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Patterned liquid permeation through the TiO₂ nanotube array coated Ti mesh by photoelectric cooperation for liquid printing
1. Introduction

In recent years, considerable interest has arisen in responsive, smart surfaces which can respond to an external stimulus, such as temperature, light, electricity, pH, solvent, and magnetic fields. However, these single-responsive surfaces have limitations in many areas, especially precise controllable wettability. The cooperation of different stimuli, particularly photoelectric cooperation, has become a hot topic, due to its potential applications in controlling the behaviors of conductive liquids. Chiou et al. proposed an opto-electrowetting mechanism for the light actuation of a liquid droplet, by integrating a photoconductive material underneath the electrowetting electrodes. Oroszi et al. introduced a technique for the optical control of electro-osmosis, through illuminating the photoconductor, to reduce the electro-osmotic driving force.

Despite much progress in this field, the patterning of controllable surface wettability is still a challenge, which is a very important issue for printing techniques. Our group has reported an approach to precisely control the patterned wettability transition on a superhydrophobic aligned ZnO photoconductive nanorod array surface via a photoelectric cooperative wetting process. Lately, an aligned nanoporous array surface of the TiO2-coated nanoporous anodic aluminum oxide (AAO) film was used to demonstrate a similar process, with high mechanical strength and excellent controllability. However, the adhesion force of the aligned nanoporous array surface was higher than that of the aligned nanorod array structure, moreover, the responsive voltage in the above work was high, so that the liquid was easily electrolyzed, to some extent.

Herein, we have developed a patterned liquid permeation method by photoelectric cooperation, on a micro/nano hierarchical structured mesh film. Namely, the patterned permeation of a liquid through the mesh can be controlled just on the illuminating sites, when applying a voltage lower than the electrowetting induced permeation threshold voltage. The permeation process and mechanism are discussed in detail. The results indicate that the microscale movement of a liquid can be controlled precisely by the surface micro/nano hierarchical structure of the device, with a low adhesion and responsive voltage. Therefore, this work is important in the research and application of liquid printing, moreover, it provides a new approach to develop and apply novel devices such as micro/nanofluidic systems, microreactors and micro-nano electronic technologies.

Patterned liquid permeation through the TiO2 nanotube array coated Ti mesh by photoelectric cooperation for liquid printing†

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The surface wettability response has been intensively studied under external stimulus, and the cooperation of different stimuli seems a trend for more effective surface wetting. Despite much progress in this field, the patterning of controllable surface wettability is still a challenge, which is a very important issue for printing techniques. Here, we have developed an approach for the photoelectric cooperative wetting induced liquid permeation through a TiO2 nanotube array coated Ti mesh. The patterned liquid permeation can be realized by patterned light illumination under a voltage which is lower than the electrowetting induced permeation threshold voltage. The permeation process and mechanism are discussed in detail. The results indicate that the microscale movement of a liquid can be controlled precisely by the surface micro/nano hierarchical structure of the device, with a low adhesion and responsive voltage. Therefore, this work is important in the research and application of liquid printing, moreover, it provides a new approach to develop and apply novel devices such as micro/nanofluidic systems, microreactors and micro-nano electronic technologies.

2. Experimental section

2.1. Fabrication of TiO₂ nanotube array coated Ti mesh

The original Ti mesh was cleaned by acetone, ethanol and deionized water in order, then dried at 60 °C for 30 min. The TiO₂ nanotube array coated Ti mesh was fabricated by an electrochemical anodization method. One piece of Ti mesh (2.5 cm × 2.5 cm) was used as a working electrode, while Pt foil was the counter electrode and the spacing distance between them was about 3 cm. The anodization of the Ti mesh was processed in an electrolyte which was consisted of 0.25 wt% ammonium fluoride and a 98 vol% ethylene glycol aqueous solution, at 50 V for 3 h, to fabricate the TiO₂ nanotube array. The as-prepared TiO₂ nanotube array was annealed at 500 °C for 3 h to induce an anatase crystallization.

