

Constructing Versatile Hydrophilic Surfaces via *in-situ* Aminolysis^①

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ABSTRACT Surface hydrophilization is required for numbers of applications such as biosensor, biomedical implants and marine coating. However, the preparation of hydrophilic surface from a solid substrate still suffers from limited thicknesses, complex procedures, restricted substrates and harsh conditions. Herein, a method based on *in-situ* aminolysis of poly(pentafluorophenyl acrylate) (pPFPA) capable of generating arbitrary hydrophilic surface is proposed, enabling high design freedom and abundant choices of hydrophilic molecules. Simply immersing pPFPA coated substrates into 3-((3-aminopropyl)dimethylammonio)propane-1-sulfonate (ADPS), β -alanine and amine-terminal poly(ethylene glycol) (NH₂-PEG) solutions for two hours drastically reduces the water contact angle of the corresponding surfaces, indicating the high efficiency and excellent generality of such method. Systematical studies reveal that these coatings are able to mitigate fog formation, self-clean the oil contaminant and exhibit excellent antifouling performance against algae. Notably, relying on the fast and quantitative feature of the aminolysis, these hydrophilic surfaces possess excellent regeneration capability and well-recover their hydrophilic feature after being physically damaged. This work represents a facile and universal way to fabricate versatile hydrophilic surfaces for multi-functional applications such as self-cleaning, patterning, sensing, antifogging and anti-biofouling.

Keywords: surface hydrophilization, *in-situ* aminolysis, antifogging, self-cleaning, antifouling, regeneration;

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1 INTRODUCTION

Antifouling coatings have played crucial roles in the field of biosensors^[1, 2], biomedical implants^[3, 4], and especially marine coatings^[5, 6]. To prevent marine organisms growing and residing on the surfaces, three types of coatings are mainly employed, including fouling resisting coating, fouling releasing coating and biocides releasing coating^[7]. Among these, fouling resisting coating based on hydrophilic surface is

particularly attractive as it prevents biofouling *via* forming a robust water-binding layer which is unfavorable for the marine organisms^[8-12], rather than releasing toxic agents. As a result, fouling resisting coating is much more environment-friendly and enables sustainable developments. Further, fouling resisting coating can also efficiently inhibit protein adhesion^[13] and various oil contaminants^[14], rendering the capability for long-term service in complicated environments.

To achieve fouling resisting coating with hydrophilic surfa-

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ces on a variety of substrates, two approaches are frequently used: (1) surface-initiated radical polymerization of hydrophilic monomers. For example, Ishihara *et al.* grafted hydrophilic poly(2-methacryloyloxyethyl phosphorylcholine) from PDMS surface pre-embedded with photo-initiator by surface-initiated photo-induced radical polymerization^[15]; Zhou's group realized a hydrophilic three-dimensional network of PEG from bisphenol A epoxy acrylate primer by UV irradiation^[16]; Zhao and his coworkers prepared hydrogel skin through *in-situ* photo-polymerization of hydrogel monomer on the polymer substrate containing a hydrophobic initiator^[17]. Although this method has been widely used, it still suffers from several disadvantages. For instance, the hydrophobic substrates are hard to be wetted by the hydrophilic monomers, leading to non-uniform surficial modifications. Despite that *in-situ* hydrolysis *via* acid or base could help to alleviate the wetting issue^[18], this approach is only suitable for limited hydrophilic molecules, such as carboxylic derivatives or zwitterions. In addition, the radical polymerization generally requires oxygen-free atmosphere, severely compromising the handleability of such method. (2) self-assembled monolayers (SAMs). SAM possesses a larger number of chains per unit area than most other grafting techniques. Typical examples include PEG-based SAM anchor to the gold surface *via* thiol terminal group and silane-chemistry based SAM formation^[19, 20]. Although SAM has been proved effective, it is only suitable for limited substrates, most of which are noble metals^[21]. Moreover, the resulting hydrophilic layer only has very limited thicknesses, and therefore is susceptible to oxidation^[22, 23], giving rise to poor long-term stability.

