

# Plasma-controlled surface wettability: recent advances and future applications

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## Abstract

Materials with the desirable surface wettability and controlled surface-liquid interactions are of key importance in diverse applications. However, most of the existing chemical processes used for surface wettability control are often energy-inefficient, environmentally unfriendly, and rely on harsh processing conditions. Therefore, highly-selective, green, and low-cost alternative fabrication techniques are in urgent demand. Low-temperature plasma processing is one such promising approach that satisfies the above requirements. In this Review, we present recent advances in plasma processing for surface wettability control for diverse emerging applications in the environment, energy, and biomedicine fields. The underlying mechanisms of the plasma surface engineering, key features of the fabrication processes, and water-surface interface properties induced by the plasma are discussed. The emerging applications and future challenges in the field of plasma-controlled surface wettability are also critically analyzed and evaluated. This Review aims to guide further development of the plasma processing to effectively control surface wettability of various surfaces with minimum environmental impact. This effort is poised to contribute to the development of advanced functional materials with the unique properties targeting a broad range of applications.

## Keywords

plasma surface modification; surface wettability control; hydrophilic surface; hydrophobic surface; water uptake

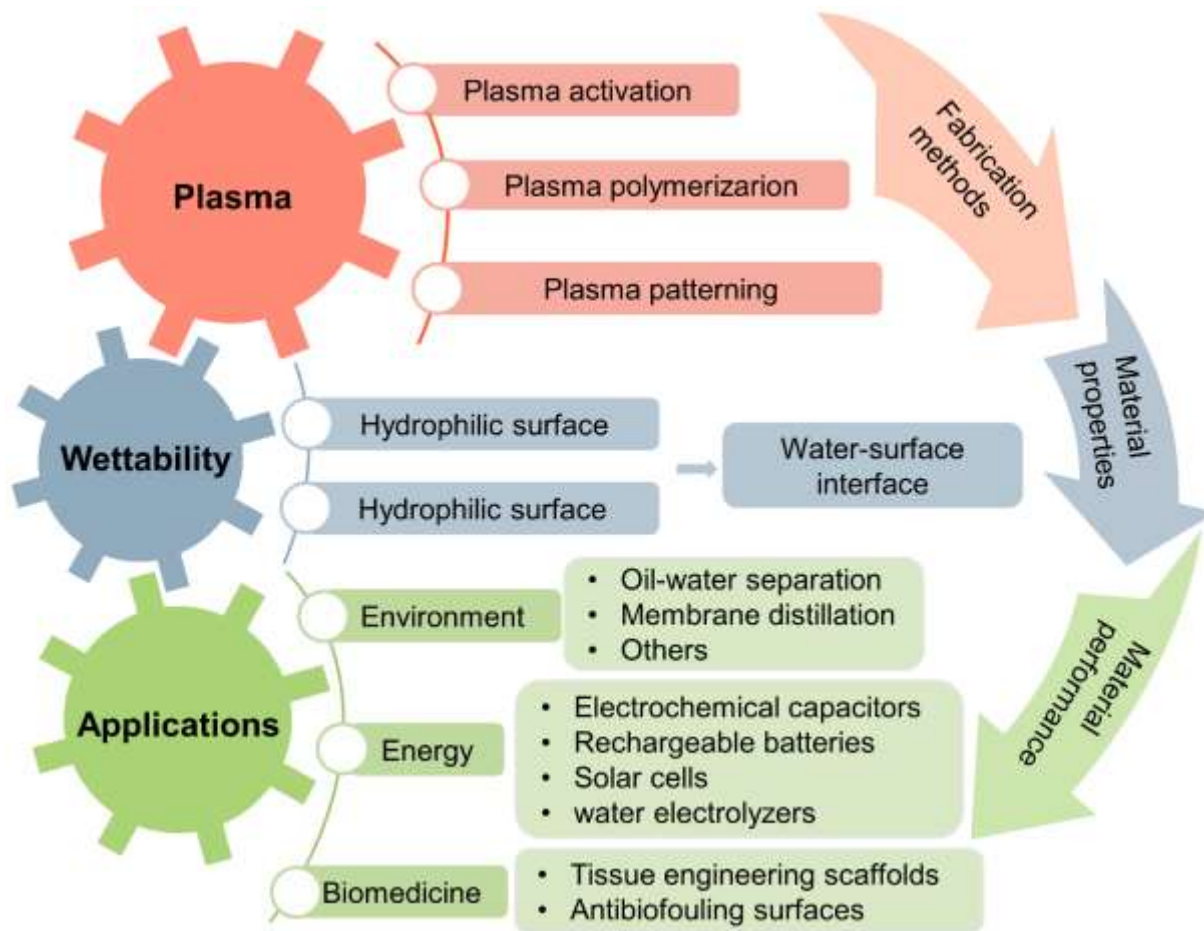
## 1. Introduction

Surface wettability is a fundamental property of a solid surface and plays a vital part in almost all applications of solid materials in diverse fields spanning from the environment and energy to biomedicine and many others [1-6]. Common materials and products that can benefit from precise control of surface wettability are ubiquitous, such as advanced membranes (from water purification to biopharmaceuticals), energy storage devices, windows, raincoats, roofs, disposable diapers, microfluidics, bandages, tissue scaffolds, bio-implants, and many others. With the continuous development of modern society, the demand for advanced functional materials with the desirable surface wettability is increasing faster than ever before. This is why precise control over surface wettability is expected to provide materials with superior properties leading to unprecedented applications in diverse fields.

Over the past decade, conventional wet chemistry approaches have been among the most frequently used methods for surface wettability control [7-10]. However, they are often energy-inefficient, pollute the environment, and rely on harsh synthesis conditions. Therefore, developing highly-selective, environmentally friendly, and low-cost alternative fabrication techniques is of high importance for a sustainable future. Considering that surface wettability is determined by the interplay of surface chemistry and surface micro/nanotextures, the low-temperature plasma processing has recently attracted major attention. The plasma processing meets all the above requirements and is widely acknowledged as a highly promising and rapidly emerging approach due to its unique ability to modify both the surface chemistry and surface topography for a wide range of materials. Plasma surface engineering has been applied to metals, polymers, and ceramics at mild operation conditions including room temperature, atmospheric pressure, and open-air processes.

Plasma is defined as the fourth state of matter apart from solid, liquid, and gas, which remains macroscopically neutral while containing a sufficiently large number of negatively- and positively-charged particles that interact with each other as well as with neutrals and the plasma reactor walls [11]. In most cases, plasma is generated through ionizing a gas by supplying a sufficient amount of electromagnetic energy, and the highly reactive species in the plasma can thus be controlled by adjusting the energy input (e.g., electric power). Importantly, plasma offers an ideal reactive physicochemical environment that can be used for surface activation, coating deposition, and nanostructuring of diverse materials. The unique plasma-specific conditions and effects allow precise control of microscopic surface chemical composition and surface nanostructures by adjusting the macroscopical energy input, leading to the effective control of surface wettability of a broad range of hard and soft materials.

To date, although many comprehensive reviews have already discussed the role of the plasma in controlling the surface chemistry by functionalization and/or nanostructuring [12, 13], there is only a very limited number of reviews focused on the relationships between the surface wettability and plasma surface functionalization, especially at atmospheric pressure operation conditions [14, 15]. Moreover, critical reviews of recent advances in plasma-controlled surface wettability and the relevant advanced applications in the environmental, energy, and biomedical fields remain limited.



**Figure 1.** The scope and focus of this review.

In this Review, we aim to highlight the start-of-the-art in plasma surface functionalization for wettability control of various materials and the diverse targeted applications that can benefit from the plasma modified surfaces. The overview of this emerging field aims to facilitate the uptake of the efficient and sustainable plasma technology by the materials science and engineering community, leading to future applications well beyond the current capability. The scope and focus of this review are summarized in **Figure 1**. First, we briefly introduce the fundamentals of the theory of surface wettability. Second, the key features of the plasma processing for surface wettability control are analyzed. We then discuss how the advanced plasma techniques, such as plasma activation, plasma polymerization, and plasma surface patterning, affect surface wetting behavior. After that, we introduce the mechanisms leading to the plasma-enhanced wettability and important aspects of kinetics of water interaction with surfaces. The emerging applications in environmental, energy and biomedical fields such as oil-water separation, energy storage devices, and tissue engineering scaffolds are also reviewed with the emphasis on material wettability properties and plasma fabrication methods. Finally, we present our vision for the applications and challenges ahead of the plasma technology in the near future.

## 2. Mechanisms of surface wettability control

Surface wettability refers to the ability of a liquid to maintain contact with a solid surface, and a liquid contact angle (CA) is usually used to quantify surface wettability [16]. Herein, to explain the underlying

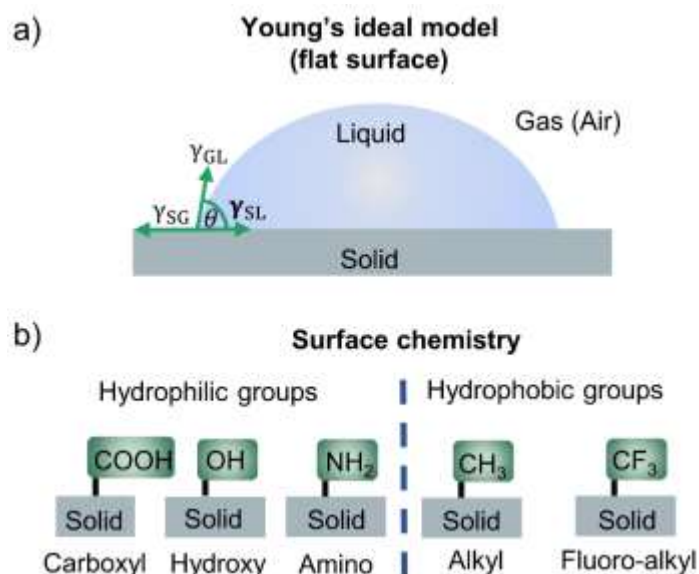
mechanisms for surface wettability control, we introduce several well-known theoretical models, namely Young's model, Wenzel model, and Cassie-Baxter model.

## 2.1 Young's model and surface chemistry

In 1805, Thomas Young proposed his famous wettability model that describes the relationship between the static CA of a liquid droplet and the three interfacial (i.e., solid-liquid, solid-gas, and gas-liquid) tensions on an ideally smooth, rigid, chemically homogeneous, insoluble, and non-reactive surface (**Figure 2 a**) [17]. The relationship can be explained by the following equation:

$$\cos \theta = \frac{(\gamma_{SG} - \gamma_{SL})}{\gamma_{GL}}, \quad (1)$$

where  $\theta$  is Young's CA ( $\theta$  is also defined as intrinsic CA),  $\gamma_{SG}$ ,  $\gamma_{SL}$ , and  $\gamma_{GL}$  represent the solid-gas, solid-liquid, and gas-liquid interfacial tensions, respectively. Note that in reality, the CA method is sensitive to a depth of 1-2 atomic layers [18]. For water, the most widely applied liquid to sense surface wettability characteristics,  $90^\circ$  is defined as the limit between surface hydrophobicity ( $\theta \geq 90^\circ$ ) and surface hydrophilicity ( $\theta < 90^\circ$ ) based on Young's equation [2]. Recent advances in wettability science have extended the types of wettability surface properties, defining superhydrophobic surfaces ( $\theta \geq 150^\circ$ ) and superhydrophilic surfaces ( $\theta < 10^\circ$ ) as important cases in the material science [19, 20]. The water droplet can stand on a superhydrophobic surface maintaining a spherical shape but spread completely on a superhydrophilic surface.



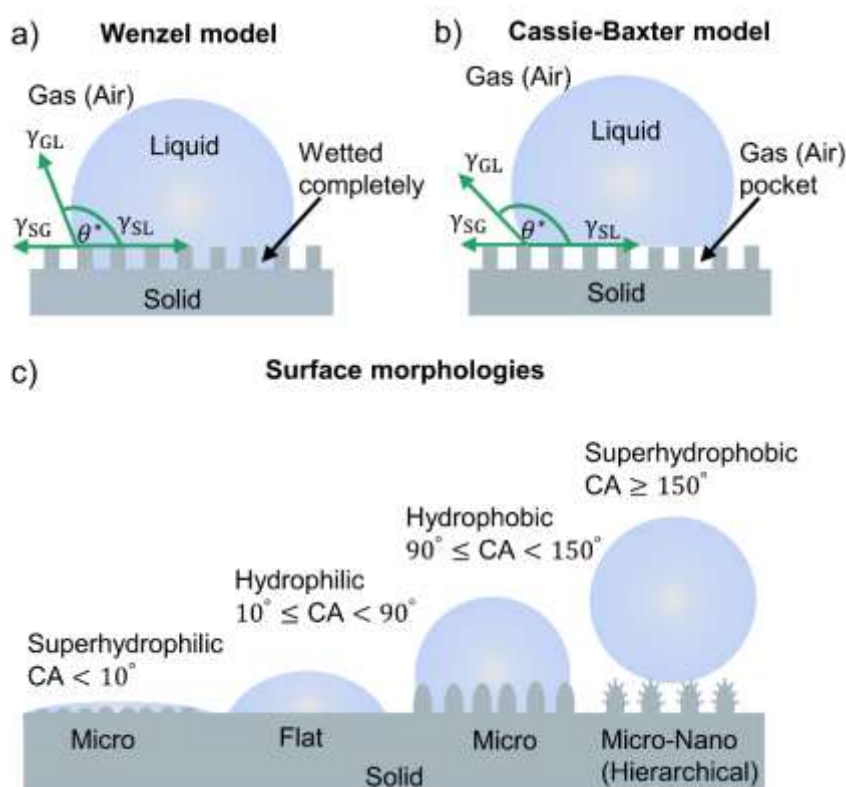
**Figure 2** Surface chemistry is one of the critical factors for surface wettability control. a) Young's ideal model on a flat surface. b) Typical chemical functional groups used to make surfaces more hydrophilic or hydrophobic. Redesigned and redrawn using information from [6]. © 2020 Wiley-VCH.

As the surface free energy of a solid surface is largely determined by chemical composition [21, 22], according to Young's model, modifying surface chemistry with advanced surface functionalization techniques results in a relevant change in surface wettability. Several typical examples of chemical functional groups that can lead to surface hydrophilicity or hydrophobicity are shown in **Figure 2 b**). However, only changing the surface chemistry on a flat surface has certain limitations in terms of

wettability control. To the best of our knowledge, the largest water contact angle (WCA) on a flat surface until now is only around 120 ° which was achieved, for example, by using -CF<sub>3</sub> as the functional group on a flat glass surface [23].

## 2.2 Wenzel model, Cassie-Baxter model, and surface morphology

Young's model is based on ideal conditions of the surfaces and can only be employed for physically smooth and chemically uniform surfaces that are rarely found in real materials. In the subsequent development, Wenzel, Cassie and Baxter in 1936 and 1944 further developed new wettability theories that took into consideration of surface textures [24, 25]. In the developed models the surface textures (micro/nanostructured morphologies) have been well-recognized as the other critical factors for controlling surface wettability.



**Figure 3** Surface morphology can significantly influence surface wettability. a) Wenzel model. b) Cassie-Baxter model. c) Typical micro/nanostructured surfaces that can lead to different surfaces wettability. Redesigned and redrawn using information from [26]. ©2008 The Royal Society of Chemistry 2008.

The Wenzel model describes the phenomenon that a sessile liquid droplet sits on a rough surface in a gas phase (e.g., air) and the whole textured surface is wetted by the liquid (**Figure 3 a**) [24, 27]. The Wenzel model can be described based on a modified Young's equation (Equation (1)) by:

$$\cos \theta^* = r \frac{(\gamma_{SG} - \gamma_{SL})}{\gamma_{GL}} = r \cos \theta \quad , \quad (2)$$

where  $\theta^*$  is the CA of the liquid on the rough surface (apparent CA);  $\theta$  is the corresponding ideal smooth surface of the same materials (Young's CA, intrinsic CA);  $r$  is the surface roughness defined as the ratio between the total surface area and the projected surface area. In the Wenzel system,  $r$  is always larger than 1, so the surface roughness will always amplify the intrinsic CA  $\theta$  (i.e., an initial hydrophilic surface will be more hydrophilic while an initial hydrophobic surface will be more hydrophobic after an appropriate surface roughing treatment under the Wenzel's contact mode). For most cases, the surface wettability in the Wenzel state is a typical characteristic indicating that the water droplets are usually immobile due to the high adhesion induced by surface micro/nanostructures [28, 29].

The Cassie-Baxter model is another type of surface wettability state in which the sessile liquid droplet is supported by the micro/nanostructured surface while the gas (air) is trapped in the "pocket" between the droplet and the solid surface (**Figure 3 b**) [25]. The Cassie-Baxter CA  $\theta^*$  can be calculated as:

$$\cos \theta^* = f_{SL} \cos \theta + f_{SL} - 1 \quad (3)$$

where  $f_{SL}$  represents the area fractions of the solid-liquid interface. Due to the trapped "air pockets" that support the droplet, the apparent CA  $\theta^*$  is always larger than intrinsic CA  $\theta$  no matter that the intrinsic surface is hydrophilicity or hydrophobicity [2]. Differently from the Wenzel model, superhydrophobic surfaces in the Cassie-Baxter state often present liquid-repellent and self-cleaning properties with very low surface adhesion (e.g., lotus leaves) [30].

Both the Wenzel and Cassie-Baxter models suggest the high importance of surface morphology in tailoring surface wettability. Interestingly, many kinds of surface morphologies with different surface wettability can be found in nature [26, 31]. **Figure 3 c** summarizes several typical surface structures from natural plants that have different CAs and wetting properties ranging from superhydrophilicity to superhydrophobicity [26]. These surface structures enable a better understanding of surface wetting phenomena both in industry and in nature and promote a better control over surface wettability for practical applications by adopting modern nanofabrication techniques. Based on the above discussion, it can be concluded that both surface chemistry and surface morphologies play a significant role in controlling materials wettability. Usually, surface chemistry determines the intrinsic CA while surface morphologies enhance the effect. Therefore, the precise control over surface wettability needs advanced micro/nanofabrication techniques coupled with surface functionalization.

