The Research Progress of Photoswitchable Wettability Materials

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Abstract. Surfaces with photo-responsive wettability can convert between hydrophobic and hydrophilic state via visible light or ultraviolet ray reversibly, which have attracted considerable attention and continue to be appealing and challenging. In this review, the classification based on their mechanism is introduced. The common fabrication approaches are outlined and also presented are the current and optional applications.

Keywords: superhydrophobic, photo-responsive, superhydrophilic.

1. Introduction
The smart materials with reversible and controllable wettability have great potential in many fields, including cell culture devices, biomedicine [1], printing techniques, microfluidic devices, and others [2]. Various materials can response to different stimulus, such as temperature, pH, light etc.

Among these materials, the manipulation and transformation of surface wettability utilizing light irradiation have obvious advantages including fast in transmutation, non-contact, relatively simple devices, and others [2]. Thus it has attracted intensive attention.

In this review, the classification based on their mechanism is introduced. The common fabrication approaches are outlined and also presented are the current and optional applications.

2. What is Photoswitchable Wettability Materials
Photoswitchable wettability materials refer to those whose wettability is reversible and controllable through Light irradiation. According to the recently published paper, two different kinds are included for photoresponsive materials. At first, the inorganic metal oxides, which mainly include V2O5, SnO2, ZnO, and TiO2 etc., are known for the conversion between the oxygen boosting (hydrophilic) state and the oxygen vacancy (hydrophobic) state. In the second place, the organic molecules can be transformed from high energy cis to low energy trans by means of altering the molecular configuration, such as spiropyran and azobenzene, which achieves the transformation between hydrophilic and hydrophobic [2].

Both of the varieties have their own merit and shortcoming. Inorganic materials generally dominate in toxicity (lower) and photochemical/thermal stability (higher) compared to organic materials. However, the relatively long response times (often days or even weeks) of dark storage pose notable barriers to their application in practice [3]. It is well known that organic molecules are rapidly and reversibly trans-photoisomerized, which would lead to the large variation of geometrical shape and
dipole moments, resulting in fast photoswitchable wettability. In the next section, some approaches to fabricate these two kinds of materials are introduced.

3. How to Fabricate Photoswitchable Wettability Materials

3.1. Inorganic Transition-Metal Oxide Surfaces

Fujishima et. al were the first to explore the wettability of semiconductor [12]. They indicated that the water contact angle of TiO2 decreased from 72° to 0°, showing superhydrophobicity, which inspired people’s interest of the switchable wettability surface of the inorganic semiconductor with wide forbidden band [4]. ZnO, SnO2, Fe2O3, TiO2, V2O5 as significant inorganic semiconductor with wide forbidden band, have become widely used to fabricate light-responsive materials.

In the beginning stage of this field, for those materials, UV is the only irradiation tool, and the recovery is by staying in the dark, which is very slow. Liu et al. reported ZnO films, with rapid reversible transition properties of superhydrophobicity and superhydrophilicity under vacuum ultraviolet (VUV) irradiation, were prepared by a simple and low-temperature solution method by controlling the pH value with hydrofluoric acid. The fresh film shows the superhydrophobic one, turning into a superhydrophilic one after 30min VUV irradiation and can be recovered to superhydrophobic through being placed in the dark for 6 d. [4] And then Shi et. al fabricated a Superhydrophobic Titanium Oxide which can be changed to Superhydrophilicity induced by Irradiation of Ultraviolet Light. A flower-like TiO2 thin film with micro and nano composite structure was deposited on the glass substrate by the hydrothermal reaction, using TiCl3. After being modified by octyltrimethoxysilane the film showed perfect superhydrophobicity, which was changed to superhydrophilicity after being irradiated under ultraviolet light for 4 ~6 hours, which can turn back to superhydrophobicity after 20d in dark[5]. New double response superhydrophobic hybrid materials ZnO/ SIMS with different counterions (I−, BF4−, PF6− and TF2N −) self-assembled monolayers have been synthesized (Xin et al., 2014). Firstly, They deposited zinc oxide nanoparticles on the surface of the glass to generate roughness. Then, the SAMs of fluorinated alkyl -3 -(3-triethoxysilylpropyl)-4, 5-dihydroimidazole-iodide (abb. [C8Ftespin]I) were inarched onto these surfaces by a -Si-O- covalent bond via self-assembly skills. The exchange reaction of aqueous anion can achieve exchanges between I-ions and BF4 -, PF6 -, or TF2N -. The wettability of the ZnO/[C8Ftespin]X hybrid layer can be reversibly transformed via altering ultraviolet irradiation (UV) at dark storage [7].

After that, scientists started to explore those materials that can turn back by heating, which shortens the time of turning back. Nano vanadium pentoxide / octadecylamine (nanoV2O5 / ODA) was covered on copper wire gauze by hydrothermal reaction to prepare photosensitive materials. The material can be transited reversibly between superhydrophobic and superhydrophilicity suffering from UV light with 254 nm. The prepared network can be transformed into superhydrophobic by heating on the oven with 60°C for 2 hours [6]. In Reza Norouzbeigi’s research, ZnO / CuO nanocomposite surfaces with adjustable dual response superantiwetting hierarchical were prepared by chemical bath deposition with different initial molar ratios of copper nitrate and zinc nitrate solutions. After 11 h of UV irradiation, the surface can reversibly change from superhydrophobic state to hydrophilic state, and can return to superhydrophobic state after 150 °C heat treatment ° C 30 minutes later [8].