2.2. Fabrication of superhydrophobic dye-sensitized TiO₂ nanotube-array surface

The annealed TiO₂ nanotube array coated Ti mesh was sensitized in a solution (10⁻⁴ mol L⁻¹) of N719 dye in ethanol (GR) for 24 h and dried, then treated in a heptadecafluorodecyltrimethoxysilane (FAS) atmosphere for 20–30 min and dried. The superhydrophobic dye-sensitized TiO₂ nanotube-array surface was achieved for a water droplet’s permeation, induced by photoelectric cooperation.

2.3. Instruments and characterization

The SEM images were characterized using a JEOL JSM-6700F SEM at 5 kV. The contact angles were measured by a Data-physics OCA20 CA system at ambient temperature. The X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffraction meter, in the range 3–90°. The UV-vis reflection spectra were recorded on a GBC Cintra 10e spectrophotometer, equipped with an integrating sphere. The electrochemical impedance measurements were carried out using a Zahner IM6e impedance analyzer (Germany) in the frequency range 0.02 Hz to 100 kHz. The photoelectric activity was measured by illumination with a monochromatic light, obtained by a series of light filters with different wavelengths. A solar simulator (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) was used as the light source, with a wavelength of 200–900 nm. The intensity of the light was 400 mW cm⁻², which was checked using a power and energy meter (Model FZ-A, Beijing). The voltage applied in the photoelectric cooperative response process was provided by an AC power supply.

3. Results and discussion

3.1. Fabrication of superhydrophobic TiO₂ nanotube array coated Ti mesh

As reported, the chemical composition and geometric structure are the two main factors to govern the surface wettability.¹⁶,¹⁷ TiO₂, a kind of inorganic light-sensitive semiconductor material with a wide bandgap of 3.2 eV,¹⁸ is an ideal micro-structure material, such as TiO₂ nanotubes with an excellent photoelectric performance and high photoelectric conversion efficiency.¹⁹ In this work, we fabricated TiO₂ nanotubes by the anodization of a Ti mesh. The preparation process and schematic diagrams of the TiO₂ nanotube array coated Ti mesh are illustrated in Fig. 1a. The TiO₂ nanotubes were grown in a radically outward direction, symmetrically, with a tubelike and hollow internal structure. The scanning electron microscope (SEM) images of the anodized Ti mesh, with a pore size of ~156.2 μm, showed that the surface of the Ti mesh became rough with a micro/nano hierarchical structure, because of the growth of TiO₂ nanotubes with similar inner diameters of ~58 nm, a wall thickness of ~7 nm, an interspace of the nanotubes of ~19 nm. The TiO₂ nanotubes were highly ordered and neatly arranged (Fig. 1b and c). The TiO₂ nanotubes were compactly formed and tightly bound to the Ti mesh surface with a nanotube length of ~7 μm (Fig. 1d and e). The length-diameter ratio of the TiO₂ nanotubes was high, which can increase the specific surface area to adsorb more dye molecules and improve the photoelectric conversion efficiency. The X-ray diffraction (XRD) pattern of the annealed TiO₂ nanotubes (500 °C for 3 h) shows that the crystallization of the TiO₂ nanotubes was an anatase phase, which has excellent photoactivity from the diffraction peak of the anatase (101) crystal face at 2θ = 25.2° and other diffraction peaks at 2θ = 37.6°, 48.1°, 62.8°, 70.5° (see Fig. S1 in the ESI†). Then, the prepared TiO₂ nanotubes were sensitized by the N719 dye, to improve the ability of the photoelectric response. Finally, the sensitized TiO₂ nanotubes were treated by FAS to obtain a superhydrophobic surface.

Fig. 1 Schematic diagrams of the preparation process and SEM images of the as-prepared aligned TiO₂ nanotube array coated Ti mesh. (a) Schematic diagrams of anodization reactor (left) and aligned TiO₂ nanotube array coated mesh structure (right). SEM top view of the anodized Ti mesh (b) and the enlarged view of TiO₂ nanotube array on the anodized Ti wire (c). (d) and (e) are side views of TiO₂ nanotube array on the anodized Ti wire.
3.2. Photoelectric cooperative permeation workaround of the aligned TiO$_2$ nanotube array coated mesh

The photoelectric cooperative water permeation process was experimentally investigated on the superhydrophobic aligned TiO$_2$ nanotube array coated Ti mesh (Fig. 2). When only an electric field was applied, water droplet permeation would not occur, until the voltage increased to 3.5 V, which can be called an electrowetting induced permeation threshold voltage ($E_t$), and the contact angle (CA) decreased from $\sim 172^\circ$ to $\sim 90^\circ$.