Herein, we develop a facile yet efficient approach to hydrophilize targeted substrates based on the *in-situ* aminolysis reaction between poly(pentafluorophenyl acrylate) (pPFPA) and desired alkylamines (*e.g.*, zwitterionic, anionic and neutral hydrophilic amines, Scheme 1a and 1b). As demonstrated by previous reports, pPFPA and its derivatives were often used as a precursor to prepare various functional materials *via* post-modification owing to their fast and quantitative reactions with alkylamines^[24-27]. Nevertheless, to the best of our knowledge, pPFPA used as a primer for hydrophilic coatings *via* post-modification with diverse hydrophilic molecules has been rarely explored. In this work, the substrates coated with pPFPA are immersed into given alkylamine solutions for a certain amount of time, dependent on the demanded thickness of the hydrophilic layer. The fast

and quantitative aminolysis between pentafluorophenyl ester groups and alkylamines allows the replacement of pentafluorophenyl groups with hydrophilic groups, resulting in diverse hydrophilic surfaces with desired functions. To evaluate the generality of such method, three alkylamines including 3-((3-aminopropyl)dimethylammonio)propane-1-sulfonate (ADPS), β -alanine and amine-terminal poly(ethylene glycol) (NH₂-PEG) are employed, respectively. Detailed studies reveal that the resulting hydrophilic surfaces show good transparency, high thermal stability, good antifogging and self-cleaning capabilities. Notably, attributed to the high efficiency of this method, patterned surface hydrophilization could be realized by applying a patterned filter paper containing alkylamine solutions on the surface of substrate, which shows potential applications in anticounterfeiting and data encryption. In addition, by culturing these hydrophilic surfaces in *P. tricornutum* and *N. closterium* suspensions for 5 days, respectively, undetectable algae are observed for these hydrophilic surfaces, indicating their good antifouling feature. Further, we have demonstrated that these hydrophilic surfaces could be regenerated simply by immersing the physically-damaged surfaces into desired amines. This work opens a new door for surface hydrophilization and may find potential applications in numbers of fields including but not limited to sensing, patterning, coating, and data encryption.

2 EXPERIMENT

2.1 Materials

Acryloyl chloride (99%) was purchased from Beijing Ouhe technology Co., Ltd. Propane sultone (99%), azobis(isobutyronitrile) (AIBN, 99%) and di-tert-butyl decarbonate (99%) were purchased from Aladdin (China); β -alanine (99%), 3-dimethylaminopropylamine (99%) and citric acid ($\geq 99.5\%$) were purchased from Macklin Inc.; Benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (Bop, 98%) and pentafluorophenol (98%) were purchased from Jiangsu Aikon Biopharmaceutical R&D Co., Ltd; Bis(benzylsulfanyl)methanethione (98%) was purchased from Shanghai Xushuo Biotech Co., Ltd. Methoxypolyethylene glycols (HO-PEG, $M_w = 350$ g/mol) and 4-dimethylaminopyridine (DMAP, 98%) were purchased from Bide Pharmatech Ltd. Anion exchange resin, FLUORIDE ON AMBERLYST(R) A-26, was purchased from Alfa Aesar Co., Inc. All these materials were used as received unless where

noted.