### 3. Key features of plasma processing for wettability control

As defined previously, plasma refers to the fully or partially ionized gases in which various charge carriers such as electrons, ions, and reactive radicals are present and define the chemical activity of the plasma media [32, 33]. Depending on the energy of species and state of equilibrium between them, the two types of technically used plasmas are often defined as [34]:

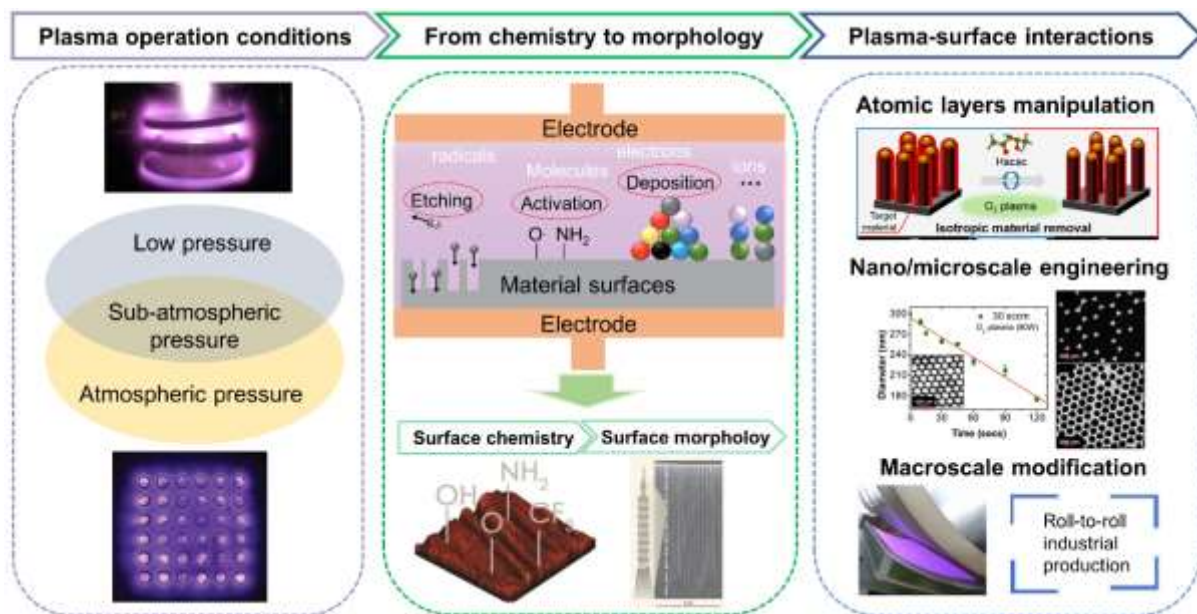
- thermal plasmas, where energy (temperature) of all states is in equilibrium;
- non-thermal plasmas (NTP), where the temperature of electrons is typically much higher than the temperature of heavy particles which remain at low-temperature.

In the area of wettability control, the former has limited applications due to the high (typically in the 1,000-10,000 degrees range) temperatures of the gas leading to too high a thermal load on treated materials, except for some specific applications in metals treatment [35, 36] and deposition of ceramic coatings on metal substrates and implants [37, 38]. NTP, on the other hand, is a very versatile tool in



both surface morphology engineering and surface chemical functionalization. The attractiveness of the plasma treatment amongst other conventional modification techniques is that plasma-assisted surface processing can be localized within a few nanometres on the top surface with no change in the excellent (as selected) bulk characteristics of the treated materials [39]. Plasma processing under non-thermal conditions is one kind of macro/micro/nanofabrication technique that uniquely features several advantages over the traditional wet chemistry approaches.

- Plasma surface engineering allows the fabrication of materials on micro, molecular, and even atomic scale with precise control over surface morphology and chemical composition, the two factors that are indispensable for surface wettability control;
- The plasma-based approach is well-known as a solvent-free technique, which is one of the most promising environmentally friendly green methods and an alternative to conventional wet chemistry;
- Plasma engineering is reliable, reproducible, relatively inexpensive, energy-efficient, and can be applied to complex 3D geometries which are often extremely challenging to other methods [40, 41];
- Plasma approach can be considered as a universal method and applied to different materials such as metals, polymers, ceramics, and composite;
- Plasma processes can be scaled up to industrial production relatively straightforwardly;
- Plasma techniques are compatible with other techniques, e.g., 3D printing, mask techniques, and wet chemistry approaches, to enable surface patterning and surface functionalization.



**Figure 4** Some of the key features of plasma processing for wettability control. Plasma can be operated at various conditions, e.g., different pressures at low pressure [42], sub-atmospheric pressure, and even atmospheric pressure [43]. By carefully operating the plasma conditions, plasma technology can tune surface properties both in terms of surface chemistry and surface morphology [44]. Importantly, the processes can be cross-scaled from atomic layers manipulation (e.g., by plasma-enhanced atomic layer etching [45]), nano/microscale engineering [46], and macroscale modification with potential for roll-to-roll industrial production [47]. Some of the figures are adapted from [42-47] with permission. [42], © 2014 Elsevier. [43], © 2016 Chinese Physical Society and IOP Publishing Ltd. [44], © 2008

Some of the key features of plasma processing for surface wettability control are illustrated in **Figure 4**. Based on the possibility to control the plasma species chemical composition and the energy of charged and excited species in the plasma, several well-developed approaches of plasma-enabled physical and chemical surface modifications are available for researchers for the surface wettability control. These include (i) plasma activation; (ii) plasma polymerization and (iii) plasma-patterning by either sputtering, etching, or nanotexturing. The choice of the method is defined by the area of application, type of substrate, and required wettability level. In general, plasma sputtering is known as a highly effective technique for the deposition of hard coatings on flat materials including metals [48] whereas nanoscale control of the surface morphology can be achieved with the use of plasma etching [49]. On the other hand, both methods of plasma activation and plasma polymerization provide a possibility for tailoring surface chemistry combined with controlled surface morphology and often can be used to modify the only top surface of the substrate at a nanometre scale [50, 51]. Uniquely, plasma methods are very versatile and can be adapted to a very wide range of operational parameters. That includes (i) the methods of plasma excitation (e.g. from direct current to alternating current of low, radio and microwave frequency); (ii) plasma sources configuration; (iii) gas composition and pressure from ultrahigh vacuum to atmospheric (or even well above) pressure; (iv) targeting atomic, nano and microscale [13, 52, 53]. Correspondingly, the plasma approach allows engineering new surfaces with precisely defined wettability characteristics. It can be scaled to almost any level with precise control over surface morphology and chemical composition. As such, the flexibility of the plasma methods in terms of adaptation to the needs of the targeted applications is unique in comparison with other methods currently available for researchers and industry.

#### 4. Surface wettability by plasma engineering

Plasma processing can provide flexible fabrication options to modify a surface for imparting it with the required wettability properties depending on the envisaged application. In this section, we review the recent advances in tailoring surface wettability properties using the most widely applied plasma-based techniques, namely plasma activation, plasma polymerization, and plasma surface patterning (**Table 1**). We also highlight their technical characteristics and state-of-the-art, assessing their efficiency, and discussing the challenges to overcome for future research.

**Table 1** Overview of the potential for surface wettability control based on plasma activation, plasma polymerization, and plasma patterning. Certain aspects are further discussed in the text.

Compounds used for plasma processing	Potential to control surface wettability LP: at low pressure; AP: at atmospheric pressure		
		Hydrophilicity	Hydrophobicity
<b>Plasma activation</b> using non-polymerizing gases	LP	O, N, or S containing gases yield incorporation of polar groups on polymers yet with pronounced hydrophobic recovery; surface roughening can reduce hydrophobic recovery; super-hydrophilicity	Hydrogen-containing gases and surface roughening might enhance hydrophobicity on hydrophobic polymers



		can be observed on textured substrates	
	AP	Similar as at LP; typically stronger hydrophobic recovery due to temperature-driven "overtreatment"	Less suited for hydrophobicity
<b>Plasma polymerization</b> using polar group-containing monomers	LP	Limited energy retains polar groups yielding high hydrophilicity; limited hydrophobic recovery by crosslinking (at the expense of polar group density); surface patterning and/or nanoporosity enhance hydrophilicity	Not suited for hydrophobicity but high energy and strong fragmentation avoids polar group retention ( $WCA \leq 70^\circ$ )
	AP	Plasma chemistry-driven deposition similar as at LP; sufficient crosslinking required to limit hydrophobic recovery	Similar as at LP
<b>Plasma polymerization</b> using siloxanes	LP	Addition of oxygen results in CH oxidation and formation of SiOx films; incorporation of silanols yields high hydrophilicity and nanoporosity as favored by limited energy; surface patterning can yield super-hydrophilicity; high energy and/or high O/Si ratios yield dense SiO <sub>2</sub> -like films	Compounds with CH <sub>3</sub> -Si-O groups favor PDMS-like films ( $WCA \leq 105^\circ$ ); high energy yields increased CH <sub>3</sub> abstraction and trapped radicals forming silanols (lowered hydrophobicity); surface patterning can yield super-hydrophobicity
	AP	Plasma chemistry-driven deposition (same as at LP) favoring hydrophilicity upon oxygen addition (air as carrier gas possible); also super-hydrophilicity possible as at LP	Plasma chemistry-driven deposition (same as at LP); oxygen addition to Si-O-Si compounds up to about 1:1 possible to retain hydrophobicity; also super-hydrophobicity possible as at LP
<b>Plasma polymerization</b> using metal organics	LP	Addition of oxygen results in inorganic metal oxides; (photo)catalytic activity favors super-hydrophilicity (e.g. TiO <sub>2</sub> )	Retention of hydrocarbons at limited energy but limited hydrophobicity due to affinity to react with oxygen ( $WCA \leq 70^\circ$ )
	AP	Similar as at LP requiring high process control due to affinity with oxygen	Not suited due to affinity with oxygen
<b>Plasma polymerization</b> using fluorocarbons	LP	F/C ratios >2 and/or addition of oxygen favor plasma etching: a thin FC surface layer can turn more hydrophilic by oxygen reactions	F/C ratios $\leq 2$ or addition of hydrogen favor hydrophobicity ( $WCA \leq 120^\circ$ ) and oleophobicity; high energy yields trapped radicals and lowering of hydrophobicity by oxygen reactions (can be reduced by substrate temperature); surface

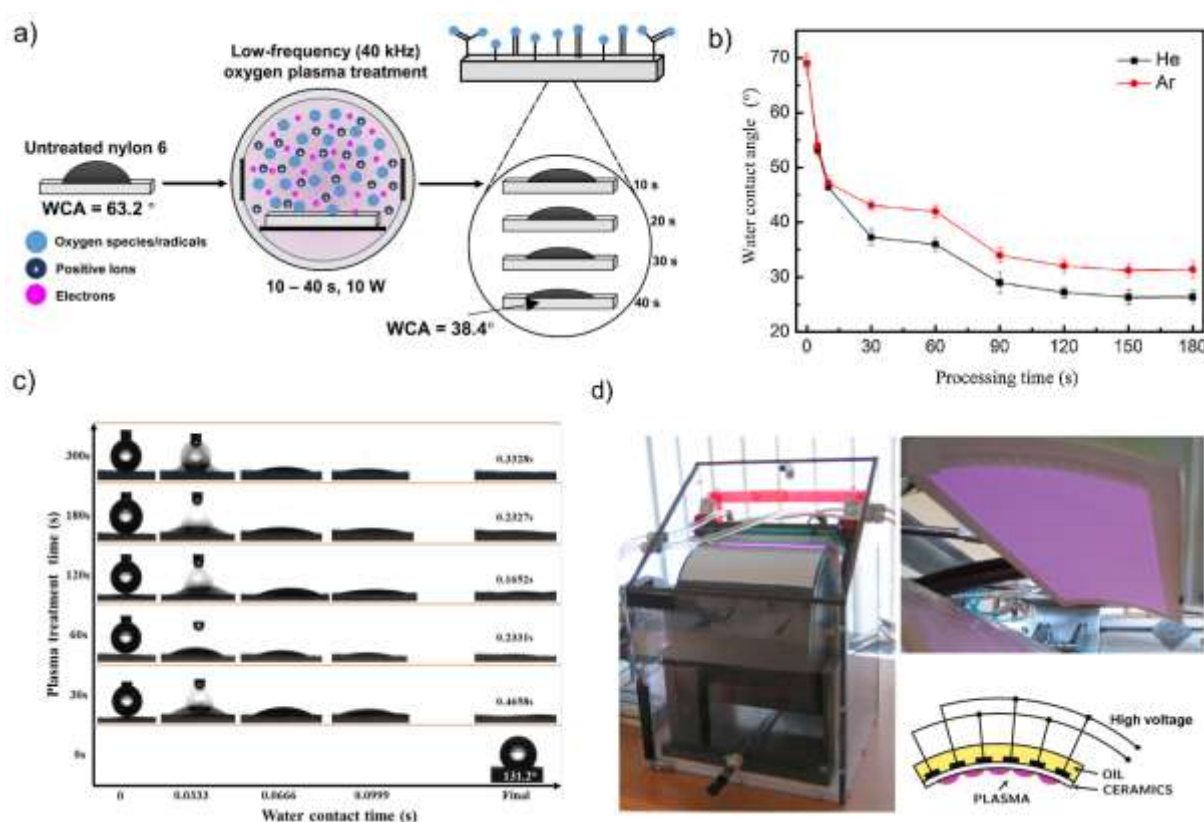
			patterning can yield super-hydrophobicity
	AP	Even proper housing leaves residual oxygen to favor oxygen incorporation limiting hydrophobicity	Addition of oxygen not recommended due to formation of toxic side products (full capsulation required)
<b>Plasma polymerization</b> using hydrocarbons	LP	Addition of O, N, or S containing gases favors incorporation of polar groups with high hydrophilicity; limited hydrophobic recovery by crosslinking (at the expense of polar group density); surface patterning and/or nanoporosity enhance hydrophilicity	Limited energy and hydrogen-surface interactions favor hydrophobic polymer-like films with enhanced H/C ratios ( $WCA \leq 90^\circ$ ); increased energy favors DLC-like films; surface patterning enhances hydrophobicity
	AP	Addition of O, N, or S containing gases possible similar to LP; sufficient crosslinking required to limit hydrophobic recovery	Plasma chemistry-driven deposition and hydrogen-surface interaction are similar as at LP; limited impurities required (not suited for DLC-like films)
<b>Plasma Patterning</b>	LP	Plasma etching/sputtering at high energy favors nano-patterning as used to support super-hydrophilicity/super-hydrophobicity (combined with film deposition); incorporation of nanoparticles allows desired surface wettabilities	
	AP	Aerosol injection allows surface nano-patterning with various chemistries	

#### 4.1 Plasma activation

Plasma activation usually refers to the process that uses a gas discharge plasma without injection of chemical precursors for direct treatment of materials, and it can introduce the desired functional groups generated in the gas phase onto the treated material surface and sometimes even change surface roughness without changing its bulk property [54]. Since the surface wettability is determined by the surface chemistry and surface roughness as discussed in Section 2, plasma activation can thus lead to tuneable surface wettability [39]. In the past decades, considerable research has been conducted on the surface hydrophilicity of polymeric materials by non-thermal plasma activation [55-57]. Generally, the effect induced by the plasma activation can be controlled through variations of the operational treatment parameters such as working gas, plasma treatment time, plasma power and frequency as well as plasma source configuration. O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, and air are the most frequently used working gases in plasma activation that can lead to surface hydrophilization due to their capacity to functionalize materials with hydrophilic groups such as -COOH, -C=O, -OH, and -NH<sub>2</sub>. Inert gases like Argon (Ar) or Helium (He) are also commonly used in plasma activation that can create free radicals on polymer surfaces and incorporate functional groups when exposed to ambient environment subsequently.

It is known that plasma activation is highly versatile and substrate-independent, which is quite different from the wet chemistry methods that typically strongly rely on the reaction between the substrates and the applied solution-based chemicals [58, 59]. From the technical point of view, plasma activation is a relatively straightforward approach, as it generally only requires a single-step process

with the treatment time in minutes (or even less), showing much higher efficiency than other established methods. For example, Thompson et al. [60] employed the low-pressure oxygen plasma activation for surface hydrophilicity of nylon 6, and the 40 s treatment time led to the WCA changing from the untreated 63.2° to oxygen plasma-treated 38.4° (**Figure 5 a**). The enhanced surface hydrophilicity was attributed to plasma-introduced oxygen-functional groups (C-OH, C=O, COOH) rather than the surface topographies due to the mild plasma operation conditions (low power: 10 W and low frequency: 40 kHz, implying high energy-efficiency of the plasma treatment). Wang et al. [61] compared two kinds of plasma (He and Ar) activation of polymethyl methacrylate (PMMA) surfaces operated at atmospheric pressure and room temperature. Both He and Ar plasma activation resulted in improved surface hydrophilicity after 180 s treatment, and He plasma showed higher efficiency than Ar plasma (**Figure 5 b**) [61]. Here, the effects were attributed to plasma-induced changes in both surface chemistry and surface topographies.



**Figure 5** Surface hydrophilicity by plasma activation. a) Low-frequency oxygen plasma activation of Nylon 6. Reprinted with permission from [60]. © 2021 Elsevier. b) Atmospheric pressure He and plasma jet for surface activation of PMMA surfaces. Reprint with permission from [61]. © 2016 Elsevier. c) Increasing plasma treatment time resulted in much high superhydrophilicity with short water spread time. Reprinted with permission from [62]. © 2019 Elsevier. d) A representative example of scalable plasma reactors for larger-scale production. Reprinted with permission from [63]. © 2020 The Authors. Published by Elsevier.

Through rigorous optimization of the operation parameters, the superhydrophilic surfaces can be obtained easily using plasma activation. Martins et al. [64] optimized different plasma working gases (O<sub>2</sub> and Ar), plasma treatment time, and plasma power for surface hydrophilicity of electrospun poly( $\epsilon$ -caprolactone) (PCL) nanofibers, and the superhydrophilicity (WCA  $\approx$  0°) was attained with O<sub>2</sub> plasma

after only 10 min activation at 30 W plasma power. Similarly, Corraera et al. [65] have applied oxygen plasmas to activate hydrophobic poly(vinylidene fluoride) (PVDF) nanofiber membranes which resulted in superhydrophilic behavior by optimizing the plasma power and plasma treatment time. Recently, oxygen plasma activation was used to functionalize electrospun biodegradable poly(butylene succinate) (PBS) nanofibrous membranes, and increasing plasma treatment time has led to much higher superhydrophilicity with a short water spread time (water spread completely in  $< 0.4$  s for 300 s plasma treatment (**Figure 5c**)) [62]. Indeed, increasing the plasma power and plasma treatment time can lead to surface etching, thus leading to the enhanced surface roughness and wettability.

