



Fast formation of hydrophilic and reactive polymer micropatterns by photocatalytic lithography method



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ABSTRACT

An approach is developed for the fast formation of a hydrophilic pattern on superhydrophobic substrates with good contrast due to the large wettability contrast between superhydrophobic and superhydrophilic areas. It can be used for forming a polymer pattern with reactive functional groups. TiO₂ nanoparticles were grafted with long alkyl chains and then coated on substrates to produce superhydrophobic films. Photocatalytic degradation of the grafted alkyl chains was effected with UV light irradiation and resulted in transition from superhydrophobicity to superhydrophilicity. After UV light irradiation through a mask for 30 s, dyes or polymers were adsorbed on the photoinduced superhydrophilic areas to make micropatterns. The photoinduced superhydrophilic switching properties can be tuned by changing the alkyl chain length. The ninhydrin assay was adapted to identify free amino groups of polymers on the patterned area. Polymer patterns with free amino groups can be achieved.

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1. Introduction

Switching between superhydrophilicity and superhydrophobicity can be achieved by tuning the surface morphology and surface chemistry of the substrate [1–3]. Photolithography/laser interference lithography [4], photocatalytic remote oxidation/photocatalytic lithography [5], photocatalytic Ag nucleation on TiO₂ thin film and electroless Cu deposition [6] can be used to make alternative superhydrophilic and superhydrophobic patterns on the substrate. Organic molecules such as *n*-octyltriethoxysilane and dodecyl phosphate can be used to form the hydrocarbon self-assembled monolayer (SAM) layer [7,8]. The alignment of a hydrocarbon SAM on the hydrophilic surface of TiO₂ creates a hydrophobic or super-hydrophobic surface. A process for patterning hydrocarbon monolayers by UV irradiation has previously been developed [9]. After UV irradiation, the organic SAM layer on TiO₂ surface is ablated [10,11], and the surface becomes hydrophilic.

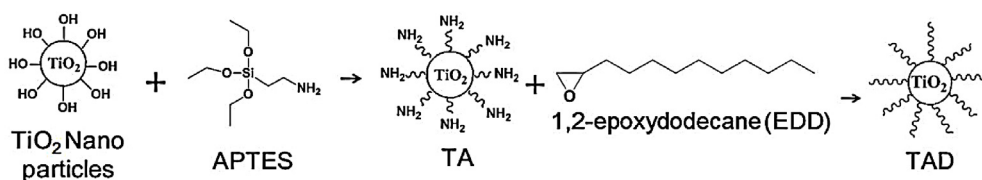
If the surface is exposed to UV light through a photomask, the grafted aliphatic chains on a TiO₂ surface can be photo-ablated to produce a superhydrophilic pattern. Then oligomers can be selectively attached to the surface and cured to obtain a chemically micropatterned, superhydrophilic surface to which cells or

proteins can be attached. This patterning of micrometer-scale proteins or cell patterns on substrates can be used in applications such as protein microarrays, biosensors, and portable diagnostic devices [12,13]. For the fabrication of protein micropatterns, dispensing and microcontact printing methods have been developed to deliver protein solutions to the designated locations on the substrates [14]. However, the above-mentioned methods still face some challenges, such as contamination from stamps in the microcontact printing process. One solution to this issue may be to form protein micropatterns on a surface with chemical micropatterns [15,16].

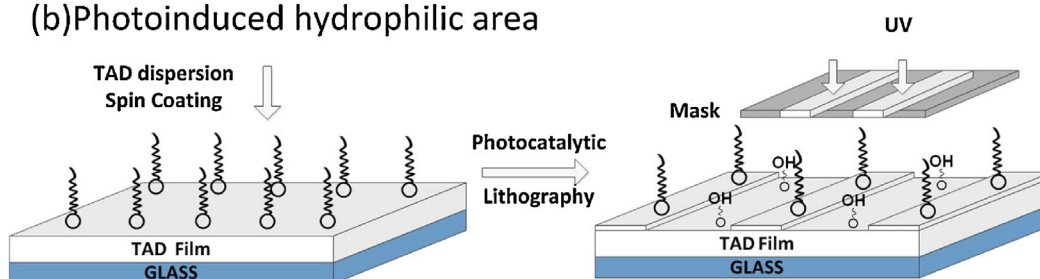
For the functional groups without strong absorption or fluorescence properties in the UV/Vis spectrum, detection requires functionalization with a marking agent [17,18]. The reaction of ninhydrin with a primary amino group forms a colored reaction product, diketohydrindylidene-diketohydrindamine (Ruhemann's purple). This reaction has previously been used for the analysis of amino acids. Curotto [19] and Sabina [20] described the use of the ninhydrin reaction for quantitative determination of chitosan, together with the amount of free amino groups. Sotgia [21] reported a reaction between ninhydrin and aminothiols that acted as an indirect method for the chiral recognition of stereoisomers of penicillamine.