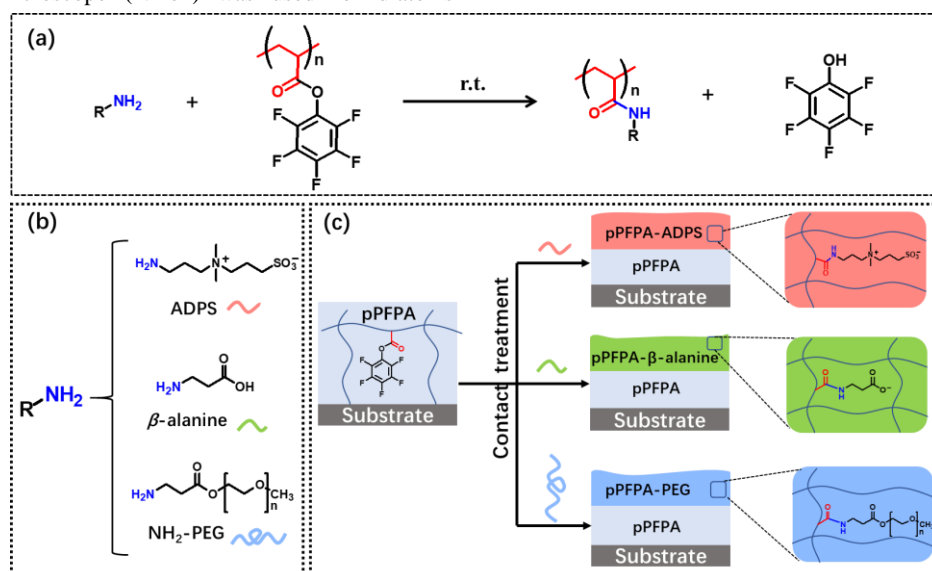
2.2 Characterization

Nuclear Magnetic Resonance (NMR) measurements were performed on a Bruker AVANCE III NMR 400M instruments; Fourier-transform infrared (FTIR) spectroscopy analyses were carried out with a NICOLET iS5 spectrometer (Thermo Fisher Scientific, USA) by attenuated total reflectance (ATR) method; Thermogravimetric Analysis (TGA) measurements were carried out with a Netzsch STA449F3 analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere. The water contact angle (WCA) was measured using a contact angle analyzer (Powereach, China), which uses the micro-lens and camera to obtain the shape of the droplets on the surface of the coating sample, and automatically calculates the contact angle of the droplets with respect to the coating surface. Fluorescence microscope (Nikon) was used for diatoms

observation with a wavelength of 475 nm. We used ImageJ for color addition, as well as brightness and contrast adjustment.

2.3 Preparation of hydrophilic surfaces

Firstly, the crosslinked pPFPA coating with a thickness of 830 ± 250 nm was formed by spin-coating the mixture of pPFPA and 1,3-diaminopropane toluene solution on the substrates that is pre-modified with 3-aminopropyltrimethoxysilane. Next, amine end-functionalized PEG (NH₂-PEG) and ADPS were synthesized and unambiguously characterized by NMR analysis (Scheme 1b and Fig. S1). Finally, the pPFPA coated substrates were immersed in ADPS, β -alanine and NH₂-PEG solutions, respectively, giving rise to three hydrophilic surfaces donated as pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG, respectively (Scheme 1b and 1c).



Scheme 1. Schematic illustration of (a) aminolysis reaction between alkylamine and pPFPA; (b) chemical structures of ADPS, β -alanine and NH₂-PEG, respectively; (c) surface hydrophilization procedure

3 RESULTS AND DISCUSSION

To confirm the success of surface treatment, the resultant coatings are characterized by FTIR-ATR. As shown in Fig. 1a, pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG give new peaks at 3380 and 1654 cm⁻¹, which are assigned to the stretching of amide N-H and C=O, respectively. Meanwhile, the peak at 1787 cm⁻¹ assigned to C=O of ester groups notably attenuates or disappears. Further, ¹⁹F NMR provides additional evidence for the fast reaction between pPFPA and three alkylamines (Fig. S2). The absence of “F1s” peak in X-ray Photoelectron Spectroscopy (XPS) surface analysis for the coatings also confirms the completion of surface modification

(Fig. S3). All these results clearly indicate the successful reaction between pPFPA and alkylamines. TGA indicates that the aminolysis only causes slight impact to the thermal stability of the surfaces (Fig. 1b). It should be noted that all these hydrophilic coatings barely swell in DI water probably due to their highly-crosslinked feature (Fig. S4). The hydrophilization depth is estimated to be around 200 nm according to the capacitance measurements (see supporting information for detail).

Fig. 1c shows the images of the glass substrates coated with pPFPA, pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG on a piece of paper written with Chinese characters, respectively.

The easy observation of the characters through the samples indicates high transparency of the coatings both before and after amine treatment. UV-vis spectra at the transmittance

mode shown in Fig. 1d demonstrate the transmittance of all samples is above 86% from 400 to 700 nm, clearly verifying their high transparency.