![Electrowetting and photoelectric cooperative wetting induced water permeation on the superhydrophobic TiO$_2$ nanotube array coated mesh.](image)

(a) Electrowetting induced water permeation: with no voltage applied, the CA was $\sim 172^\circ$ (left), water droplet kept stable on the mesh surface; at 3.5 V ($E_t$, electrowetting induced permeation threshold voltage), the CA decreased to $\sim 90^\circ$ and water began to permeate the mesh (middle); after the voltage was turned off, the permeate state remained almost the same (right). (b) Photoelectric cooperative wetting induced water permeation: upon applying a bias of 2.5 V, water droplet with original CA of $\sim 172^\circ$ changed little (left); added light illumination, water droplet permeated at 2.5 V with CA of $\sim 91^\circ$ (middle); after the light and voltage were turned off, the permeate state almost kept the same (right). (c) The CA change curve with the voltage increasing: (■) without light illumination; (▲) with light illumination. The applied voltage can be divided into three parts: In region I, water would not permeate the mesh film with the voltage increase even with light illumination. In region II, water would permeate the mesh film with light illumination, but that could not occur without light illumination. In region III, water permeation would occur no matter with or without light illumination. Consequently, region II is considered as the suitable workaround for photoelectric cooperative wetting induced water permeation.

While the CA and the permeation state had little change after the voltage was turned off (Fig. 2a). Similarly, the permeation process of a water droplet controlled by photoelectric cooperation is shown in Fig. 2b. Upon applying a bias of 2.5 V, the water droplet, with an original CA of $\sim 172^\circ$, changed little. When light illumination, with an intensity of 400 mW cm$^{-2}$ and a wavelength of 200–900 nm was added, the water droplet would permeate through the mesh, while the CA decreased to $\sim 91^\circ$. Notably, the responsive speed of the photoelectric wetting induced liquid permeation was very fast and it took tens of milliseconds (less than 1 s) to realize the permeation process. When the light and voltage were turned off, the CA and the permeation state remained almost the same. It can be seen that with illumination, the water can permeate the mesh film at a voltage lower than the electrowetting induced permeation threshold voltage. To demonstrate the photoelectric cooperative water permeation result, the curve of CA versus voltage is sketched with and without light illumination in Fig. 2c.

The curve can be divided into three parts: in region I, water droplet could not permeate the mesh film with the increase of voltage, even with light illumination. In region II, water would permeate the mesh film with added light illumination. It can also be seen that the photoelectric cooperation induced permeation threshold voltage ($E_c$) was 2 V. In region III, water droplet permeation would occur, no matter with, or without light illumination. Consequently, region II is considered as the suitable workaround for a photoelectric cooperation controlled water permeation. These results made a strong indication that photoelectric cooperative permeation can be realized only at the illumination sites on the superhydrophobic mesh film at a voltage which is lower than the electrowetting induced permeation threshold voltage. Accordingly, the patterned permeation of a liquid can be obtained by the patterned light illumination.

![Schematic diagrams of red ink permeation controlled by photoelectric cooperation are illustrated in Fig. 3.](image)

3.3. Photoelectric cooperative liquid permeation patterning on the aligned TiO$_2$ nanotube array coated mesh

In order to demonstrate the process of the mesh film, the schematic diagrams of red ink permeation controlled by photoelectric cooperation are illustrated in Fig. 3. When a commercial, water soluble ink was added to the TiO$_2$ coated mesh surface and a voltage applied higher than photoelectric cooperation induced permeation threshold voltage ($E_c$) but lower than electrowetting induced permeation threshold voltage ($E_t$), air was trapped in the micro/nano-hierarchical structure owing to the Cassie state$^{22}$ of the superhydrophobic mesh surface (Fig. 3a). With patterned light, e.g., a “+” pattern, illuminating the TiO$_2$ coated mesh surface through a photo mask, the wettability of the patterned site transferred from the Cassie to the Wenzel state$^{21}$ simultaneously and thus the ink entered the micro structure and an ink pattern “+” permeated the mesh film, even after the light and the voltage were turned off (Fig. 3b). At the same time, a printing paper was put in contact with the bottom of the mesh film, then the “+” pattern was transferred onto the paper (Fig. 3c). The patterned liquid
permeation controlled by photoelectric cooperation for printing was processed successfully. Similarly, other reprographic images can also be obtained.