To provide a method for preparing chemically micropatterned surfaces onto which covalently-bonded protein micropatterns can be formed, we developed a fast UV lithography process that allows the patterning of hydrophilic polymers with reactive functional groups in this study. Unlike previous UV surface modification

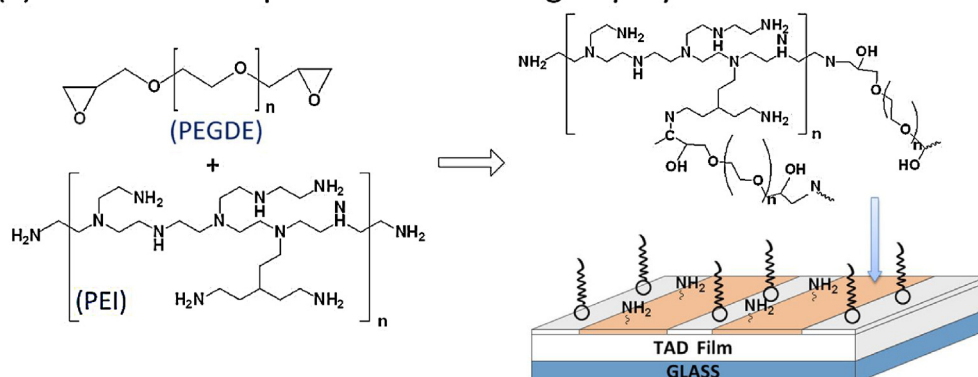
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(a) Grafting on TiO₂

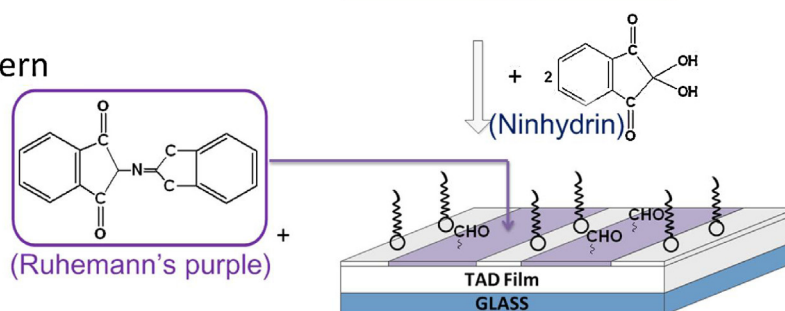
(b) Photoinduced hydrophilic area



(c) Selective adsorption & crosslinking of polymer



(d) Color pattern



Scheme 1. Schematic illustration of (a) synthesis of grafted TiO₂ nanoparticles (b) formation of hydrophilic micropattern (c) fabrication of polymer micropattern with free amino groups (d) marked purple patterns by the reaction of ninhydrin with primary amino groups.

methods, this method can be performed under ambient conditions with a fast response time (30 s) by taking advantage of the photocatalytic properties of TiO₂. The substrate used for the patterning was glass coated with titanium dioxide nanoparticles with alkyl chains grafted to them to produce a hydrophobic surface. Films with hydrophobic/hydrophilic micropatterns were fabricated by UV light irradiation through a mask. Hydrophilic dyes or polymers were selectively adsorbed on the hydrophilic areas to make the micropatterns. A aqueous solution of poly(ethylene glycol) diglycidyl ether with excess polyethylenimine was coated and selectively adsorbed on the photoinduced superhydrophilic areas. After curing, the pattern will not be washed away during biochip

or biosensor applications. Ninhydrin was used for confirming the primary amino groups of the polymer patterns.

2. Materials and methods

2.1. Materials

3-Aminopropyltriethoxysilane (APTES) was supplied by TCI. 1,2-epoxydodecane (EDD), polyethylenimine (Mw: 1200–1300), and 1,2-epoxyoctadecane (EOD) were purchased from Aldrich Chemical. Poly(ethylene glycol) diglycidyl ether, and ninhydrin

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