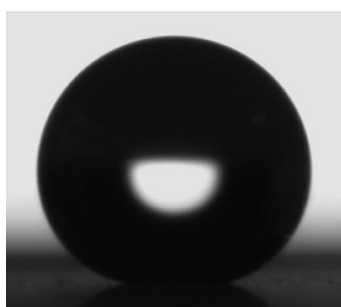


Figure S15. The FPSH-coating plastic transparent ITO-PET film possesses a high WCA of about $160.5^\circ \pm 1^\circ$.

Movie S1. The 4- μL water droplet dripped on the FPSH film surface with a small tilt angle of about 4 degree can roll off rapidly the surface.

Movie S2. Lateral movement of the water droplet (4 μL) hanging at the tip of a needle on the surface of the FPSH-enclosing stainless steel woven wire mesh.

Movie S3. The video of the water droplets (20 ~ 30 μL) dripping on the surface of the FPSH-enclosing stainless steel woven wire mesh. The water droplets do not be stuck but roll off rapidly the surface.

Movie S4. The video of the water droplets (20 ~ 30 μL) dripping on the FPSH-coating plastic transparent ITO-PET film and the water droplets rolling off rapidly the FPSH film surface, leaving the surface dry.