### 3.4. Photoelectric properties characterization of the aligned TiO$_2$ nanotube array coated mesh

To achieve the photoelectric cooperative liquid permeation, the special micro/nano structure and the photoconductivity properties are important. The micro/nano hierarchical structured mesh has an excellent photoelectric performance and high photoelectric conversion efficiency, due to the large surface area and high interface energy of the aligned TiO$_2$ nanotube array. When sensitized by the N719 dye, the aligned TiO$_2$ nanotube array would have a higher photoelectric performance. The UV-vis diffuse-reflectance spectra of the TiO$_2$ and N719-dye-sensitized TiO$_2$ nanotube array indicate that when modified by N719 dye, the TiO$_2$ nanotube array can absorb much more visible light, which benefited the process of the photoelectric response (Fig. 4a). The photocurrent action spectrum in Fig. 4b suggests that the N719-dye-sensitized TiO$_2$ nanotube array has a high photoelectric conversion efficiency, in a broad range, 380–700 nm, which indicates that the N719 dye can sensitize the TiO$_2$ nanotube array, strongly. Fig. 4c shows the Nyquist diagram of the electrochemical impedance contrast in the dark and under light illumination for the N719-dye-sensitized TiO$_2$ nanotube array. It can be seen that the electrochemical impedance of the TiO$_2$ mesh under illumination was much lower than that of the mesh in the dark. These results indicate that light can excite the N719 dye molecules into an excited state, and photogenerated electrons can be transferred from the excited dye molecules to the TiO$_2$ conduction bands, because the former electric potential energy was higher, and then to an external circuit by an electrode to form the photoelectric current (Fig. 4d). As a result, the N719 dye improves the photoelectric activity of the TiO$_2$ nanotube array evidently when light is illuminated on the layer, which equivalently decreased the effective thickness. As eqn (1) (ref. 22) demonstrates, the threshold voltage drops, then the CA decreases ($\theta_v < \theta_0$) and photoelectric cooperative wetting induced liquid permeation happens.

$$\cos\theta_v = \cos\theta_0 + \frac{\varepsilon_0\varepsilon_r(V - V_T)^2}{2d}\gamma_{LV}$$  

where $\theta_0$ is the initial contact angle when no voltage is applied, $\theta_v$ is the contact angle at a voltage, $\varepsilon_0$ is the permittivity of a vacuum, $\varepsilon_r$ is the permittivity of the dielectric layer, $d$ is the thickness of the dielectric layer, $\gamma_{LV}$ is the surface tension of the liquid–vapor interface, and $V_T$ is the voltage that needs to compensate the influence of the trapped changes.

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**Fig. 3** Schematic diagrams of the integrated procedure of photoelectric cooperation controlled red ink permeation for liquid printing. (a) When a commercial water soluble red ink was added to the TiO$_2$ nanotube array coated Ti mesh surface above the photoelectric cooperation induced permeation threshold voltage, but below electrowetting induced permeation threshold voltage, the ink kept the Cassie superhydrophobic state. (b) When patterned light illumination, e.g., a “+”, was added by a photo mask, the wettability of the patterned site transferred to the Wenzel state, meanwhile the patterned red ink would permeate through the illumination sites. (c) The “+” ink pattern was achieved, and transferred onto the paper through a printing paper contacting with the bottom of the mesh film.

**Fig. 4** The photoelectric properties characterization of the N719 dye sensitized TiO$_2$ films. (a) UV-vis diffuse-reflectance spectra of TiO$_2$ and N719-dye-sensitized TiO$_2$ nanotube array film. (b) Photocurrent action spectrum of the N719-dye-sensitized TiO$_2$ nanotube array film. (c) Nyquist plots of the electrochemical impedance spectra obtained in the dark and under illumination for N719-dye-sensitized TiO$_2$ nanotube array film. Inset is the corresponding enlarged drawing of the high-frequency region. (d) Schematic diagram of the electron transportation process between the N719 dye and the TiO$_2$. 