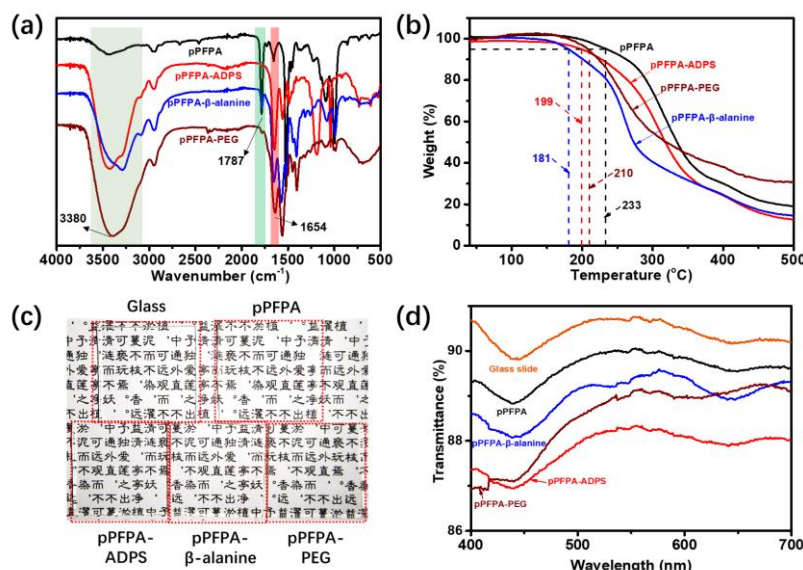


Fig. 1. (a) FTIR-ATR spectra, (b) TGA analysis of pPFPA, pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG, respectively.

(c) Image of the glass substrates coated with pPFPA, pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG on a piece of paper written with Chinese characters. (d) UV-vis spectra at the transmittance mode of glass slide, pPFPA, pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG, respectively

Next, the hydrophilicity of the coatings is measured using a contact angle analyzer. Fig. 2a shows the WCAs of these coatings after 10 hours of immersion in the solutions of ADPS, β-alanine and NH₂-PEG. Owing to high hydrophilicity of the alkylamines, the WCAs are $20 \pm 3^\circ$, $20 \pm 1^\circ$ and $29 \pm 1^\circ$ for pPFPA-ADPS, pPFPA-β-alanine, and pPFPA-PEG surface, respectively. As a control, the WCAs of glass and pPFPA are $60 \pm 1^\circ$ and $95 \pm 2^\circ$. Besides, to monitor the progress of the surface modification, the WCAs of the pPFPA coatings after different immersion time are also measured, as shown in Fig. 2b. It is worth noting that the WCAs of pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG decrease sharply within the first 2 hours, and then slightly decrease from 2 to 10 hours, and are nearly constant from 10 to 20 hours. This demonstrates high efficiency of the surface reaction between pPFPA substrate with ADPS, β-alanine and NH₂-PEG. After 20 hours of soaking, pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG show WCAs of $24 \pm 2^\circ$, $6 \pm 1^\circ$ and $26 \pm 1^\circ$, respectively, which are comparable to the values in the previous reports *via* other approaches^[28, 29]. Considering no obvious additional decreases in WCA after 10 hours, we thus choose the samples with 10 hours' aminolysis for the

following tests.

To further confirm the surface hydrophilicity, we conduct underwater oil contact angles (UWOCAs) measurement for the coatings using dichloroethane droplet. Owing to the robust water binding layer, the dichloroethane droplet cannot adhere to the surfaces of pPFPA-ADPS and pPFPA-PEG, even by the slight press (Fig. 2c, Movie S1 and S3); however, the dichloroethane droplet can easily adhere to the pPFPA-β-alanine surface (Fig. 2c and Movie S2), though their WCAs are comparable. This may be ascribed to the low strength of hydration layer on the pPFPA-β-alanine surface. Moreover, the adhesive force of the oil droplet to pPFPA-PEG is lower than that of pPFPA-ADPS (Fig. 2c), probably due to strong steric repulsion of the long chain of PEG. All pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG express underwater superoleophobicity, and corresponded oil contact angles are $156 \pm 3^\circ$, $156 \pm 3^\circ$ and $152 \pm 5^\circ$, respectively. In contrast, the dichloroethane droplet can easily wet the bare glass substrate and pPFPA surface underwater, and their UWOCAs are $85 \pm 9^\circ$ and $28 \pm 2^\circ$, respectively. These results further verify the successful hydrophilization of surface by the *in-situ* aminolysis approach. It should be noted that this

hydrophilization method is substrate-independent, and a variety of substrates including silicon wafer, plastics, and

metals could be adapted to such method (Fig. S5).