Recent advances in the development of atmospheric pressure plasma sources have made it possible for the scalable production of desired surface wettability by plasma activation [66]. Upscaling plasma sources and using movable treatment areas are the main strategies to integrate plasma treatment into the industrial roll-to-roll industrial production line for large-scale production. A scaled-up diffuse coplanar surface barrier discharge (DCSBD) reactor (**Figure 5 d**) has been used to treat polyamide (PA) 6 foil surface resulting in improved surface hydrophilicity (WCA was changed initial  $65^\circ$  to  $28^\circ$ ) [63]. Importantly, the treatment was conducted under ambient air conditions, which can reduce the cost significantly as there is no need for expensive vacuum equipment and high-cost gases. Movable treatment areas can be achieved either by moving the powered plasma head (electrodes) [67] or by moving the sample or sample holder [68]. The well-developed scalable plasma treatment systems are generally cost-effective and can be re-used for a long period of time. On the other hand, the movable plasma (e.g., microplasma printer [69]) also allows the precise position control for the precision position treatment, which may enable desired surface property pattern without the use of masks.

Some reports have confirmed that surface hydrophilicity induced by plasma activation treatment can be unstable, showing the aging effect (hydrophobic recovery) with time when stored in open-air [70, 71]. This is due to the tendency of a surface to minimize the interfacial energy by the reorganization of chemical polar groups [72]. The drawback can be overcome to some extent by storing the plasma-treated samples in polar liquids such as water [73], or boiled water post-treatment [74]. However, the long-term surface hydrophilicity induced by the plasma activation still remains a significant challenge under mild conditions.

#### **4.2 Plasma polymerization**

Different from plasma activation that only activates the very top layer of a material surface, plasma polymerization (sometimes also called plasma deposition, plasma-enhanced chemical vapor deposition (PECVD)) is a particular type of thin film plasma-based technique that can impart the treated material with a new layer of thin coating [12, 75]. Depending on the nature of the material to be covered and the final objective, plasma-enabled thin films are currently used for a multitude of applications owing to the advantageous and tuneable properties that they impart to a surface without affecting the bulk of the substrate, whereas conventional solution-based approaches tend to alter the bulk properties due to partial penetration of the grafting into the substrate bulk (especially for polymeric substrates) [76].

Regarding the surface wettability control, plasma polymerization is also one of the most popular techniques, as the coating thickness together with the surface chemistry and surface topographies can be precisely controlled by manipulating the relevant plasma operation parameters and the applied chemical precursors. Most of the plasma polymerized coatings are very stable with negligible long-term aging effect due to the relatively higher degree of crosslinking of the plasma polymers compared

to the conventional polymers [77, 78]. In addition, compared to other wet chemistry methods, plasma polymerization can be applied much easier and faster for synthesizing functional coatings with desirable surface wettability as it can be realized by simple injection of chemical precursors (in the form of gases, liquids, and aerosols) into the plasma treatment area directly or indirectly [79, 80]. Therefore, plasma polymerization allows single-step processing, it is scalable, and operations at mild conditions often applicable even to very heat-sensitive materials.

Recently, Durán et al. [81] employed the single-step plasma polymerization approach to fabricate superhydrophilic coatings. As illustrated in **Figure 6 a)**, four different siloxane precursors with different structures and different number of Si-H and Si-CH<sub>3</sub> groups (i.e., 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), 1,1,3,3-tetramethyldisiloxane (TMDSO), and hexamethyldisiloxane (HMDSO)) were injected to the N<sub>2</sub>/N<sub>2</sub>O plasma region which was operated at atmospheric pressure condition, and the formed thin films showed different hydrophilic properties [81]. The formation of superhydrophilic coating (WCA < 5° for TMCTS) was attributed to the hydrophilic functionalities, such as hydroxyl (C-OH), carboxyl (COOH), ester (COOR), and amino (NH<sub>2</sub>) groups at the coating surface and the relatively high surface roughness, which were induced by the plasma-precursor-surface interactions.

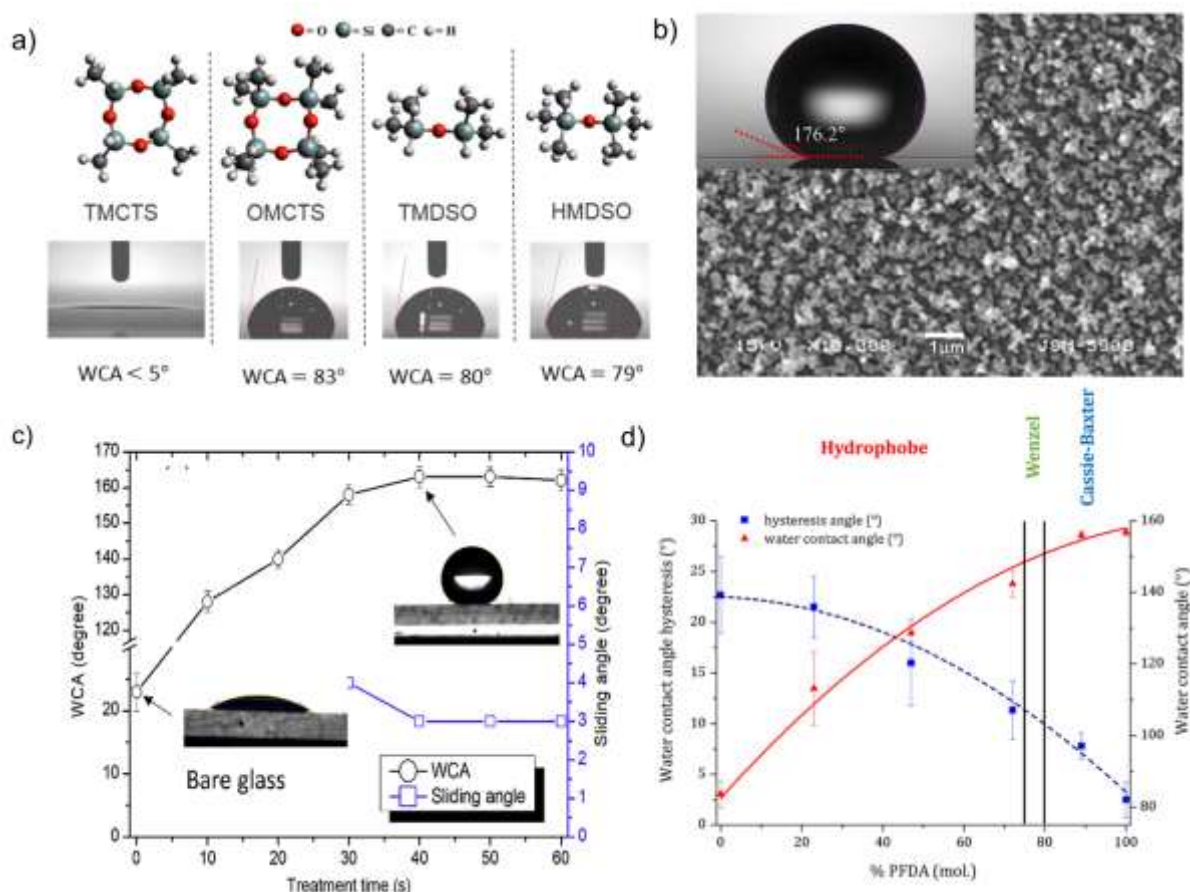
Mun et al. [82] have demonstrated the single-step synthesis of superhydrophilic polydopamine-based plasma polymer by using atmospheric pressure plasmas and a dopamine solution mist formed by a piezoelectric module. The study confirmed the clear advantage of plasma polymerization in the fabrication efficiency as the whole fabrication time was only ~ 70 s (including plasma-on and plasma-off time), whereas it usually takes more than 1 day for the traditional wet chemistry methods in which the materials need to be immersed in the dopamine solution for self-polymerization. Indeed, probably due to the high efficiency and versatility of plasma polymerization, a huge number of chemical precursors that possess the polar hydrophilic functional groups have been investigated by this method for surface hydrophilicity. Those plasma polymerized coatings usually contain polyethylene glycol (PEG), polyethylene oxide (PEO), and acrylamides such as *N*-isopropylacrylamide (NIPAM) and have attracted much interest in biomedical applications [83].

On the other hand, recent attention has been paid to superhydrophobic surfaces as they have shown great potential in a wide variety of advanced applications, such as self-cleaning, antifouling, and sensors, which can benefit sustainable future devices [84-86]. However, most wet chemistry strategies to prepare superhydrophobic surfaces require harsh conditions such as high temperatures, toxic gases, and a large amount of solvents to satisfy the indispensable requirements on both surface chemistry and surface micro/nanostructures for a superhydrophobic surface. As an ideal alternative tool, plasma polymerization is a new paradigm for fabricating superhydrophobic surfaces with merits such as no toxic gases, fewer or even no solvents, room temperature processing, and faster, enabling solutions with superior resources efficiency and sustainability.

Han et al. [87] have applied a single-step and solvent-free He plasma polymerization using C<sub>4</sub>F<sub>8</sub> and CF<sub>4</sub> gases as precursors for surface hydrophobicity. The atmosphere pressure room temperature plasma facilitated the formation of superhydrophobic coatings with WCA as high as 176.2° with a slippery property having low hysteresis of 4.9° owing to the plasma deposited micro/nanostructured surfaces and hydrophobic functional groups (**Figure 6 b)**) [87]. Likewise, Hossain et al. [88] have employed an atmospheric pressure plasma jet for co-polymerization of stable superhydrophobic coatings with tetramethylsilane (TMS) and 3-aminopropyl(diethoxy)methylsilane (APDMES) as precursors. It was found that the surface wettability can be tailored from 23° for untreated bare glass to superhydrophobicity with WCA 162° and sliding angle (SA) below 5°.

Noticeably, the treatment time was only in the range of 0 – 60 s (**Figure 6 c**) [88]. With a short treatment time of 0 to 20 s, the surface roughness and coverage were relatively poor, and a longer treatment time allowed the deposition of additional APDMES-TMS co-polymer on the surface, leading to a thicker coating layer with more roughness and surface coverage. Therefore, the plasma co-polymerization allows precise control of the surface coating thickness and surface roughness, thereby controlling the surface wettability from hydrophilicity to superhydrophobicity. Moreover, the short treatment time (in minutes) can enable the fast production of superhydrophobic surfaces for translation towards real-world applications.

Similar superhydrophobic coatings with fast plasma polymerization have been achieved by using a variety of chemical precursors like HMDSO [89], HMDSO + toluene [90], hexamethyldisilazane (HMDSN) [91], and benzene + cyclohexane [92]. In general, the superhydrophobic coatings induced by the single-step plasma polymerization are caused by the particles in the coating for surface roughness enhancement, and the formation of these particles is highly dependent on the nature of precursor chemical structures and the density of reactive species in plasma that can trigger condensation reactions in the gas phase [14].



**Figure 6** Plasma polymerization for surface coating with different wettability. a) Plasma polymerized 4 kinds of siloxane precursors showed different WCAs. Reprinted with permission from [81]. © 2019 Elsevier. b) He/C<sub>4</sub>F<sub>8</sub>/CF<sub>4</sub> plasma polymerized superhydrophobic coatings with WCA 176.2° and rough surface topographies. Reprinted with permission from [87]. © 2015 WILEY-VCH. c) WCAs and SAs of plasma co-polymerization of TMS and APDMES as a function of treatment time. Reprinted with permission from [88]. © 2019 Elsevier. d) Plasma-controlled wetting state from Wenzel state to Cassie-Baxter state by fine-tuning the ratio of two precursors: DOCA and PFDA. Reprinted with permission from [93]. © 2018 WILEY-VCH.

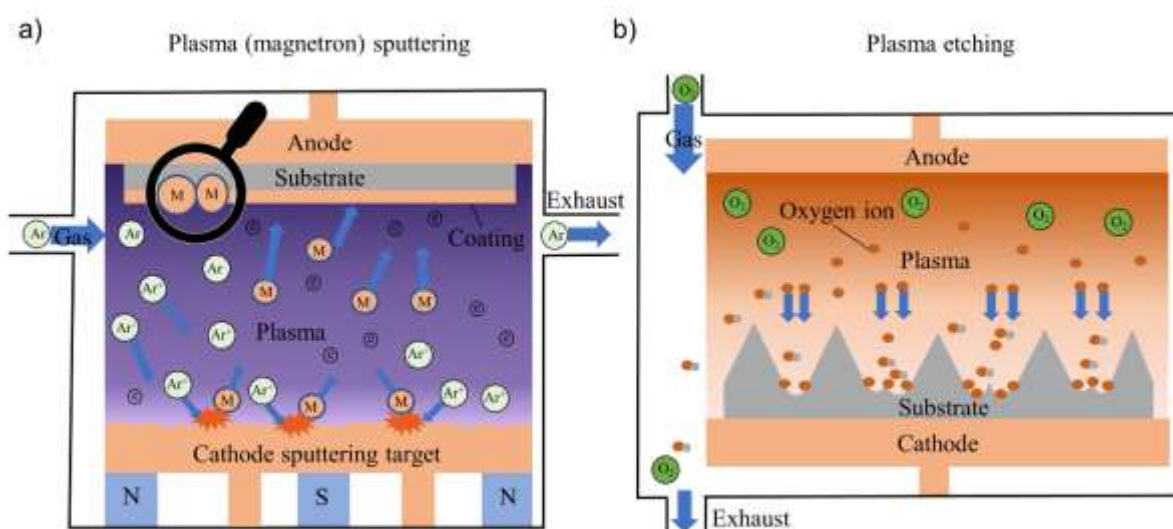


A recent study has shown that by fine-tuning the ratio of two precursors (dodecyl acrylate (DOCA) and 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA)), the surface wettability can be controlled from hydrophobic to superhydrophobic bearing two different wetting states from Wenzel to Cassie-Baxter, as shown in Figure 6 d) [93]. Therefore, plasma polymerization also allows the precise definition of the wetting state within the selected area. Together with the above other examples, we can conclude that plasma polymerization is a truly versatile technique that can be used to tailor surface wettability. However, the studies on the robustness of plasma polymerized coatings (especially those superhydrophobic coatings) seem rare in literature, which should be the foci in future research.

### **4.3 Plasma patterning**

Surface morphology plays a crucial role as chemical composition in defining wettability. Both Wenzel and Cassie-Baxter models, presented in Section 2.2, directly relate the morphological properties of the surface with the behavior of the surface/liquid interface. Among other methods, the control over surface morphology on atomic/nano and microscale provides a promising way to tune wettability in a very large range from superhydrophobicity to superhydrophilicity [94]. The fabrication of advanced nanostructured materials has become the heart of modern plasma technology that facilitates many innovative applications in the field of materials with enhanced surface wettability. Among modern nanofabrication techniques, non-thermal plasma that uniquely features highly reactive species enables the precise control of surface morphology by a variety of plasma-based surface engineering approaches including plasma etching [52] and plasma sputtering [95]. Recent years have also witnessed advances in nanopatterning by atmospheric pressure plasmas [96].

Sputtering is a process of knocking atoms off a surface by bombardment with energetic particles, such as ions, atoms, molecules, or clusters of atoms/molecules. Starting from the 1970s magnetron sputtering has been mainly used to prepare high-quality thin films for numerous applications as well as for engineering well-defined nanopatterned surfaces [97]. In a typical magnetron discharge, high sputtering yield is achieved by adding a magnetic field behind the cathode, which created a specifically configured, ring-shaped non-homogeneous magnetic field above the target surface [98]. Due to the Lorentz force, the high fluxes of ions bombarding the target surface can be achieved, yielding much higher fluxes of sputtered atoms and increasing their deposition rate in comparing with other methods [99, 100]. The mechanism behind the magnetron sputtering is presented in **Figure 7 a)** [101]. Recently, the magnetron sputtering method has been adapted to the needs of very precise control of the size and distribution of nanostructures on the surface by the development of the gas aggregation source method (GAS) [48]. GAS is a top-down approach capable of deposition nanoclusters and nanoparticles on almost any surface. In the 1990s, Haberland's group [102, 103] realized the first cluster source based on the use of magnetron sputtering operated at rather high pressures. This facilitates the nucleation processes of the sputtered atoms in the gas phase. With the use of appropriate cluster separation techniques, the beam of nanoparticles of well-defined geometry and size distribution can be obtained [104]. GAS is used to prepare surfaces with the desired surface wettability by the incorporation of nanoparticles with very high control of their deposition parameters [105, 106].

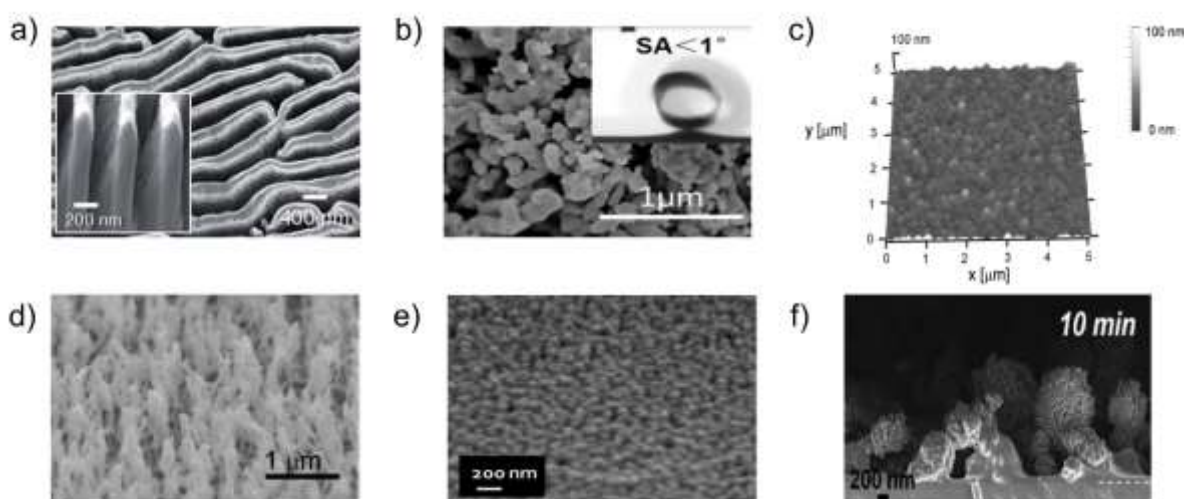


**Figure 7** Schematic representation of typical approaches for plasma processing of nanopatterned surfaces. a) plasma (magnetron) sputtering, and (b) plasma etching (reactive ion etching). Reprinted with permission from [101]. ©2021 The Authors. Published by Elsevier B.V.