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3.5. Mechanism of micro/nano hierarchical structure on the patterned liquid permeation

To further understand the mechanism of the micro/nano hierarchical structure on the photoelectric cooperative patterned liquid permeation, we modelled the wetting induced permeation process of the micro/nano hierarchical structure of the TiO₂ array coated mesh, seen in Fig. 5. Initially, the liquid was kept stable on the superhydrophobic mesh surface and an external pressure $\Delta P$ existed in the micro mesh pores, the open ends of nanotubes and the interspaces of the nanotubes (Fig. 5a). As illustrated in eqn (2), $\Delta P$ largely depends upon the ratio of $l$ to $A$.

$$\Delta P = \frac{l}{A} \cos \theta_A$$

where $l$ is the circumference of the micro/nano structure, $A$ is the cross-sectional area of the micro/nano structure, and $\theta_A$ is the advancing angle of the liquid on the single Ti wire surface.

By calculation, the ratio of $l$ to $A$ of the micro pores was the minimum ($2.6 \times 10^4 \text{ m}^{-1}$), the open ends of the nanotubes second place ($6.9 \times 10^4 \text{ m}^{-1}$), and the interspaces of the nanotubes was the maximum ($2.1 \times 10^8 \text{ m}^{-1}$). Thus, the corresponding $\Delta P$ was $8.8 \times 10^2 \text{ Pa}$, $2.3 \times 10^6 \text{ Pa}$, and $7.1 \times 10^6 \text{ Pa}$, respectively, which meant the energy barrier of the micro pores for liquid permeation was much smaller than the others. The photoelectric cooperation induced a CA decrease and electric capillary pressure (ECP), to cause the liquid to merge into the micro-structure.

$$\text{ECP} = \frac{l}{A^2} \left(V - V_A\right)^2$$

The ECP can promote the influx of the liquid to the micro/nano structure, as long as $\text{ECP} > \Delta P$ is satisfied. Calculated by eqn (3), the ECP was $1.8 \times 10^3 \text{ Pa}$, which was just enough to overcome the energy barrier of the micro pores. Accordingly, when patterned light illuminated the mesh film during the photoelectric cooperative liquid permeation process, the permeation would happen only into the micro pores, but not the open ends of the nanotubes and interspaces of the nanotubes (Fig. 5b).

The detailed permeation description of the relationship of $\Delta P$ versus $l/A$ is shown in Fig. 5c; in region I, liquid permeation would not happen; in region II, the liquid would only permeate into the micro pores, which is the case suitable for liquid printing; in regions III and IV, liquid would permeate into the open ends of the nanotubes and interspaces, subsequently. Therefore, the special micro/nano-hierarchical structures of the mesh film are important in the patterned liquid permeation process. On the one hand, the micro pore size is a critical factor for the resolution of the printed pattern. In general, a smaller pore size leads to a higher image resolution, in theory. While the smaller the pore size is, the smaller the wire diameter is; it was noted that its mechanical strength was very low after the Ti mesh was treated by the electrochemical anodization method.

In this paper, we chose a relative small pore size, with a certain mechanical strength, to explain the photoelectric wetting induced liquid permeation through the micro/nano hierarchical structured mesh. On the other hand, the micro/nano hierarchical structured mesh film also has many advantages, such as a low adhesion and low responsive voltage.

4. Conclusions

In conclusion, we have developed an approach for photoelectric cooperative wetting induced liquid permeation, through an aligned TiO₂ nanotube array coated Ti mesh. The patterned liquid permeation can be realized by patterned light illumination under a voltage which is lower than the electrowetting induced permeation threshold voltage. The permeation process
and mechanism have been discussed in detail. The results indicate that the microscale movement of a liquid can be controlled precisely by the surface micro/nano hierarchical structure of the device, with a low adhesion and responsive voltage. Therefore, this work has an important impact in the research and application of liquid printing, moreover, it provides a new approach to develop and apply novel devices, such as micro/nanofluidic systems, microreactors and micro-nanoelectronic technologies.

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