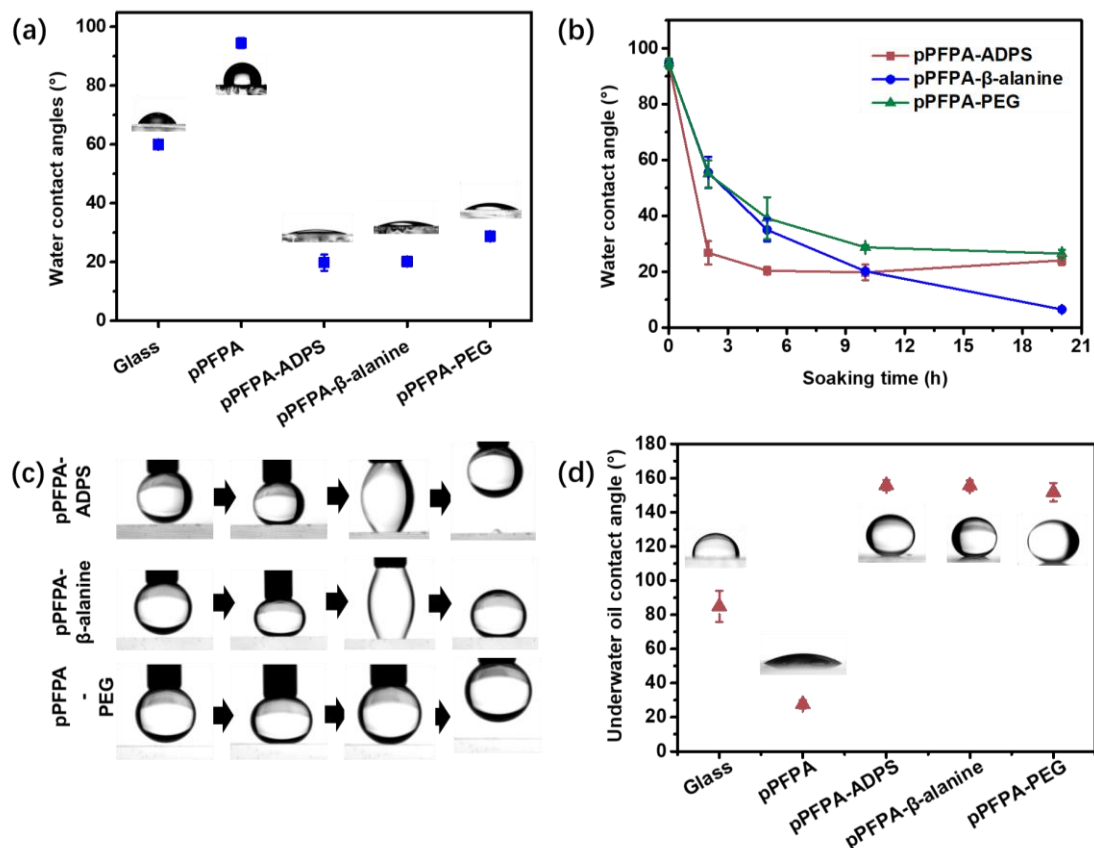


Fig. 2. (a) WCAs of the glass, pPFPA, pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG, respectively. The insets are the water droplet images on the coating surfaces. (b) WCAs of the coatings at different amination time. (c) Different adhesive behaviors of dichloroethane droplet on three coating surfaces under water. (d) Underwater oil contact angles of the coatings and the insets are the oil droplet on the coating surfaces

Having demonstrated the successful hydrophilization of the substrates, we next assess their antifogging properties. The fog condensed on the eyeglass or windscreen in cold weather severely obstructs the view and imposes potential danger to our life. A highly hydrophilic surface is known to facilitate the microdroplet spreading out and eliminate the fog^[30, 31]. Considering the high transparency and hydrophilicity of these coatings, they are expected to show a good antifogging feature. To verify this, the antifogging tests are carried out for these coatings. We first immerse an 'A' shaped paper into ADPS, the β -alanine and NH_2 -PEG solutions, respectively. Then, the wetted papers containing amine solution are attached to the pPFPA coating surfaces for 2, 5 and 10 hours, respectively (Fig. 3a). After removing these papers from the coating surfaces, the coatings well-maintain their original transparency, and the modified area cannot be discerned by