Another method of surface nanopatterning is plasma etching that can be regarded as a plasma-chemistry-enabled extension of the physical sputtering technique. The plasma etching has become one of the cornerstones in semiconductor manufacturing and has also been widely extended for surface nanopatterning in multidisciplinary fields such as biology and energy [107]. In general, both chemical and physical etching processes occur simultaneously in the plasma etching, which makes it distinctive from traditional wet chemistry etching. Specifically, the species in plasmas can react with the treated materials and form volatile products easy to be removed. Importantly, the energetic ions in plasmas can be accelerated directionally during the etching process by a sheath potential developed on surfaces exposed to the plasma, which enables a fast etching rate in the vertical direction, leading to deep anisotropic etching via ion bombardment on the treated surface [53]. The directional/anisotropic etching is one of the unique advantages of plasma etching over wet chemistry etching. The typical plasma etching mechanism is presented in **Figure 7 b)** [101]. Since the etching mainly takes advantage of the high-energy particles in plasmas, the control over the etch rates, selectivity, sidewall profile, and etch roughness, etc., can be achievable by tuning the processing parameters such as voltage, power, temperature, chamber pressure, and gas flow rate that directly influence ion density, and electron temperature [108]. Well-designed nanostructures can be produced by plasma etching with the use of masks or with maskless or self-mask plasma etching through various methods [109, 110]. Overall, via operating the relevant parameters carefully, low-pressure plasma etching allows patterning of the surfaces at the nanometer scale with extra advantages such as no contamination issues and no hazardous chemicals. On the other hand, wet chemistry etching often fails to define a small feature size of less than 1  $\mu\text{m}$  and also needs to handle hazardous chemicals and contamination issues with much more attention [111].

Despite enormous progress of recent years in nanopatterning of the surfaces by plasma sputtering and reactive ion etching methods, the drawback of both approaches is the relatively low processing rate of some nm/min and relatively high energy demands. To overcome both issues, attention has been made more and more on plasma operation at sub- or atmospheric pressure where high particle flux can be achieved. However, the high frequency of collisions at high pressure suppresses the possibility to control the ion flux to the surface [32]. This is why atmospheric pressure plasma

nanopatterning methods are mainly based on control of the chemical composition of the gas phase and surface self-organization [112, 113]. In this area, one of the interesting approaches is the use of aerosol injection where a low volatile precursor is directly injected in the plasma or afterglow leading to the development of a well-established 3D surface with complex morphology [114, 115]. The method was used to deposit different coatings, including hydrophilic coating (WCA in the range  $49^{\circ}$ - $57^{\circ}$ ) of polyethylene oxide deposited at a rate of  $45 \text{ nm} \cdot \text{min}^{-1}$  with high control over chemical composition [116]. The application of plasma nanopatterning methods allows preparing almost any kind of surface with the intricate and well-controlled morphology as shown in **Figure 8**.



**Figure 8** Representative examples of plasma processing of materials with controlled surface morphology and wettability. a) Top-surface scanning electron microscope (SEM) image of Co–Cr obtained from substrate bias voltage of 1600 V after 60 min of target-ion induced plasma sputtering. Reproduced with permission from [117]. © 2016 The Royal Society of Chemistry. b) SEM image of the three-layered ZnO/SiO<sub>2</sub>/PTFE nanocomposite coating prepared by RF magnetron sputtering with superb anti-icing performance and SA < 1°. Reproduced with permission from [118]. © 2017 Elsevier. c) Atomic force microscope (AFM) scans of Ti nanoclusters deposited by GAS method at 60 s and overcoated with plasma polymerized n-hexane, WCA is 110°. Reproduced with permission from [119]. © 2012 WILEY-VCH. d) Superhydrophilic surface prepared by plasma etching. Reproduced with permission from [120]. © 2011 WILEY-VCH. e) SEM image of polycarbonate surfaces randomly roughened by plasma etching under 100 W RF power. Reproduced with permission from [121]. © 2014 Elsevier. f) Aerosol-assisted plasma nanocomposite coating deposited during 10 min, characterized by WCA 165°. Reproduced with permission from [115]. © 2014 American Physical Society.

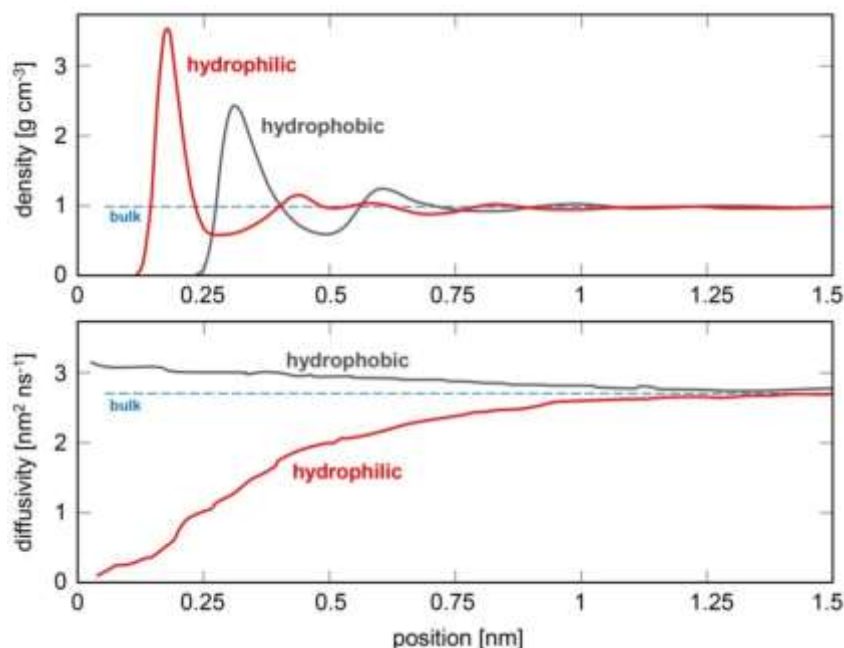
Such precise control over the surface structure provides a unique opportunity to prepare materials where only the top surface is modified by the plasma methods. The wettability of such materials can vary from superhydrophilicity to superhydrophobicity, and even more importantly, the contact angle can be tuned to the desired value through the variation of the plasma operational conditions [122]. Nowadays, this tool starts to be available for many research groups and can help to create novel materials with superb surface properties never achieved before.

## 5. Kinetics of water interactions

Despite obvious progress in the field of surface wettability control by plasma-assisted methods, highlighted in Section 4, the complexity of coatings/liquid phase interactions is a key aspect of our understanding of surface engineering. The ultimate goal of the plasma engineering of either hydrophobic or hydrophilic surfaces is not only to create the coatings with specific chemical properties and morphology but also to define the mechanisms of water (or any other liquid or solution) interaction with the top surface of the material. In the following section, the insights on coating interaction with liquids are presented based on the examples of surfaces modified by the plasma methods and specific water uptake processes.

### 5.1 Water interaction at surfaces

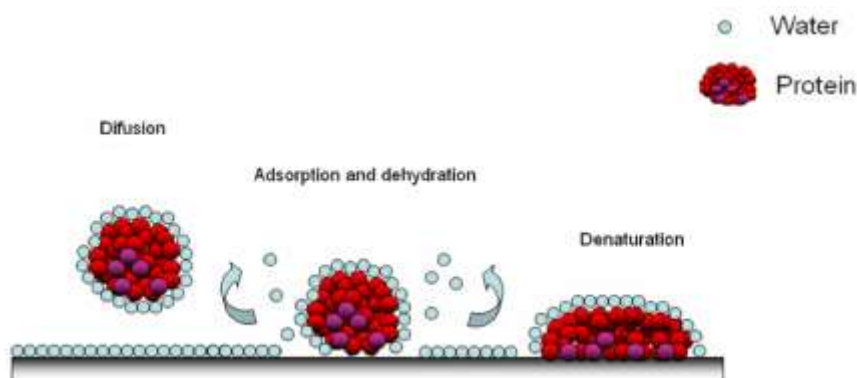
Many characteristics of water molecules near the real surfaces differ greatly from those in bulk water [123, 124]. Approaching a surface, the density of water molecules is increasing forming a hydration layer (**Figure 9**) – more pronounced for hydrophilic interfaces due to hydrogen bond formation [125]. Accordingly, the diffusivity of such interfacial water is reduced at hydrophilic interfaces, whereas it is slightly enhanced at hydrophobic interfaces [126]. Moreover, the effective polarizability increases for interfacial water following the density profile of the water molecules.



**Figure 9** Density and (lateral) diffusivity of water molecules near hydrophilic and hydrophobic flat solid surfaces based on molecular dynamics simulations. Upper part: Reproduced with permission from [125]. © 2015 American Physical Society; lower part: Reproduced with permission from [126]. © 2013 American Physical Society.

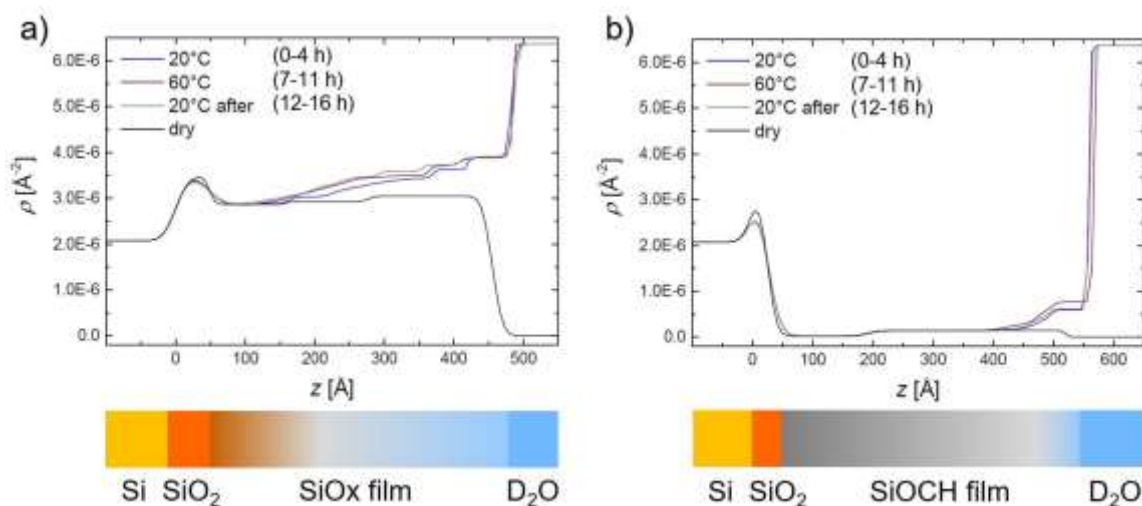
Depending on hydrogen-bonding opportunities at surfaces, an ordered arrangement of water molecules can occur, further influenced by electrostatic and dipolar interactions as well as specific interactions with the surface such as at crystallographic faces [127]. Most of all, fixed dipoles at a surface might further enhance the interaction forces creating long-range dipolar interactions [128]. Hence, when solvated biomolecules encounter a solid surface, significant changes in their shape may be expected as a consequence of the interfacial water structure [129]. Typically, more proteins adsorb

on hydrophilic surfaces, while denaturation is favored at hydrophobic surfaces (**Figure 10**). This indicates that protein adsorption strongly depends on the structure of the interfacial water and of the binding force of the water to the interface, which is higher at surfaces of high surface energy. The situation, however, can change when additional forces prevail such as van der Waals interactions, which can even arise from the subsurface composition of a material by its polarizability such as for a few nanometer thick films on Si wafers [130].



**Figure 10** Schematic representation of protein adsorption on a solid surface showing diffusion of the solvated protein, adsorption, and dehydration possibilities. Reprinted from [129]. © 2012 Poncin-Epaillard et al.

Surfaces with varying wettability and high stability based on similar or specifically combined chemistry can efficiently be provided by the plasma deposition allowing high precision at the nanoscale [15]. In particular, plasma polymerization from HMDSO is a well-studied process forming Si-O-(CH<sub>3</sub>) radicals as building blocks in the plasma that allow film growth with defined properties down to 0.5 nm in thickness [131, 132]. Depending on the energy input into the plasma, both at low and atmospheric pressure conditions, hydrophobic PDMS-like films can be deposited on various substrates by controlling crosslinking and wettability [133, 134]. The addition of oxygen in the gas phase combined with Ar or O<sub>2</sub> plasma post-treatment enabled gradually more hydrophilic plasma polymer films by increasing the inorganic SiO<sub>2</sub>-like content covering a range of stable water contact angles from about 25° to 105° with smooth surfaces and up to 135° during nanostructuring of the growing films [133, 135]. As-coated samples are, for example, well-suited for cell and protein adsorption studies [136]. Such plasma polymer films (PPFs), however, contain defects such as silanol groups and nanopores favoring water interaction yielding penetration of water molecules over a time scale of minutes to hours [137]. Based on neutron reflectometry (NR) with deuterated water, water intrusion has been detected in both hydrophilic and hydrophobic siloxane PPFs. As shown in **Figure 11**, the water uptake mainly proceeds within the first hours and slows down afterward due to a diffusion-reaction mechanism [138]. Water penetrates porous hydrophilic materials rather uniformly with a flat front, whereas it follows single channels along with polar defects in hydrophobic films also involving hydrolysis reactions [139-141]. For this reason, the water interaction with PPFs is not necessarily limited to the surface and needs to be examined in more detail.



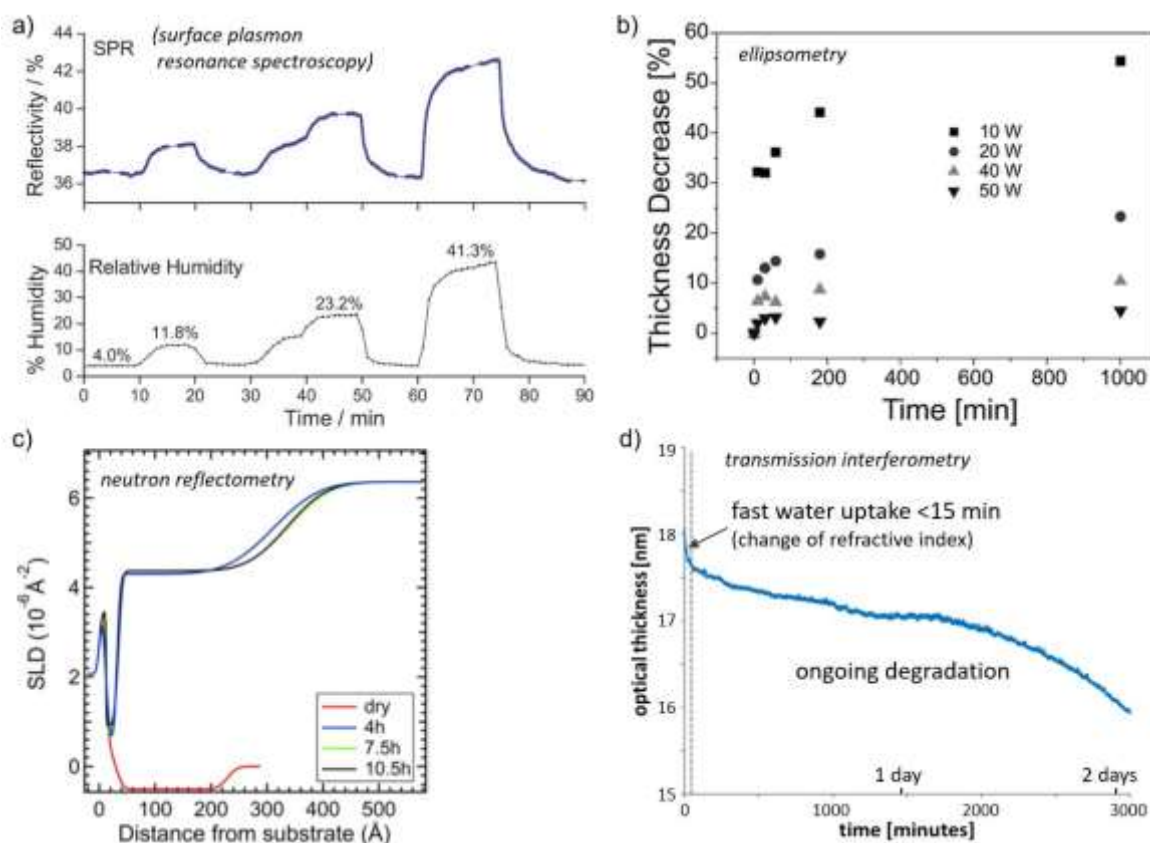
**Figure 11:** Neutron reflectivity of a) hydrophilic SiOx and b) hydrophobic SiOCH plasma polymer films measured consecutively in dry conditions and in D<sub>2</sub>O at different temperatures. Scattering length density profiles are given as a function of layer depth  $z$ , where the origin of the  $z$ -axis is set at the Si/SiO<sub>2</sub> interface. Reproduced and adapted with permission from [137].

## 5.2 Water interaction with thin films

### 5.2.1 Hydrophilic surfaces

Hydrophilic plasma polymer films comprising a wide range of functional groups such as hydroxyl, carboxyl, ether, ester, anhydride, amine, etc. have been deposited from suitable monomeric compounds including acrylic acid, allyl alcohol, maleic anhydride, allylamine, and many more [142-144]. A high retention of functional groups can be achieved, however, yielding swelling and partial dissolution of weakly crosslinked plasma polymers in aqueous environments as displayed in **Figure 12** [145-147]. Likewise, the swelling of hydrophilic PPFs such as oxygen- and nitrogen-containing hydrocarbon PPFs (C: H:O and C:H: N, respectively) deposited from maleic anhydride or allylamine has been detected by NR confirming that water penetrates readily throughout such films yielding swelling with up to 1.5 times the dry thickness at 70 vol% water content [148, 149]. While water uptake proceeds within minutes, dissolution is an ongoing process on longer timescales due to the involved hydrolysis reactions which depend on film chemistry and crosslinking [150, 151].