With the efforts of scientists, the UV is not the only irradiation tool, the surfaces that can respond to visible light or solar light were also reported. Zahed Shami et al. reported a PVDF-P25TiO2 nanotextile using a single stage method with low cost. A three-dimensional (3D) intelligent response surface was prepared by amplified electrospinning using purchasable PVDF and p25 TiO2 in market as raw materials. The surface realize a rapid and reversible transition between superhydrophobic and superhydrophobic / underwater superhydrophobic state via ultraviolet and sunlight, which can also be restored after heating [9].
3.2. Organic Molecules

Spiropyran (SP) and azobenzene are widely utilized in modifying the wettability of functional surfaces due to their famous rapid and reversible trans-cis photoisomerization, leading to great changes in geometrical shape and dipole moment [6], which can lead to the optical switch wettability of spiropyran and azobenzene modified surfaces. Most of them can be induced by both UV and visible light.

Zhang et al. found that a surface grafting polymerization of 7-[(three fluoromethoxy phenyl azo) phenoxy acrylic acid (TFMPAA) was carried out by plasma and UV light, and a method for chemical grafting of azobenzene polymer nanoparticle porous layer on the cyclic olefin copolymer (COC) substrate was developed. 1- vinyl -2- pyrrolidone (NVP) and cross-linker N,N’-methylenebis (acrylamide) (MBA). The polymer nanoparticles are formed and aggregated on the surface to form porous photosensitive layer during initiating graft polymerization on the surface of inverse microemulsion, improving their surfaceness. (Fig. 1). As a result, a photo-responsive surface achieving superhydrophobic / superhydrophilic transformation was achieved by means of UV and visible light irradiation [2].

In Lu’s research, a simple dip coating method was used to prepare the intelligent copolymer functional flexible surface with light switch wettability between superhydrophilic state and superhydrophobic state utilizing UV and visible light. The cotton fabric was cut into rectangles and immersed in the solution of poly (FAzo-co-FMA) / THF or homopolymer (poly-Azo) / THF. All samples were dried for 48 hours in the vacuum oven with 100 °C. The effects of the molar ratio of copolymer FAzo / FMA and the azo polymer solution concentration on the modification of cotton fabric were studied (Fig. 2) [1].

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Zhang et al. reported that dopamine hydrochloride was dissolved in buffer water solution (Tri-HCl) with pH of 8.5 and silica particles were added into the solution of dopamine. The solution would form silica/PD composite particles by overnight stirring at ambient temperature. The composite particles were washed by deionized water several times, and then dispersed in the solution containing molecules that would be immobilized at room temperature. Finally, the surface owns the capacity of switching between superhydrophobic and superhydrophilic state via UV and visible light. The process of preparing the surfaces is shown in Fig. 3 [11].
In Wang et al’s research, they grafted methacrylate polymer brushes containing SP from silicon and quartz substrates using ATRP. Eventually, achieve the transformation of the surfaces by alternation of UV-irradiation and visible light irradiation or utilizing dark storage [13].

4. How Photoswitchable Wettability Materials Work

4.1. Microfluidic Devices
Zhang et al. reported how the light responsive polymer surface (mentioned in section 2.2) working in controlling liquid samples loading in microfluidic apparatus. The video clip that drops load can be observed in the auxiliary materials. In the Figure S1A, the channel surface with hydrophobicity hinders the influx of deposited water droplets. In Figure S1B, the capillary force deriving from hydrophilicity of the channel surface due to UV irradiation can lead to the behavior of auto-fly of water droplets into the channel. In addition, the hydrophobic state would dominate the channel surface due to the visible light irradiation. As shown in Figure S1CE, the water droplets after re-deposition cannot flow into the channel [2].

4.2. In Situ Water Purification
The smart nano-V$_2$O$_5$/ODA-coated mesh (mentioned in section 2.1) combine wettability conversion with ROS generation characteristics, which achieves the in situ photo-switchable water purification. It can control and simultaneously remove oil and soluble pollutants. In Fig. 4, the mechanism of V$_2$O$_5$/ODA coating mesh and their matching assistant mesh involved in the light controlled water restoration was plotted. Under UV irradiation, V$_2$O$_5$ produces electron hole pairs, and then OH$^-$ becomes OH (ROS), while lattice defects are trapped and generated by water molecules, which makes the grid superhydrophilic. The oil removal by light control and pollutant degradation can be realized at the same time in that way [6].
4.3. Cell Culture Devices
The morphological changes of cell growth can be regulated by adjusting the water contact angle. Jiang et al. reported that the hydrophilic membrane with 10 μm-column structure met the needs of three-dimensional culture of cells, while the hydrophobic membrane with 3 μm-column structure was only appropriate for the three-dimensional culture of cells with small size and hard cuticle. Additionally, cells tend to form spheres on hydrophobic membranes, whereas cells usually grow on and adhered to the hydrophilic membranes [10]. Therefore, the photoswitchable wettability materials have great potential in cell culture device.

5. Conclusion and Outlook
In this review, we have outlined the research on the photoswitchable wettability material. The definition and common fabrication methods are introduced. The various applications of photoswitchable wettability material in microfluidic devices, in situ water purification and cell culture devices.

However, there are still challenges and large development potential. The method to fabricate the materials which can respond to both UV and visible light should be further studied. And more effort should be devoted to their novel applications, such as cell culture devices, which lack of practical research. And here we propose that the photo-responsive materials can combine with Janus membranes to realize smarter materials.

6. Appendix A. Supplementary Data
In terms of the description water droplet loading I thermal bonded COC, its corresponding video clips can be discovered in the online version, at http://dx.doi.org/10.1016/j.surfcoat.2016.12.072 [2].

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