the naked eyes (Fig. 3b). Moreover, the 'A' patterned area remains clear after the coatings being exposed to moisture (Fig. 3c), indicating good antifogging properties. Further, the antifogging performance improves with the treating time. In addition, among the three coatings, the pPFPA-ADPS shows the best antifogging performance, which can be attributed to its lowest WCA. Notably, the ranking of pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG antifogging performance is in line with their WCAs, in good agreement with the fact that the fogging resistance relies on the spread out of water droplet on the surface^[30, 31]. As a control, pPFPA and glass are easily fogged and become opaque immediately after being exposed to moisture (Fig. S6). Further, this hydrophilization method can be adapted to printing technology (Fig. S7 and Movie S4), beyond the reach of previously reported hydrophilization approaches.

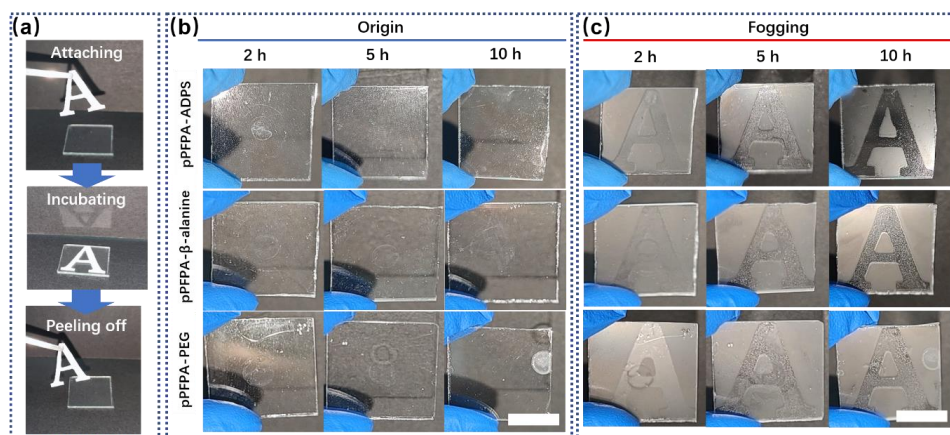


Fig. 3. (a) Schematic illustration of the process of surface patterning. (b) The pPFPA coatings patterned with 'A' character with different time length and (c) the fogging tests of the surfaces. The scale bar is 1 cm

We next evaluate the self-cleaning ability of these coatings. Self-cleaning capability is essential to maintain the original physicochemical surface properties after being contaminated by oils or other organic matters. Here, silicone oil and salad oil-stained by fluorescent dye are used as prototype contaminants for assessing the self-cleaning performance of three coatings. These dyed oils show cyan and bluish fluorescence under 365 nm UV light, enabling to track the residual oil contaminant on the surfaces. Fig. 4 shows the procedures of the self-cleaning tests. Prior to the test, these surfaces are thoroughly clean and free from oil spots (Fig. 4a and 4b). Upon dropping silicone oil and salad oil on the surfaces, cyan and bluish fluorescence drops could be clearly

observed under 365 nm UV light (Fig. 4c and 4d). After 24 hours, the surfaces are rinsed with DI water. As shown, surfaces with pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG coatings are well-cleaned, and only trace amount of oil could be observed on the surfaces of pPFPA-β-alanine and pPFPA-ADPS, whereas pPFPA-PEG surface is thoroughly clean, indicating the best self-cleaning capability (Fig. 4c and 4d). However, bare glass and pPFPA surfaces still show considerable amount of residual oil spots after being rinsed by DI water. These results clearly demonstrate that the highly hydrophilic surfaces rendered by amine modification possess good self-cleaning ability.