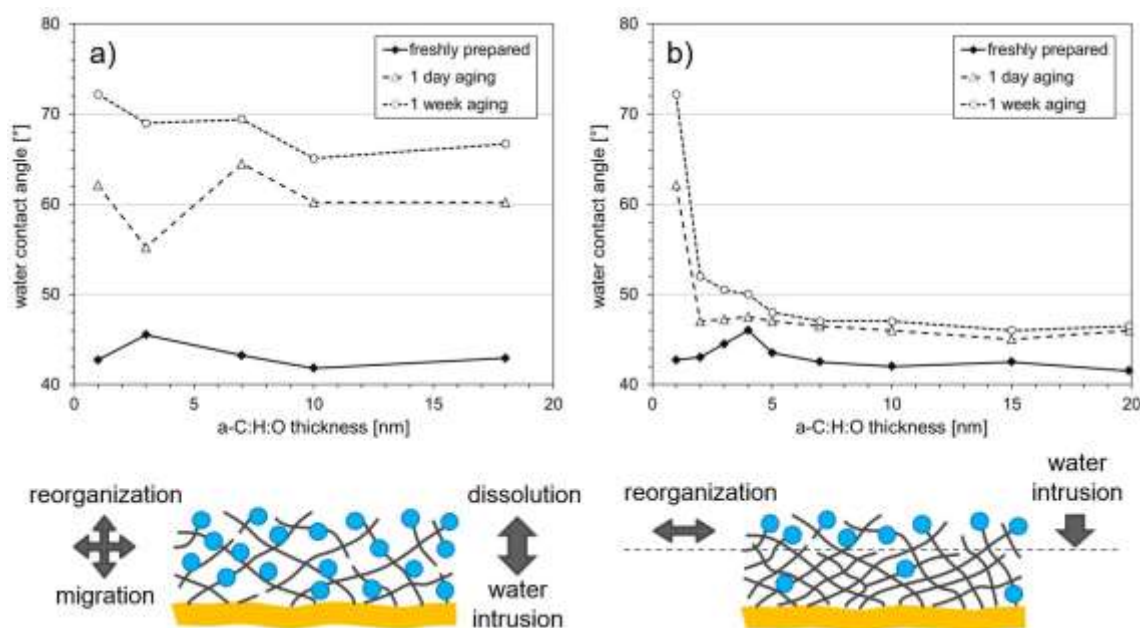




**Figure 12:** a) Swelling behavior of a C:H: N plasma polymer film deposited from allylamine at moderate power input following various relative humidities as seen by SPR kinetic measurement. Reproduced with permission from [147]. © 2015 WILEY-VCH. b) Dissolution of C:H: N plasma polymer films deposited from n-heptylamine at varying power input as a function of time of immersion in water. Reprinted with permission from [146]. © 2008 American Chemical Society. c) Change in scattering length density (SLD) upon exposure to deuterated water of C: H:O PPFs deposited from maleic anhydride showing water uptake (increase in SLD) and swelling (increase in thickness). Reprinted with permission from [149]. © 2018 American Chemical Society. d) Change in optical thickness of an 18 nm thick C:H: N PPFs using an  $\text{NH}_3/\text{C}_2\text{H}_4$  plasma with enhanced crosslinking [150]. The initial decrease in optical thickness is due to a decrease in refractive index indicating fast water uptake, whereas dissolution results in a decreasing thickness at longer timescales.

The limited stability of hydrophilic PPFs can also be an asset, e.g., for drug release or biodegradable coatings allowing high control over the degradation properties in aqueous environments, which can be adjusted by chemical composition and the energy input-related crosslinking degree of the plasma polymer film [152, 153]. In order to enhance the stability in aqueous environments, on the contrary, crosslinking needs to be increased, which is typically at the expense of functional, that is, terminal, group density [154, 155]. However, the use of simple gaseous mixtures of hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , etc.) with reactive gases ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , etc.) becomes feasible, which facilitates translation towards industrial processes. Taking advantage of the layer-by-layer growth in plasma polymer deposition, the plasma conditions can be modified in a gradual or step-wise manner within a one-step process [144, 156]. Starting with conditions yielding stronger crosslinking and thus high stability of C: H:O PPFs, a higher density of functional groups can be induced towards the surface

by adjusting the plasma conditions such as gas ratio and power input (**Figure 13**). This procedure has been proven to yield long-term stable hydrophilic surfaces for nm-thick functional top layers. Likewise, the higher crosslinked C: H:O layer can be functionalized by a post-plasma treatment without polymerizing gas, for example, a  $\text{CO}_2/\text{C}_2\text{H}_4$  plasma deposition is followed by a  $\text{CO}_2/\text{H}_2$  treatment [157]. Coated scaffolds, petri dishes, blood filters as well as metalized membranes and biosensors, to name a few substrates, were found to maintain stable wetting properties over many years stored at ambient conditions. C:H: N plasma polymers can be stabilized in a similar way retaining a constant density of amino groups of about 1 at% at least over weeks in aqueous environments [150].



**Figure 13:** Wettability of a-C: H:O PPFs deposited from  $\text{CO}_2/\text{C}_2\text{H}_4$  plasmas with the varying thickness on Au-coated chips assessed directly after coating as well as after 1 day and 1 week stored in ambient conditions: (a) uniform coating with high functional group density and (b) gradient structure with 1 nm thick highly functional top layer (higher  $\text{CO}_2/\text{C}_2\text{H}_4$  and lower power input) deposited on a crosslinked base layer of varying thickness (lower  $\text{CO}_2/\text{C}_2\text{H}_4$  and higher power input). The scheme underneath depicts restricted reorganization processes thanks to the stabilizing base layer. Reproduced with permission from [156]. © 2018 WILEY-VCH

Besides the importance of hydrophilicity, the water absorption properties of thin films are relevant for many applications, with some of them highlighted in Section 6. One of the most investigated hydrophilic surfaces allowing high water uptake are hydrogel-like coatings made of polyethylene glycol (PEG) comprising  $-\text{CH}_2-\text{CH}_2-\text{O}-$  chains as binding centers for water molecules. Surfaces coated with low molecular weight PEG brushes extending over a film thickness of about 8 nm can contain water volume fractions of more than 80%, whereby the water interaction with the thin film contributes to the PEG conformational structure [158]. Since protein adsorption involves multiple interaction sites, it is assumed that proteins cannot sufficiently influence the water structure of PEGylated surfaces as required for their attachment. Likewise, bacteria and further biomolecules are repelled at such surfaces strongly surrounded by water. Compression and steric hindrance of extended PEG brushes by protein/biomolecule adsorption restrict changes in the stable PEG/water

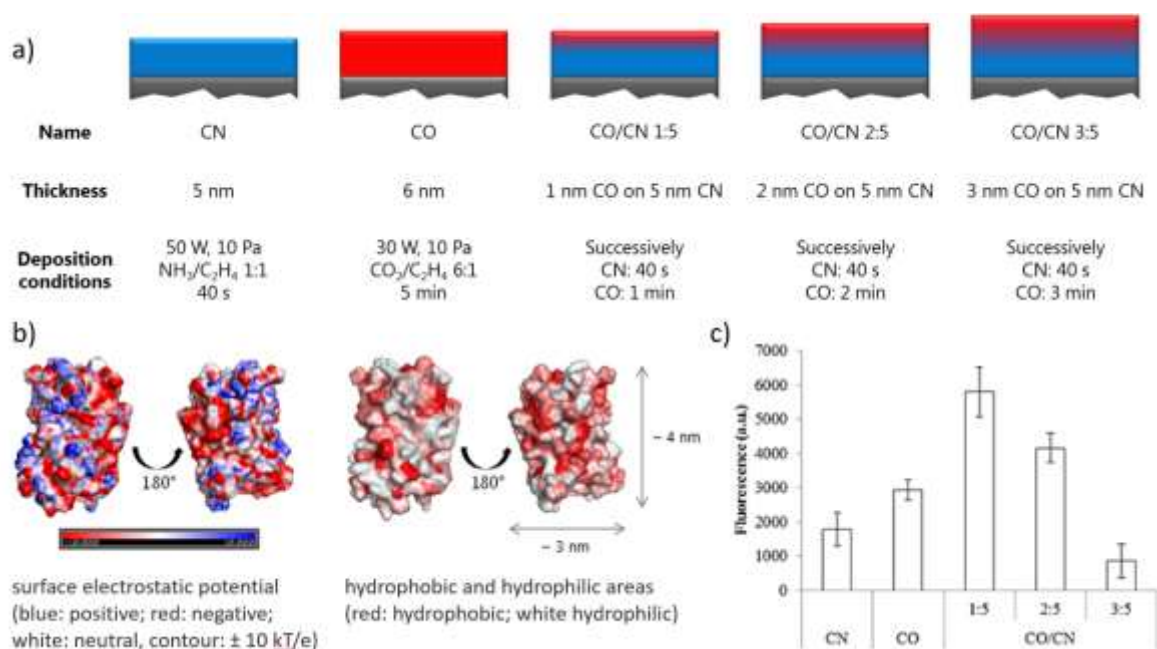
conformational structure, for which reason the biomolecule adsorption process becomes entropically nonfeasible [159].

Accordingly, plasma activation of polymer substrates has been used to graft a polycation-PEG copolymer (PLL-g-PEG) onto the oxidized surface from an aqueous solution [160]. The generated PEG/aqueous interface enabled a near-perfect resistance to nonspecific protein adsorption. The protein-repellent effect of PEGylated surfaces, however, is limited in time. Protein adsorption has been reported to occur over extended interaction periods (about one day), likely due to slow structural changes of the PEG/water and/or protein conformation finally allowing protein attachment [161]. Hence, water interaction with thin films appears as a highly dynamic process. Furthermore, limitations in stability and adhesion, as well as defects in the brush conformation, are encountered depending on the substrate material used.

To overcome such issues related to polymer brushes, plasma polymer deposition has been utilized to generate hydrogel-like surfaces with enhanced crosslink density and covalent bonding to various substrate materials. Sardella et al. performed a comparative study of low and atmospheric pressure plasma to deposit PEG-like plasma polymer films [162]. High stability of hydrogel-like coatings was obtained at low-pressure conditions (53 Pa) using diethylene glycol dimethyl ether (DEGDME,  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$ ) as the monomer. Cell-repulsive (polyethylene oxide (PEO) character of 70%) or cell-adhesive properties were observed depending on the energy input (5-50 W power input) and induced crosslinking during plasma deposition. In order to enhance the stability in the aerosol-assisted DBD process, the liquid chemical compound tetra ethylene glycol dimethyl ether (TEGDME) was mixed with ethylene in the plasma. Again, excellent cell-repulsive surfaces (PEO character around 70%) were achieved with high stability, when a 180 nm thick highly hydrophilic PEG-like PPF (without the addition of  $\text{C}_2\text{H}_4$ ) was deposited on a more crosslinked base layer (with the addition of  $\text{C}_2\text{H}_4$ ).

Similar to hydrogels grafted by means of plasma activation, zwitterionic brushes, molecules that contain oppositely charged functional end groups, have been immobilized on surfaces [163]. Such end groups can bind a hydration layer yielding durable, extremely hydrophilic surfaces. This highly hydrated ionic polymer/water structure promotes antifouling properties and might serve as a fluid lubrication film. Thin films containing both negatively and positively charged groups can also be deposited by plasma polymerization. Using hydrocarbon gases mixed with  $\text{CO}_2$  and  $\text{NH}_3$  (similar as discussed above), a multifunctional plasma polymer film can be produced containing oppositely charged groups such as  $-\text{NH}_3^+$  and  $-\text{COO}^-$  when dissociated in water yielding almost zero surface charge [164]. While not meeting the requirements for antifouling applications, varying the surface charge and surface chemistry of such films might allow effective control over protein and cell adhesion when exposed to various biological fluid environments. Plasma polymer bilayers made of an amine group-containing base layer covered by a 1, 2, or 3 nm thick layer comprising carboxylic groups revealed significantly different amounts of adsorbed proteins despite very similar surface properties (chemistry, wettability, surface charge, and roughness) as shown in **Figure 14** [165].

Plasma polymerization thus offers the unique possibility to build advanced surface architectures with mixed or graded opposite functional groups at the nanoscale allowing selective biomolecule interaction thanks to the interplay with water molecules. This potential based on nanoscaled plasma polymer films has not yet been fully exploited.



**Figure 14:** Plasma polymer deposition of bilayers with oppositely charged functional groups (CN: amine groups, CO: carboxylic groups). a) Schematic representation and conditions of the CO/CN plasma coatings. b) Properties of the green fluorescent protein (GFP) used for adsorption studies. c) Surface fluorescence after incubation in a GFP-containing solution corresponding to protein adsorption. Reproduced with permission from [165]. © 2018 Springer Science + Business Media, LLC, part of Springer Nature

### 5.2.2 Hydrophobic surfaces

To obtain hydrophobic surfaces on different substrate materials, mainly fluorocarbon, silicone, and hydrocarbon coatings are considered, which can be uniquely achieved by plasma polymerization [166]. Although fluorocarbon PPFs are considered to enable the most water-repellent surfaces, water molecules might interact with nanoscopic defects yielding slow water uptake (over days and weeks), swelling, and oxidation reactions [167]. Hydrocarbon PPFs (also named diamond-like carbon) also show water penetration via through-film defects and pinholes affecting the interface between the substrate and DLC film resulting in instability that is critical e.g., for implants [168]. Therefore, suitable interlayers are required [169]. Limited water penetration has also been detected by NR for silicone-like PPFs as e.g., deposited from HMDSO accompanied by minimal swelling [137, 149]. As shown in **Figure 11**, water penetrates about 10 nm deep into the SiOCH film within the first hours before nearly approaching saturation. As the likely mechanism of reaction-diffusion along defects such as silanol groups has been discussed that delays the water intrusion with film depth [141]. Likewise, water uptake in silicone-like PPFs deposited from hexymethyldisilane was studied by impedance spectroscopy (EIS) allowing to estimate the initial diffusion coefficient to be as low as  $10^{-14}$  cm<sup>2</sup> s<sup>-1</sup> by neglecting hydrolysis reactions [170]. Hence, sufficiently thick hydrophobic PPFs without through-film defects are required for barrier layers against water intrusion. Ultrathin films, on the contrary, can be used to control the diffusion of water, for example, for the controlled release of embedded silver deposited in a one-step plasma process, further providing anti-adhesive properties [171].

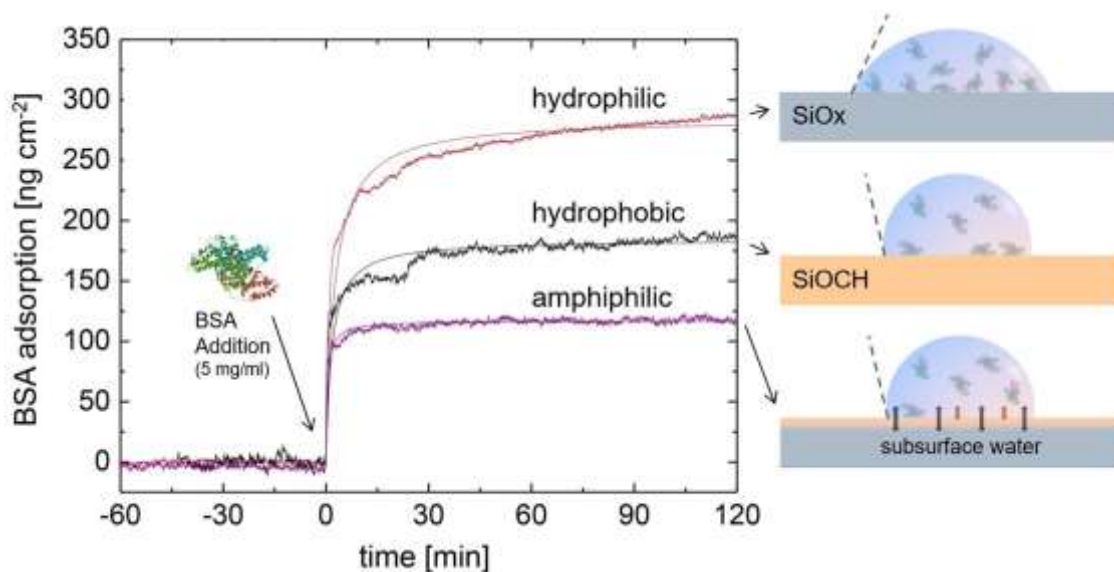
### 5.2.3 Amphiphilic surfaces

An amphiphilic surface is defined as a surface layer that consists of both hydrophilic (containing polar functional groups) and lipophilic (containing hydrocarbons) components. Amphiphilic surfaces exhibit a chemical complexity that effectively hampers biomolecules, cells, and organisms to interact. Consequently, coatings containing, for example, amphiphilic PEGylated fluoroalkyl side chains have shown antibiofouling and fouling release properties, comparable to or better than the widely used PDMS elastomers [172]. Immersed in water, surface enrichment of the PEGylated parts was observed due to chain mobility and migration. Hydrophilic organosilica-based xerogels have been modified with different hydrophobic groups such as  $-(CH_2)_n-X$  with  $X = NH_2, CF_3$ , and  $CH_3$  to cover a range of critical surface tension around 20-30 mN m<sup>-1</sup> comparable to silicone elastomers [173]. This range of surface tension is known to allow the formation of weak boundary layers and facilitated removal of biofouling by hydrodynamic shear forces – also known as Baier curve – as also met by silicone-based coatings [174]. Purely hydrophobic surfaces as silicone, however, still favor the adhesion of some microorganism. Noteworthy, the slightly less hydrophobic end groups with  $-NH_2$  on the hydrophilic xerogel films enabled higher removal of attached cells and significantly lower adhesion forces of BSA compared to silicone. It has been argued that amphiphilic biomolecules such as proteins show a lower tendency to adhere to such 'ambiguous' surfaces, which might be related to water interaction phenomena despite the hydrophobic nature of the outermost surface. Likewise, protein adsorption on PDMS (showing non-specific adsorption) might further be reduced by the attachment of hydrophilic, non-fouling polymer chains providing sufficient surface coverage, typically above 50% [175, 176].