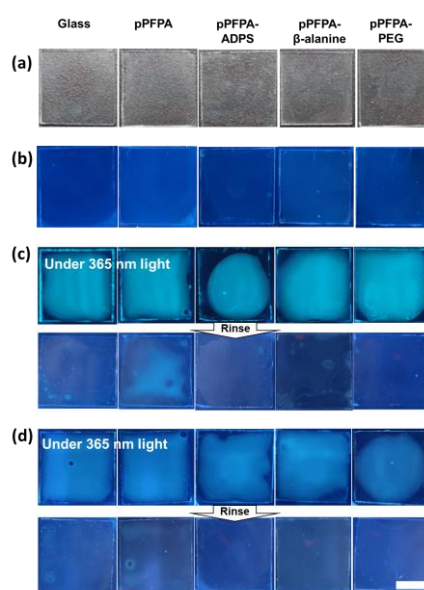


Fig. 4. Image of five different surfaces before and after oil contamination under natural light and UV light. From left to right: bare glass, glass coated with pPFPA, pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG, respectively. (a-b) Clean surfaces prior to tests; (c) The coatings are covered with silicone oil and rinsed with water after 24 hours; (d) The coatings are covered with salad oil and rinsed with water after 24 hours. The scale bar is 1 cm

We move forward to evaluate their antifouling behavior against algae. Here, *P. tricornutum* and *N. closterium* are used as the target algae to characterize the antifouling performance due to their high abundance in the ocean. After culturing in the algae suspension for 5 days, the coating surfaces are observed by fluorescence microscope. As shown in Fig. 5c, bare glass and pPFPA surfaces exhibit bright green fluorescence, indicating significant high density of algae. In sharp contrast, surfaces of pPFPA-ADPS, pPFPA- β -alanine and pPFPA-PEG remarkably reduce the algae density by

98.6%, 98.3%, and 99.7% for *P. tricornutum*, and 98.0%, 99.1%, and 99.8% for *N. closterium*, respectively, which can be attributed to the hydration and the steric repulsion of the water-binding layer^[32-35]. This result demonstrates the excellent antifouling performance of the hydrophilic surfaces^[11, 36, 37]. It is also interesting to find out that the algae density on pPFPA coatings is lower than hydrophilic glass, probably due to the easy detachment of algae from the low surface energy pPFPA coatings^[38].

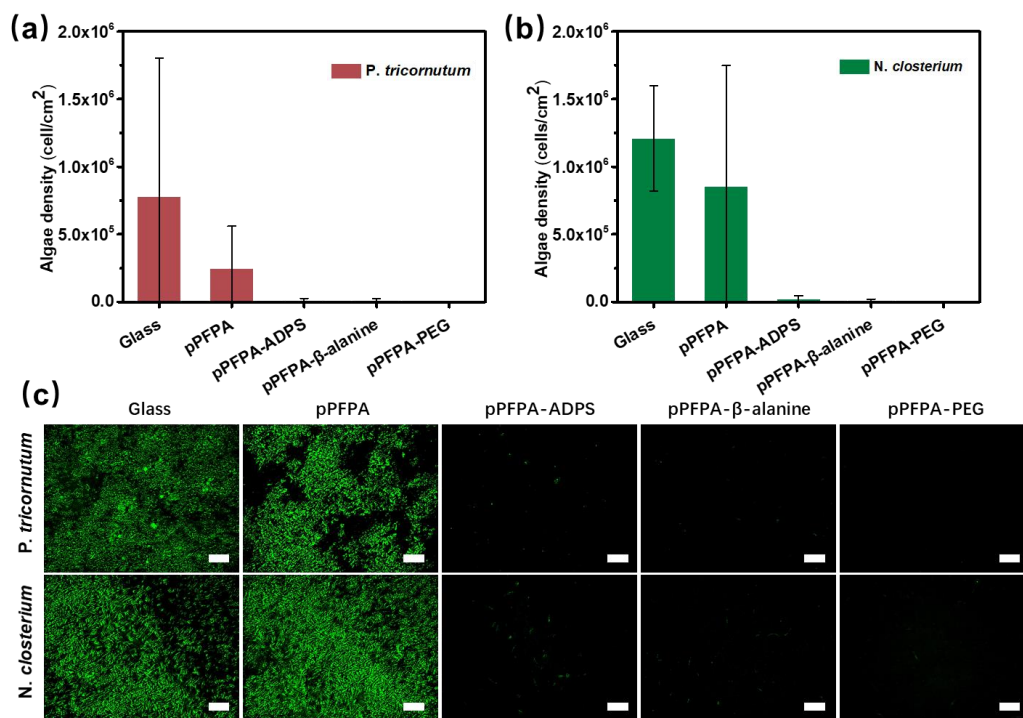


Fig. 5. Density of (a) *P. tricornutum* and (b) *N. closterium* settling on different coating surfaces, and (c) corresponding representative fluorescence images. The scale bar is 50 μ m (Excitation wavelength: 475 nm)

Remarkably, these coatings exhibit excellent regeneration capability. Regeneration is a significant and distinct process in the biological world. With such capability, creatures could efficiently renew, restore or heal the damaged parts and greatly extend their life. Introducing regeneration capability into materials would be a fascinating approach to design smart bionic system with long service period. The fast and quantitative aminolysis reaction renders the possibility of regeneration for these coatings. To verify this, we abrade the coating surfaces by 30 gram falling sand from a height of 40 cm (Fig. 6a), and then measure the WCA change. As shown

in Fig. 6b, after being abraded, the WCAs of these coatings increase from $\sim 20^\circ$ to $\sim 50^\circ$, indicating that the coating surfaces are partially damaged and the inner hydrophobic pPFPA surfaces are exposed to the air. Interestingly, immersing the damaged surfaces into corresponding amine solutions at room temperature brings the WCAs back to $\sim 20^\circ$, implying that the exposed hydrophobic pPFPA surfaces convert to hydrophilic surfaces again *via* aminolysis reaction. Moreover, several damage-regeneration tests demonstrate the good reproducibility and robustness of this hydrophilization method.

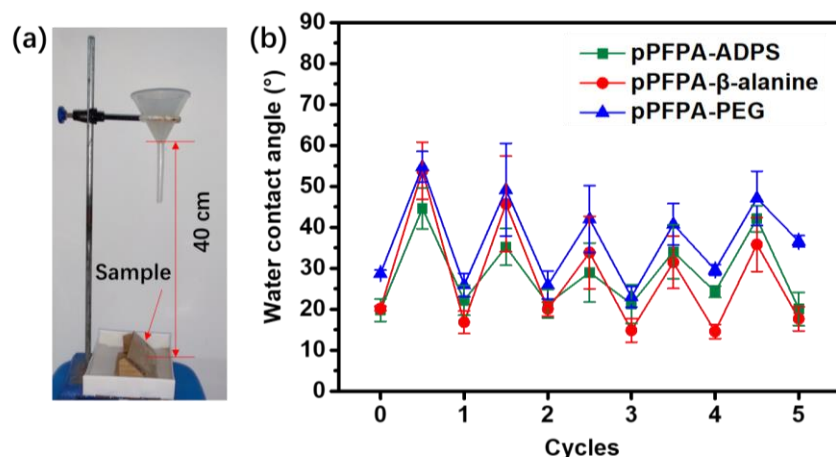


Fig. 6. (a) Schematic illustration of the abrasion tests of the coatings with a self-made device. (b) Change of WCAs during abrasion and regeneration cycles for pPFPA-ADPS, pPFPA-β-alanine and pPFPA-PEG, respectively

4 CONCLUSION

In this study, we have developed a simple yet robust approach to fabricate hydrophilic surfaces through *in-situ* site-specific aminolysis between pPFPA and alkylamines (i.e., ADPS, β-alanine and NH₂-PEG). The fast and quantitative feature of such method is evidenced by ATR, time-resolved WCA and UWOCa measurements. Moreover, this hydrophilization method shows negligible impact to the transparency and thermal stability of the surfaces. In addition, the hydrophilized surfaces exhibit excellent antifogging properties, with potential applications for anticounterfeiting and data encryption *via* patterned surface hydrophilization. Adhesion tests between fluorescent oil and hydrophilic

surfaces reveal that all three surfaces possess good self-cleaning property. Culturing *P. tricornutum* and *N. closterium* for 5 days on the surfaces results in undetectable density of algae, implying their excellent antifouling property against algae. Finally, we have demonstrated that these hydrophilic surfaces could be regenerated simply by immersing the damaged surfaces into desired amine solutions. All above results clearly indicate the unique advantages of such method for surface hydrophilization. This work provides a new approach not only for surface hydrophilization but also for a variety of surface modifications, and may find a number of applications in the fields of smart coating, sensing, precise patterning, data encryption and many others.

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