Plasma engineering thus gained increasing interest as a technology to generate amphiphilic surfaces. If a PDMS surface is simply oxidized in an O<sub>2</sub> plasma, a silica-like surface layer larger than 10 nm is easily formed, and both wettability and BSA adsorption were found to be comparable to quartz surfaces [177, 178]. Subsequent attachment of hydrophilic, non-fouling polymer chains can thus not be considered as amphiphilic surfaces. Therefore, hydrophilic/hydrophobic gradients (or bilayer systems) should be limited to the outermost surface region of about 10 nm or less. Non-plasma methods such as CVD, however, typically require a polymer coating thickness of a minimum of 10 nm, e.g., of hydrophilic poly-2-hydroxyethyl methacrylate (PHEMA) onto hydrophobic polytetrafluoroethylene (PTFE) surfaces to reach sufficient coverage to completely alter wettability [179]. Vertical hydrophilic/hydrophobic gradients deposited by plasma polymerization, on the contrary, can be attained with even thinner layers [131]. While the amount of solvents penetrating into PPFs as examined by NR typically shows a gradual decrease with depth [137], this gradient can be inverted by inverse chemical structuring of the film, that is, a hydrophobic layer on top of a hydrophilic layer. This structure resulted in an increased amount of solvent at the interface, which was shown e.g., for ~10 nm thick a-C: H films on Si wafers using NR with toluene as solvent [180]. For example, anti-fogging surfaces can be prepared by attaching PEG brushes with perfluorinated end groups at the substrate surface allowing water penetration by retaining oleophobic properties [181]. Similarly, plasma co-deposition was studied using one hydrophilic (2-dimethylamino ethyl methacrylate or acrylic acid) and one hydrophobic (1H,1H,2H-perfluoro-1-decene) monomer in a low-pressure pulsed plasma enabling anti-fogging properties when the hydrophobic portion amounts to about 10-60 % [182]. It is assumed that the fluoro-containing part in the plasma polymer maintains sufficient hydrophilicity by remaining in a relatively mobile state at the film surface able to reorganize to allow for penetration of water molecules into the hydrophilic subsurface [181].

Another approach based on more crosslinked and thus highly stable siloxane films makes use of 4 nm thick hydrophobic cover layers (HMDSO plasma) deposited on nanoporous, hydrophilic base layers (O<sub>2</sub>/HMDSO plasma) in order to control water penetration to the interface. The amphiphilic

subsurface structure was found to allow water accumulation and nanoconfinement, whereby the orientation of the water molecules is defined by the hydrophilic/hydrophobic interface different from bulk water, which significantly affects protein adsorption at the surface as depicted in **Figure 15** [141, 183-185]. Such water-mediated interactions between nanoscale hydrophilic-hydrophobic pairs able to bound water molecules forming fixed dipoles supported by the hydrophilic sites have not yet received much attention [186]. It is assumed that a long-range dipolar field can thus be created due to confined-water ferroelectric order which affects water orientation and molecular adsorption processes at the surface [141, 187].



**Figure 15:** BSA adsorption measured on different siloxane plasma polymer films after pre-immersion in water. Hydrophilic SiOx and hydrophobic SiOCH PPFs reveal an expected amount of absorbed BSA, whereas the adsorption is reduced for an amphiphilic subsurface by depositing a 4 nm thick hydrophobic cover layer on a hydrophilic base layer indicating that subsurface water affects protein adsorption. Adapted with permission from [185]. © 2016 WILEY-VCH.

To conclude this section, the unique features of plasma polymer deposition to adjust chemical film composition, functionality, and crosslinking at the nanoscale allow a variety of film architectures combining hydrophilic and hydrophobic groups within a nanoporous structure. Using appropriate plasma conditions, a subsurface region, just a few nanometers below the surface, can be adjusted introducing an amphiphilic, zwitterionic, and/or water-absorbing interface maintaining well-defined surface properties. The water interaction with such films revealed fascinating results regarding, as a selection, protein adsorption, non-fouling, and anti-fog that can further be explored for novel surface characteristics involving the near-surface structure. In the following sections some insights are given to emerging applications of plasma engineered surfaces and features of plasma prepared surfaces, indicated in Sections 3 and 5, are highlighted.

## 6. Emerging applications of plasma-controlled surface wettability

Nowadays, the research focus in materials science is on developing functional materials and advanced devices that aim to satisfy the increasing demands in the sustainable development of society and the economy. As for surface wettability, the current dominant applications are centered in environmental,



energy, and biomedical fields in which plasma processing is expected to play an important role mainly due to its versatility and advantages over conventional chemical processes. Below we select and discuss the key applications in these areas that benefit from the plasma-controlled surface wettability achieved by the methods described in Section 4. Through highlighting the specific applications the aim is to give insights into the versatile plasma techniques capable to fabricate multifunctional materials in the most demanding sectors of human life.

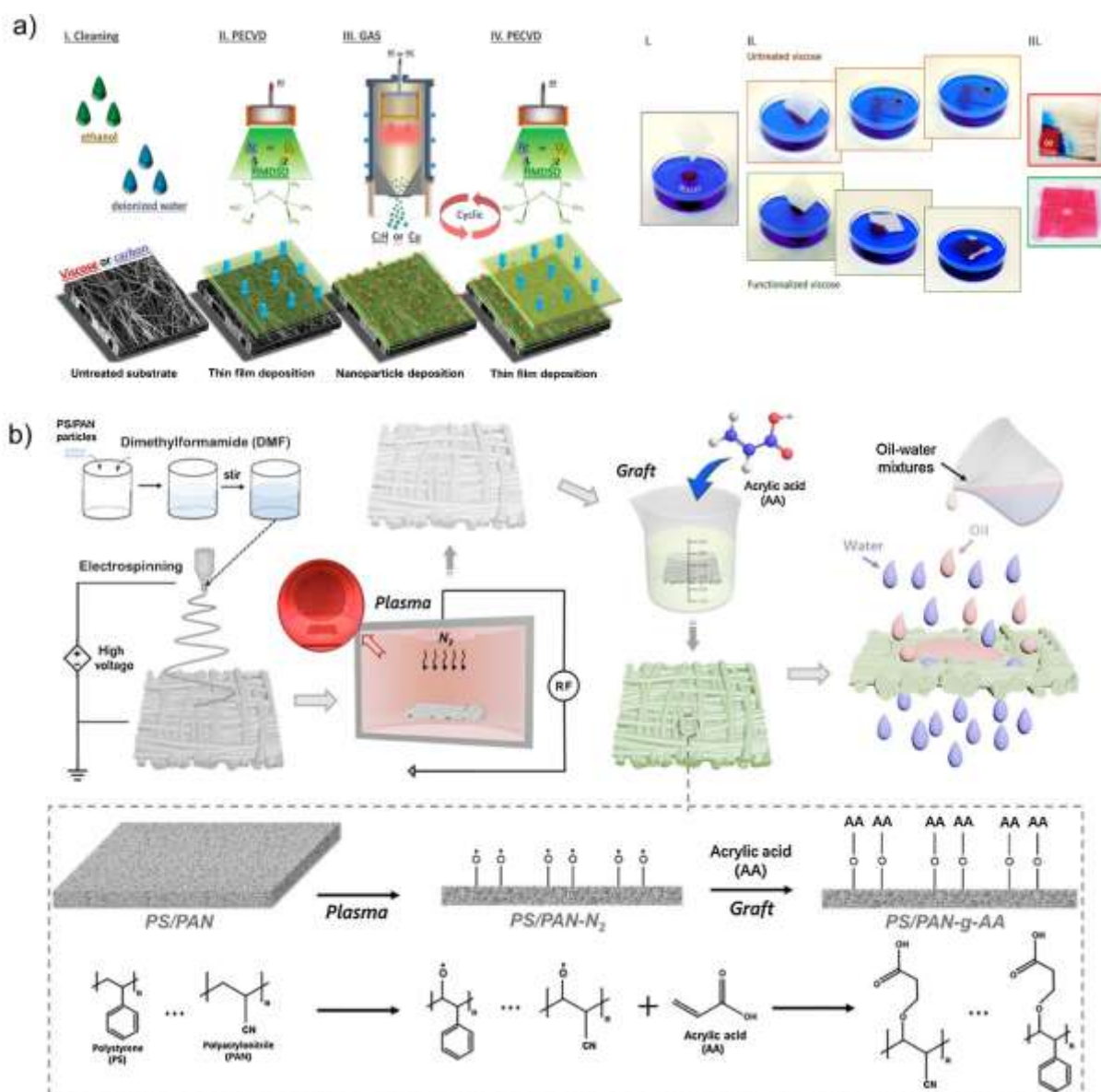
### **6.1 Environmental applications**

In environment-related applications, materials with the desired surface wettability have attracted significant attention in several processes, such as oil-water separation and membrane desalination (MD). Plasma surface functionalization has been used as an eco-friendly surface modification approach in these materials fabrication processes.

#### **6.1.1 Oil-water separation**

Oil-water separation is one of the most intensively studied environmental applications in the past decade where surface wettability defines the success of different approaches and materials [188-190]. Separating oil and water from their mixtures can facilitate their reuse and has multiple targeted applications in both resource utilization and environmental protection. Generally, materials with the specific wettability are the main focus of this application topic due to their opposing affinities toward water and oil (e.g., superhydrophobicity and superoleophilicity and vice versa), and two major types of materials are widely applied: superhydrophobic absorbents [191] and selective filters [192].

Superhydrophobic adsorbents are usually highly porous materials that are also oleophilic and they can thus selectively repel water and absorb oil from oily wastewater by the weight of the original ones up to tens of times [193, 194]. As discussed earlier, plasma techniques can be used to prepare superhydrophobic coatings and thus can be adopted to functionalize sponge-like porous polymeric materials for oil-water separation. As an example, Vaidulych and co-authors [195] reported a multi-layer superhydrophobic nanocomposite coating (WCA = 162 ° in the Cassie-Baxter state) on nonwoven viscose fabric which was achieved by plasma polymerization (PECVD) using HMDSO as precursor combined with a GAS for producing nanoparticles, and the prepared materials showed excellent selective absorption of oil from the oil-water mixture (**Figure 16 a**). In the study, the HMDSO plasma thin film was used to provide hydrophobic functional groups while the embedded Cu nanoparticles were intended to enhance surface roughness. In another example, Torasso et al. [196] used a simpler approach to fabricate superhydrophobic coatings on carbonaceous nanosponge by one-step plasma polymerization of acetylene. The resulting material can adsorb the light crude oil up to as high as 33 times its original weight. Considering the merit of plasma fabrication in the possibility of mass production, the large-scale practical applications for this kind of oil adsorbents in cleaning up oil spills on water surfaces (for example, rivers, lakes, and oceans) seem promising. However, the retrieval of oil from nanoporous materials after oil adsorption and the economical regeneration of the used materials remain immense challenges.



**Figure 16** Plasma-controlled surface wettability for oil-water separation applications. a) Plasma fabricated multi-layer superhydrophobic nanocomposite coatings for selective absorption of oil from the oil-water mixture. The left figure shows the fabrication processes, and the right figure shows the oil absorption processes of both untreated and plasma functionalized materials. Blue is water while red is oil. Reprinted with permission from [195]. © 2019 WILEY-VCH. b) N<sub>2</sub> plasma activation followed by AA liquid phase grafting resulting in superhydrophilic/underwater superoleophobic coatings on electrospun polystyrene/polyacrylonitrile (PS/PAN) nanofiber membranes for oil-water separation. The schematic diagram illustrates the fabrication process and possible reactions. Reprinted with permission from [197]. © 2019 Elsevier.

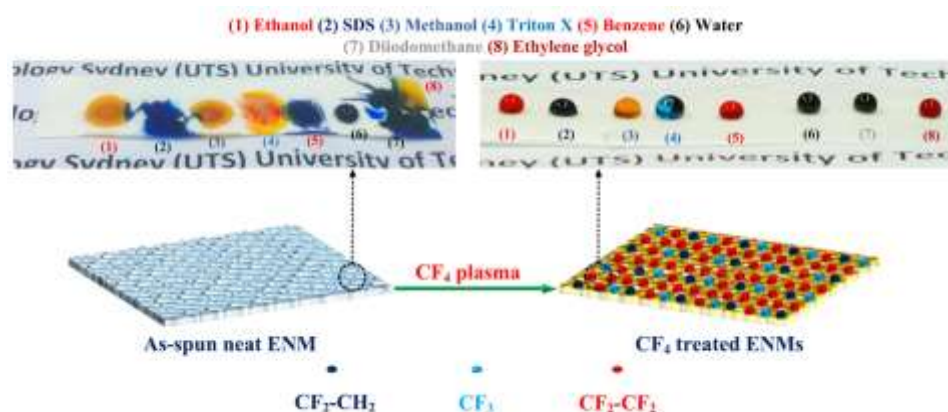
Plasma functionalized superhydrophobic/oleophilic surface can also be used as one kind of selective filter for oil-water separation in a gravity-driven separation system that allows oil permeation but rejects water. Atmospheric pressure plasma polymerized HMDSO superhydrophobic coatings on cotton have been used for separating corn oil and water mixture in a gravity-driven system with a separation efficiency up above 99% [198]. Cotton textiles processed by oxygen plasma etching followed by a diamond-like coating deposition have shown superhydrophobic properties, and thus

they were successfully used to separate a mixture of heavy pump oil and water only using gravity as an external force [199]. Indeed, due to the nature of superhydrophobic and oleophilic materials, it is easy to form a water barrier on the superhydrophobic membranes that can make the light oil stand above the water but can let heavy oil pass still [200]. Therefore, such kind of materials is more suitable for separating the phase-separated mixture of heavy oil and water if a continuous operation driven by gravity is desired.

On the other hand, plasma techniques can be employed to fabricate another type of selective filter: superhydrophilic/underwater superoleophobic membrane, which is regarded as an ideal candidate in a continuous operation for gravity-driven separating light oil and water mixture. Atmospheric pressure He plasma jet has been used as an environmentally friendly and efficient tool to activate nylon mesh for surface hydrophilicity with the aim of oil-water separation [201]. Oxygen-containing functional groups and enhanced surface roughness induced by the plasma activation resulted in the materials with superhydrophilicity with WCA  $\sim 3^\circ$  and underwater hexadecane CA  $\sim 162^\circ$ , and the materials showed excellent oil-water separation performance toward various light oils such as hexane, hexadecane, diesel, and peanut oil with separation efficiency above 97.5%. Superhydrophilic/underwater superoleophobic coatings on electrospun polystyrene/polyacrylonitrile (PS/PAN) nanofiber membranes were fabricated with  $N_2$  plasma activation followed by an acrylic acid (AA) liquid phase grafting (**Figure 16 b**)[197]. The fabricated nanofibers can separate both oil-water mixtures with permeate flux up to  $57509 \text{ L m}^{-2} \text{ h}^{-1}$  and oil-in-water emulsion with high fluxes of  $1390\text{--}6460 \text{ L m}^{-2} \text{ h}^{-1}$  and separation efficiency above 99.5%. Due to the nature of the underwater superoleophobic property, such kinds of membranes can avoid oil contamination significantly with promising for economical regeneration.

### 6.1.2. Membrane distillation

Membrane Distillation (MD) that offers the capacity to treat highly saline water including industrial wastewater, seawater, brine water from other processes, and oil-gas field-produced water is another type of surface wettability application in the environment field [202, 203]. Conventional hydrophobic microporous membranes are in general applied in MD processes, however, they are often hindered by fast wetting and severe fouling especially when the feed stream is enriched with low surface tension agents such as surfactants. Generally, membranes with superhydrophobicity [204], omniphobicity [205], and Janus hydrophilicity/hydrophobicity [206] can efficiently mitigate the wetting and fouling issues of conventional MD membranes.



**Figure 17** The capacity of retaining various low surface tension liquids for the electrospun nanofiber membrane (ENM) (left) and the one modified by  $CH_4$  plasma treatment (right). Plasma treatment can

enable the omniphobic property to PVDF MD membrane and thus improving the performance of MD membranes. Reprinted with permission from [207]. © 2017 Elsevier.

As an alternative technique to traditional wet chemistry approaches, plasma technology with eco-friendly and energy-efficient features can be applied in the fabrication processes of high-performance MD membranes. CH<sub>4</sub> plasma treatment has been employed to functionalize electrospun polyvinylidene fluoride (PVDF) membranes with superhydrophobic properties (WCA  $\approx$  162.4°), and the performance of plasma functionalized MD membranes showed a high salt rejection and about 30% higher water flux than that of the original one [208]. Woo et al. [207] have fabricated a PVDF MD membrane with omniphobic property also by the combination of electrospinning and CH<sub>4</sub> plasma treatment, and the omniphobic surface has displayed WCA larger than 160° and a high wetting resistance to various low surface tension liquids such as methanol, ethylene glycol, and mineral oil (Figure 17). The performance of the omniphobic MD membranes was thus improved significantly mainly due to the reduction of surface tension by promoting the formation of CF<sub>3</sub> and CF<sub>2</sub>-CF<sub>2</sub> bonds induced by plasma treatment. Recently, a facile layer-by-layer coating of Teflon® AF1600 and polydopamine (PDA) on oxygen plasma-treated commercial polytetrafluoroethylene/polypropylene (PTFE/PP) membrane has been used to fabricate Janus hydrophilic/hydrophobic MD membrane, and the fabricated membrane has shown robust desalination performance [209].

### 6.1.3. Others

Apart from oil-water separation and membrane distillation applications, plasma-controlled surface wettability also found other application niches in solving urgent environmental issues. For example, plasma fabricated hydrophobic/hydrophilic patterned surfaces have been proposed for fog harvesting (water collection) [210, 211], which is extremely important in areas where fresh water is scarce. Plasma-treated polymers with improved hydrophilic properties have been used as humidity-sensing materials with high sensitivity [212], which makes the possibility to produce cheap and reliable sensors for environmental monitoring. Although these highlighted environmental applications enabled by plasma-controlled surface wettability seem promising, however, compared to the widely used wet chemistry approaches the relevant studies are still quite rare, and more experimental and theoretical work is needed to further elucidate the benefits of plasma processing.

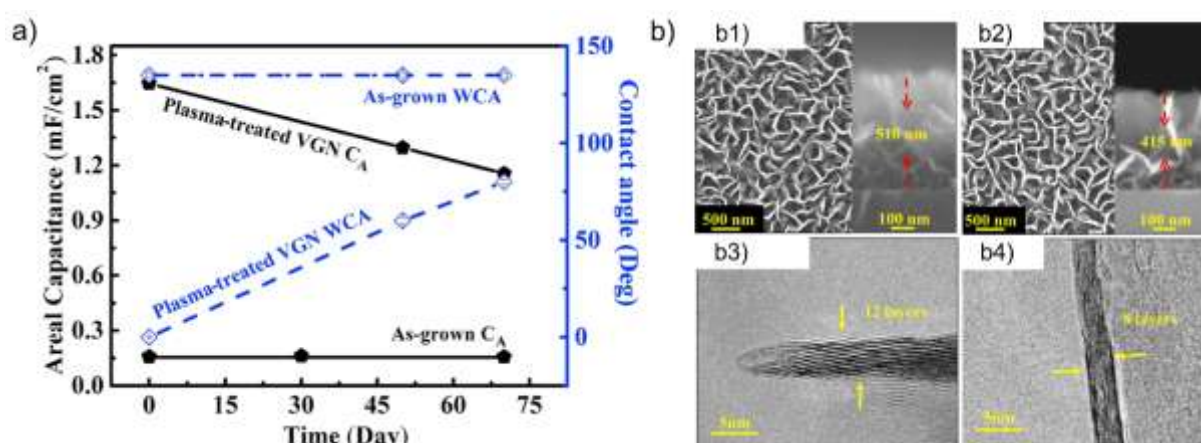
## 6.2. Energy applications

In the past decade, plasma-enabled approaches have also been used as an efficient tool for synthesizing or functionalizing energy-related materials which are mainly carbon-based materials such as graphenes, activated carbon fiber, and carbon nanotubes [213-215]. In some cases, plasma-controlled surface wettability has played a critical role in emerging energy applications ranging from energy storage devices (e.g., electrochemical capacitors and rechargeable batteries) to energy conversion devices (e.g., solar cells) and others like water electrolyzers.

### 6.2.1 Electrochemical capacitors

Nowadays great potential is foreseen in the development of novel electrochemical capacitors having a much higher capacitance than regular capacitors and known as “supercapacitors”. Their charge storage capacity is largely dependent on the surface properties of the used nanostructured electrodes [216]. The surface wettability of the electrodes may influence their interactions with electrolyte ions, and thus affecting the energy storage performance. Sahoo et al. [217] applied O<sub>2</sub> plasma at 600 W for

surface activation of the vertical graphene nanosheets (VGN) used as supercapacitor materials, and the hydrophobic nature (WCA = 134 °) of as-grown VGN was changed to superhydrophilicity (WCA = 0 °). The plasma-induced superhydrophilic VGN showed the improved supercapacitor performance with the maximum areal capacitance of 1.65 mF/cm<sup>2</sup>, while the hydrophobic as-grown VGN surface possessed a specific capacitance of about 0.15 mF/cm<sup>2</sup> only. Although the plasma-treated materials suffered a quite significant aging effect due to the reduction in the oxygen content, the supercapacitor performance was still better than the as-grown one (the measured capacitance value was 1.2 mF/cm<sup>2</sup> for the 90 days aged sample with stable WCA = 80°) (**Figure 18a**) [217]. This study also confirmed that plasma treatment can retain the distinct nanostructured features of VGN when imparting VGN surface with desired surface wettability (**Figure 18b**), showing great potential in surface functionalization of supercapacitor materials for improving the relevant electrochemical performance. Meng et al. [218] obtained a high-performance graphene fiber-based supercapacitor by using air plasma surface treatment. The 33.1% enhancement of areal specific capacitance (36.25 mF/cm<sup>2</sup>) and a higher energy density (22 times) in comparison to the as-prepared one were obtained after only 1 min treatment. The improved performance was attributed to simultaneously tuning the pore size distribution with high microporosity and enhancing hydrophilicity (WCA was changed from 109.4° to 63.6°) by ultrafast plasma treatment.



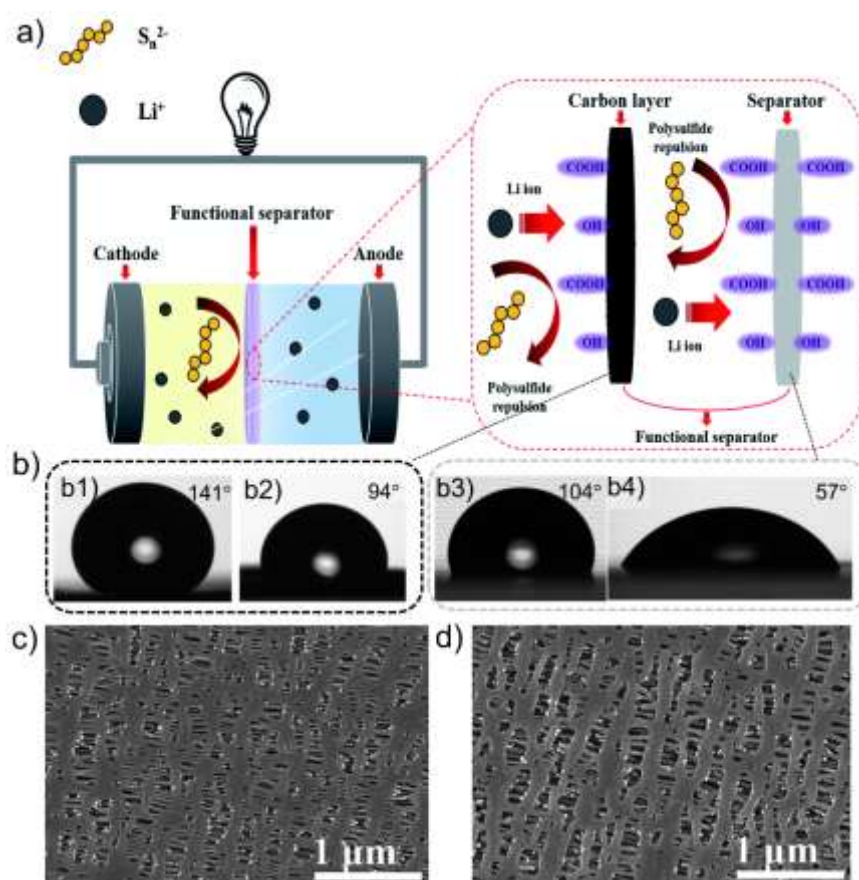
**Figure 18** Plasma treatment of VGN for surface hydrophilicity leading to the enhanced supercapacitor performance. a) Change in areal capacitance ( $C_A$ ) and WCA with aging for 600 W plasma-treated VGN (as-treated WCA 0°). b) SEM and High-resolution transmission electron microscopic (HRTEM) micrographs of VGN before and after O<sub>2</sub> plasma treatments: The top and cross-sectional SEM view of b1) as-grown VGN b2) plasma-treated VGN at 600 W for 2 min, and HRTEM micrographs of as-grown b3) and the plasma-treated VGN b4). Reproduced with permission from [217]. © 2018 Elsevier.

### 6.2.2. Rechargeable batteries

Rechargeable batteries are another kind of versatile and efficient renewable energy storage device. Although there have been great advances in the development of rechargeable batteries in the past decade, a new generation of batteries with much higher power density, better safety, and increased cycle stability is still increasingly on-demand [219, 220]. Generally, electrode materials, separators, and electrolytes are the essential components of a rechargeable battery, and the good wettability of electrode materials and separators has a pronounced impact on providing easy access to electrolytes and thus facilitating battery performance [221-223].



Until now, different plasma-based approaches have been used for controlling the surface wettability for various electrode materials or separators to improve battery performance. Chen et al. [224] introduced an  $N_2$  atmospheric plasma jet to treat the graphite felt electrodes for all-vanadium redox flow batteries, and the hydrophobicity of the electrodes was significantly tailored to high hydrophilicity due to the incorporation of oxygen-containing functional groups, resulting in an improved battery energy efficiency from 62% to 76%. Ouyang et al. [225] have reported a one-step and environmentally friendly strategy enabled by  $N_2$  radio frequency (RF) plasma processing for functionalizing carbon cloth as the electrodes of energy storage devices. The RF plasma activation led to N-doping, nanostructuring, and surface area increase for the treated materials, and the wettability was also distinctly enhanced from WCA =  $141.6^\circ$  to WCA=  $21.3^\circ$ . All these properties resulted in an enhanced storage performance toward the applications in both Lithium-ion batteries and supercapacitors [225], showing the advanced features of plasma processing. Jin et al. [226] employed oxygen plasma functionalization of polyethylene (PE) battery separators with improved electrolyte wettability and retention of PE separators (WCA was changed from  $114^\circ$  to  $8.1^\circ$  after 10 min treatment while the electrolyte CA was changed from  $62.1^\circ$  to  $0^\circ$ ), and the battery cell with oxygen plasma-treated PE separators showed charge-discharge capability with lower interfacial resistance and stable cycling performance. Likewise, Li et al. [227] applied oxygen plasma to activate commercial separators (Celgard 2400) for Lithium-sulfur batteries, and the plasma treatment resulted in the enhanced surface wettability and increased pore sizes eventually leading to effectively maintaining the electrolyte solutions and facilitating the electrolytes to diffuse well into the cell and better ionic conductivity.



**Figure 19** A representative example of plasma treatment of rechargeable battery separators to enhance battery performance. a) Schematic configuration of a lithium-sulfur cell employing a functional

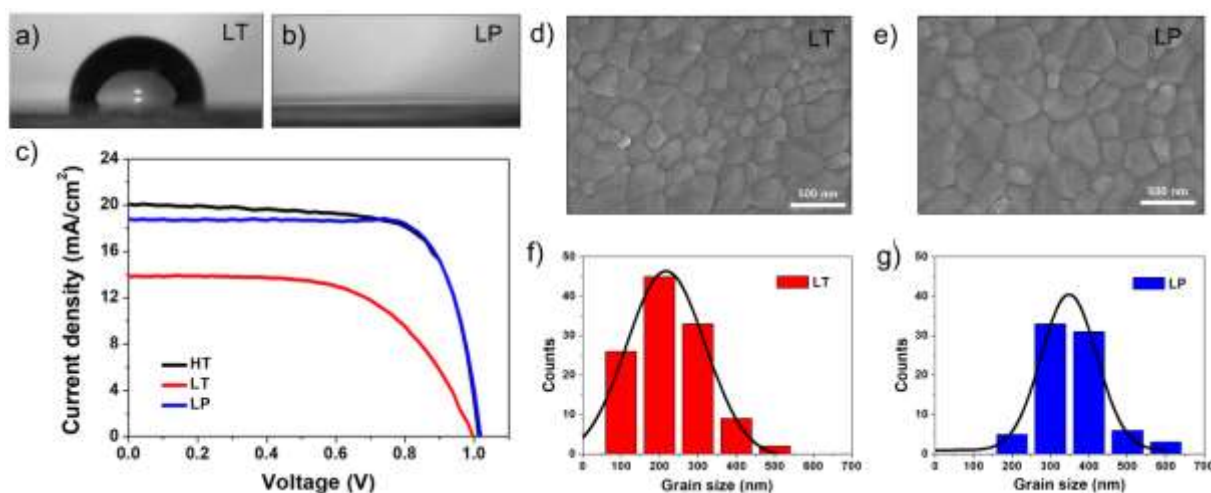


separator; i.e., a carbon-coated separator modified by a plasma. b) WCA images for different samples: b1) Water on a pristine carbon layer, b2) water on a CO<sub>2</sub> plasma-treated carbon layer, b3) water on a pristine separator, and b4) water on a CO<sub>2</sub> plasma-treated separator. c) SEM of a pristine separator surface and d) SEM for the separator after CO<sub>2</sub> plasma treatment, showing a slightly enlarged pore structure as compared to the pristine one. Reproduced with permission [228]. © 2019 The Royal Society of Chemistry.

It has been reported that CO<sub>2</sub> plasma was more efficient than N<sub>2</sub> and O<sub>2</sub> plasma for enhancing the surface wettability of the battery separators (**Figure 19**) [228]. In the study [228], a multi-step plasma-based approach was applied for a functional battery separator. Firstly, CO<sub>2</sub> plasma was used to treat a commercial polymer separator (Celgard 2320), which significantly improved its surface wettability [228]. Then, a carbon layer was coated on the plasma functionalized separator. Finally, CO<sub>2</sub> plasma treatment was performed again on the carbon layer coated separator. The surface wettability of the carbon layer was also improved quite a lot [228]. The lithium-sulfur battery performance was eventually enhanced due to the excellent wettability to the electrolyte, enhanced separator pore structure, a high lithium-ion conductivity, and an electrostatic repulsion toward negatively charged polysulfide. In addition, plasma-enabled polymeric coatings [229] and coatings containing metal oxides such as TiO<sub>2</sub> [230] and Al<sub>2</sub>O<sub>3</sub> [231] have also been reported for improving surface wettability of the battery separators aiming to improve battery performance.

### 6.2.3. Solar cells

Plasma-controlled surface wettability can also be applied in some energy conversion devices such as solar cells. Oxygen plasma has been employed to process a low-temperature deposited mesoporous-structured TiO<sub>2</sub> layer for a flexible perovskite solar cell by Nam et al. [232]. The photovoltaic performance was significantly enhanced (the relevant power conversion efficiency was improved from 8.27% to 14.82%) due to the improved surface wettability which increased MAPbI<sub>3</sub> grain size and the infiltration depth of MAPbI<sub>3</sub> into the mesoporous-structured TiO<sub>2</sub> layer, and also due to the passivated the oxygen vacancy related traps in TiO<sub>2</sub> induced by the plasma (**Figure 20**) [232]. In another study [233], a low-temperature (< 40 °C) He plasma jet treatment of nickel oxide (NiO) thin film for p-i-n perovskite solar cells also improved the surface hydrophilicity, thereby leading to the improved energy harvesting performance. Importantly, the study was performed at atmospheric pressure ambient conditions, which shows a great prospect for further development of more efficient solar cells under mild conditions. On the other hand, self-cleaning hydrophobic/superhydrophobic coatings can also benefit solar cells by preventing contamination by dust, snow, and so on in practical applications [234]. Liang et al. [235] have developed a superhydrophobic coating (WCA = 153 °) with self-cleaning, transparent, durable properties by a PECVD process under low pressure combined with wet chemistry approaches. The fabricated coatings have also shown stability against strong acid, strong alkali, and the impact of water drops and sand. Moreover, when the plasma-based coating was applied to a solar cell, the power conversion efficiency of the coating-covered one was much higher than that of the bare cell after two months of outdoor experiment tests [235].



**Figure 20** Oxygen plasma treatment of mesoporous-structured TiO<sub>2</sub> layer for a flexible perovskite solar cell, showing significantly enhanced photovoltaic performance. a) and b) are WCA images for low-temperature sintered (LT) TiO<sub>2</sub> and low-temperature sintered TiO<sub>2</sub> with oxygen plasma treatment (LP) TiO<sub>2</sub>, respectively. c) J-V curves of the best performing perovskite solar cells fabricated with high-temperature sintered (HT) TiO<sub>2</sub>, LT TiO<sub>2</sub>, and LP TiO<sub>2</sub>. The LP TiO<sub>2</sub> shows comparable performance to that of HT TiO<sub>2</sub>. Top-view SEM images of MAPbI<sub>3</sub> layers on d) LT TiO<sub>2</sub> and e) LP TiO<sub>2</sub>. Grain size distribution histogram of MAPbI<sub>3</sub> layers on f) LT TiO<sub>2</sub> and g) LP-TiO<sub>2</sub>. Reproduced with permission [232]. © 2020 American Chemical Society.

In addition, the fabrication of barrier film for encapsulation of solar cells can also use plasma technologies. For example, a flexible perovskite solar cell with improved stability and efficiency was achieved by using HMDSO plasma polymerization for depositing the barrier film [236].

#### 6.2.4. Water electrolyzers

Plasma-controlled surface wettability could also be used in other energy fields such as electrolyzing water for hydrogen production. For example, a graphdiyne (GDY) based water splitting electrode was changed from hydrophobic (WCA 139.2 °) to superhydrophilic (WCA 0 °) by Li et al. [237] using a simple air plasma treatment method. The obtained superhydrophilic electrode was used to support cobalt/aluminum layered double hydroxide catalysts, exhibiting superior activity with an overpotential of  $\approx 258$  mV to reach  $10 \text{ mA cm}^{-2}$  and a turnover frequency of  $0.60 \text{ s}^{-1}$  at an overpotential of 300 mV. The boost of water oxidation activity was ascribed to the increased electron density, enhanced interactions with catalysts, and improved interfacial mass/electron transfer by using the plasma fabricated superhydrophilic graphdiyne.

According to the above-highlighted energy applications enabled by plasma-controlled surface wettability, further studies into the fabrication of energy-related materials and devices with more functions using efficient plasma-based methods, are envisaged in the near future.

### 6.3. Biomedical applications

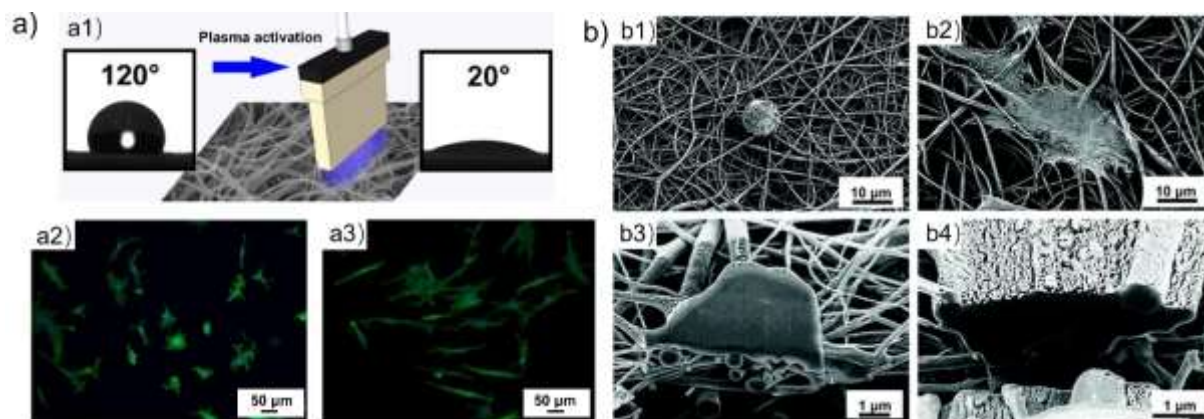
The dynamic liquid environment of live cells makes the surface wettability of a biomaterial critically important for relevant biomedical applications. In general, surface wettability has an immense influence on protein adsorption and cell adhesion, etc., thus affecting the performance of a biomaterial [6, 238, 239]. As the plasma approach is a rapid, dry, economical, effective, and environmentally friendly materials processing technique, it is also becoming increasingly popular in the biomedical

community in recent years [240]. In this section, we briefly summarize and discuss the role of plasma-controlled surface wettability in the most popular biomedical fields such as tissue engineering scaffolds and antibiofouling surfaces.

### 6.3.1 Tissue engineering scaffolds

Tissue engineering scaffolds are typically porous materials that are mainly synthesized by an electrospinning technique because the electrospun polymeric nanofibers generally possess suitable properties such as biodegradation capacity, appropriate mechanical properties, and, most importantly, the nanoscale structures that mimic the native extracellular matrix (ECM) [241-243]. However, they usually have the inherent hydrophobic nature with low surface energy, and thus showing poor cell-surface interactions. Therefore, post hydrophilic surface modification is generally required to facilitate better tissue regeneration performance for such kinds of scaffolds in which plasma approaches have played a significant role [244-246].

Dolci et al. [247] have employed a linear corona (LC) discharge plasma jet operated at atmospheric pressure open-air (working gas:  $N_2$ ) to functionalize the electrospun poly(L-lactic acid) (PLLA) scaffolds (**Figure 21 a**). The plasma-activated nanofibrous scaffolds showed a significantly improved surface hydrophilicity with WCA changing from  $120^\circ$  for the pristine one to  $20^\circ$  after plasma activation treatment which was attributed to the introduction of carboxyl groups on scaffold surface as there was no significant modification on surface morphology in terms of fiber shape, uniformity, and diameter. Moreover, the average percentage of water uptake was increased from around 10% for the untreated one to around 400% for the plasma-activated one, and the ability was preserved for different aging times, up to at least 120 h. Furthermore, it was found that the scaffolds treated by plasma activation significantly enhanced mouse embryonic fibroblast (MEF) vitality (**Figure 21 a**) [247]. Therefore, this study confirms the effectiveness of plasma activation and shows the feasibility of the plasma technique in the functionalization of polymeric scaffolds.



**Figure 21** Plasma-controlled surface wettability applied in tissue engineering scaffolds. a)  $N_2$  plasma activation of PLLA electrospun nanofibrous scaffolds: a1) illustration of the plasma activation process and WCAs of pristine and plasma-activated surface, a2) MEF cells morphologies on the pristine scaffolds, showing small, rounded, and star-like fibroblasts with short processes, and a3) MEF cells on the plasma-activated scaffolds, exhibiting elongated with dendritic morphologies. Reproduced with permission from [247]. © 2014 WILEY-VCH. b) Saos-2 cells cultured on  $O_2$  plasma activation of electrospun piezoelectric PVDF nanofibrous scaffolds. b1) and b2) are SEM images of the cultured Saos-2 cells on untreated hydrophobic and plasma-treated hydrophilic electrospun PVDF scaffolds, respectively; b3) and b4) are SEM-FIB cross-sections of Saos-2 cells grown on hydrophobic and hydrophilic scaffolds, respectively.

hydrophilic electrospun scaffolds, respectively. Reproduced with permission from [248]. ©2019 The Royal Society of Chemistry.

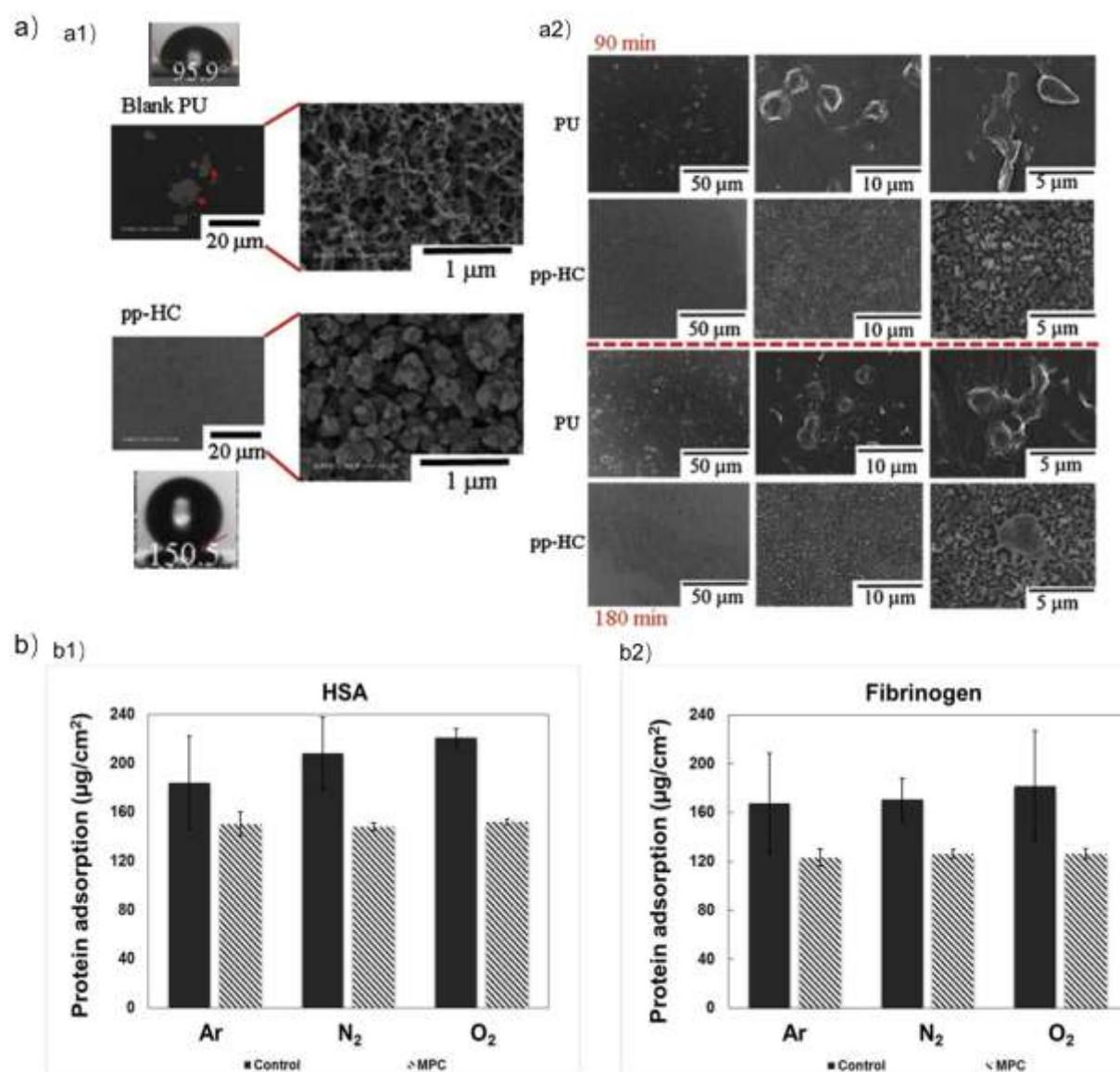
In another study, to improve the inherent hydrophobic nature of electrospun PVDF, Kitsara et al. [248] applied O<sub>2</sub> plasma activation for obtaining high-performance hydrophilic PVDF scaffolds. The surface wettability (WCA) of PVDF was significantly changed from untreated 130° to superhydrophilic immediately after 2 min plasma treatment. However, it suffered a slight aging effect to become hydrophilic (WCA = 35 °) in one month. The plasma-treated 35° hydrophilic materials finally did not change over 2 years after the treatment, which can be regarded as permanently hydrophilic surfaces induced by the plasma processing. More importantly, osteoblast cultures showed better cell spreading and scaffold colonization in the plasma functionalized electrospun scaffolds due to the improved surface hydrophilicity (**Figure 21 b**) [248]. In addition, similar studies have been conducted on different electrospun materials such as polyurethane (PU), poly( $\epsilon$ -caprolactone) (PCL), and polylactic acid (PLA) with different plasma such as Ar, O<sub>2</sub>, and NH<sub>3</sub> for surface activation [249-251], and some of them give the electrospun scaffolds not only desired surface wettability but also targeted functional groups that can result in better cell-surface interactions for better performance in practical usage.

### 6.3.2 Antibiofouling surfaces

Biofouling usually occurs on biomedical devices where cells and microorganisms such as bacteria, protein, and even viruses can be attached to their surface, and thus largely threatening human health and the life-cycle of the devices [252]. Surface engineering for antibiofouling has become one of the most popular strategies for antimicrobial/antiviral applications [101, 253, 254]. Regarding the surface wettability, low adhesion and self-cleaning superhydrophobic surfaces (in the Cassie-Baxter state) can avoid water droplets “standing” on the surface, and thus can prevent biofouling, which is one of the most investigated antibiofouling strategies [255, 256]. As discussed above, plasma surface engineering can be used to fabricate superhydrophobic surfaces efficiently and easily, and thus may provide a viable way for the preparation of high-performance antibiofouling surfaces. For example, Hsiao et al. [257] have employed an HMDSO/CF<sub>4</sub> plasma polymerization for obtaining superhydrophobic coatings on PU biomaterials, and the fabricated superhydrophobic surfaces showed remarkable antifouling properties with no both platelet adhesion and fibrinogen adsorption (**Figure 22 a**). Moreover, the plasma fabricated coatings also showed non-cytotoxicity and favorable hemocompatibility. This study thus shows the great potential of the plasma approach in biomaterial functionalization. Similar superhydrophobic coatings with excellent antibiofouling properties have also been fabricated by using the plasma polymerization method with different precursors such as PFDA and the mixture of TMCTS and perfluorooctyltriethoxysilane (PFOTES) [258, 259].

On the other hand, some high hydrophilic or even superhydrophilic surfaces also have antibiofouling properties due to their high affinity for water and the reaction between hydrophilic chains and water, forming a hydration layer where bio-contaminants can hardly adhere [260-262]. The plasma approach could also be applied for fabricating such kind of antibiofouling surface. Chen et al. [263] have used a multi-step plasma method for grafting a zwitterionic 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer brushes on the silicone (polydimethylsiloxane, PDMS)-based contact lenses. N<sub>2</sub> plasma was first used for cleaning the PDMS-based contact lenses. Then, they were immersed in an isopropanol solution containing 10 wt% of the MPC monomers. Thirdly, the samples were treated with Ar, N<sub>2</sub>, and O<sub>2</sub> plasma again for fast polymerization. The fabricated plasma coatings showed high hydrophilicity (WCA 20 – 30 °) resulting in approximately 25 – 30% protein adsorption,

compared with those of the pristine silicone contact lenses due to the immobilization of the MPC zwitterionic polymer brushes and the suitable hydrophilic surface (**Figure 22 b)**) [263]. This effect is similar to the formation of zwitterionic polymers discussed in Section 5.



**Figure 22** Plasma-controlled surface wettability for antifouling applications. a) Plasma polymerized HMDSO/CF<sub>4</sub> (pp-Hc) superhydrophobic coatings on PU surfaces: a1) the WCA images of and SEM images of the fibrinogen adsorption for blank PU samples and pp-Hc films, and a2) the platelet adhesion test incubated in platelet-rich plasma (PRP) for 90 min and 180 min on the blank PU substrate and pp-HC films coated specimens. Reprinted with permission from [257]. © 2015 Elsevier. b) Multi-step plasma-induced zwitterionic MPC polymerization for antibiofouling applications: two proteins b1) human serum (HSA) and b2) human plasma fibrinogen on the silicone surface after only the plasma gas treatment (without the MPC monomers, as a control) and atmospheric plasma-induced polymerization of the MPC (n = 5). Reproduced with permission from [263]. © 2018 Elsevier.

## 7. Summary, future directions, and challenges

As the selected and by far non-exhaustive examples in this review suggest, plasma processing has revealed its unique potential as a versatile tool for the effective control of surface wettability in a broad

range of materials and practical applications. The plasma processes allow unique and very effective control of the surface chemistry and surface morphology – the two key factors that determine the surface energy, and hence, the ability of the surface to either repel or attract the liquid. In respect to water, wetting responses characterized by water contact angles ranging from zero (complete hydrophilicity) to over 150 degrees (superhydrophobicity) have been demonstrated. Similar effects have been shown for other liquids and solutions, with varying degrees of success.

The ability to effectively control the surface wettability by plasma treatments has been extended for more sophisticated processes including the production of porous and composite materials which were engineered with nanoscale (e.g., by surface texturing) and even atomic (e.g., vacancy or substitutional doping) precision. This precise materials engineering has led to the demonstration of a versatile toolbox to manipulate water across sub-nanometer to microscopic scales, as evidenced by the numerous examples of active water control by the plasma-treated outer and inner surfaces of the materials. Indeed, it becomes possible to repel, absorb, capture, diffuse, transport, or evaporate water molecules, and also to separate them from contaminants (e.g., salts or oil).

The plasma-modified surfaces have revealed the ability to actively control the interactions with other molecules, e.g., to manipulate the adsorption and conformation of proteins in biomedical applications or infuse perovskite precursors inside porous metal oxide in the fabrication of next-generation solar cells. The range of applications of the plasma-enabled surface wettability control is broad, spanning water purification and desalination in the environmental field, energy storage, and water electrolysis active materials and devices in the clean and renewable energy field, as well as biomolecule manipulation and biofouling control in the biomedical field.

Importantly, the above plasma-enabled processes have been demonstrated for both low-pressure (vacuum-based) and atmospheric pressure processing conditions, and the entire spectrum of common materials from soft hydrogels and easy-to-melt plastics to metal alloys, ceramics, as well as relatively recently discovered low-dimensional nanomaterials such as graphene. Although the more traditional low-pressure processes still prevail, the importance of atmospheric pressure plasma processing is rapidly increasing, owing to the outstanding potential for scale-up towards the industry-relevant processes.

What are the key unique features of the plasma-assisted surface processing that enable the above achievements across the broad range of materials and applications? The key to answer is in the way plasmas make the surface modifications happen. The few such features discussed in the review include fast and localized atomic manipulations through both physical (e.g., sputtering by ion impact) or chemical (e.g., by etching or polymerization) effects and reactions that make it possible for the plasma to control surface chemistry and surface morphology in unique ways, often in a synergistic way. Indeed, the plasma exposure can simultaneously lead to the enhanced surface chemical activity (e.g., functionalization or atomic reconstruction) or surface texturing, and this combined effect can produce better outcomes than when the two approaches are used separately. The plasma treatment and the associated energy and matter transfer can be localized to only the few top atomic layers without affecting the bulk of the materials. This leads to the enhanced crosslink density and atomic bonding applicable to diverse materials systems, including those where it is normally difficult to achieve otherwise. Consequently, it becomes possible to uniquely synthesize and further enhance (by defect engineering, doping, or functionalization) sophisticated surface nanoarchitectures, which in turn enable the unique and selective interactions with water and other molecules contained in the water.



From the practical materials and process engineering perspective, plasma processing has several notable features. These features include the very fast, dry, effective, scalable, environment-friendly processes with potentially generic applicability across the broad range of materials systems.

There are numerous challenges and opportunities for plasma processing to contribute even more to this rapidly evolving field encompassing fundamental research and practical applications. As the materials systems and their functionalities, along with the processes to produce such materials, become more and more advanced to meet an ever-broader range of socio-economic challenges, plasma processing has to maintain the momentum and advance faster and well beyond the current capabilities, in a close collaboration with researchers across all the research fields that benefit from the plasma processing. Put simple, materials fabrication and processing techniques, such as the plasma-based ones, should always be at the forefront of materials research and applications.

There are several examples of the areas where plasma processing is poised to contribute in the near future. For example, the rapid uptake of digital additive manufacturing technologies (AMTs) may lead to the unprecedented ability to create intricate three-dimensional (3D) structures for the effective manipulation and control of liquids and solutions for diverse applications. Synergizing atmospheric pressure plasma processing with AMTs is a promising yet underexplored way to simultaneously functionalize and nanostructure the 3D surfaces to control the wettability of all surface areas outside and within such structures, virtually at will.

The scalability and stability of the plasma wettability control is a critical issue on the way to widespread commercial applications. Indeed, scalability implies the ability to effectively and uniformly control the materials properties from atomic to micrometer scales in each square millimeter within a film of an industry-relevant scale, e.g., of the square meter area. The reported range of stability of the achieved surface wettability properties range from minutes to years depending on the specific processes and materials; this ability obviously requires to be improved in a more generic and uniform fashion.

Radically new fundamental scientific solutions are required when the processing spaces reduce to the nanometer and sub-nanometer scales. For instance, the ability to control water molecules within sub-nm spaces is presently demanded to enable next-generation energy storage, clean water, and biomedical purification technologies. This ability requires effective control of the surface energy with atomic precision, e.g., intentional defect creation within the interspaces between the atomic layers of two-dimensional (2D) materials. The fundamental limitation is that plasma as such cannot penetrate into such small spaces due to the loss of charge neutrality. However, the plasma generated species such as hydrogen ions can penetrate effectively even across the atomic layers of 2D materials such as graphene, and cause structural modifications on the inside, such as vacancies. The vacancies would substantially modify the transport and capture of water and other molecules between the atomic layers. Larger ions, such as oxygen atoms, generated by plasma, can penetrate between the atomic layers and expand the interatomic spaces, leading to the new class of molecular superlattice materials [264]. One can expect that water transport in these and many other materials, modified with atomic precision, would be substantially different compared to the pristine materials. The relevant capabilities presently exist for vacuum-based plasma systems and represent an obvious opportunity for atmospheric pressure plasma conditions.

There are many other recent and rapidly evolving materials systems offering opportunities for plasma processing to engage and actively contribute to the development of their surface wettability properties. The non-exhaustive examples include diverse nature-derived, topological, quantum, smart, responsive, flexible, memory, intelligent materials, biodegradable plastics, and many other materials

where the imagination and creativity can help grasp the unique opportunities to collaborate across several fields of science and engineering and contribute the many challenges facing humankind.

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