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Patterned hydrothermal synthesis of TiO_2 to produce droplet repelling forces

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Abstract

Hydrophilic/hydrophobic pattern on a surface repels water droplet because a driving force acts on the droplet from hydrophobic area to hydrophilic area due to the imbalance of surface tensions. In the case of oil droplet in water, the driving force acts oppositely due to the same reason. These driving forces can be applied to produce a self-cleaning function. The forces can be enhanced with tapered wettability pattern on the surface. To extend the functional life, this study applied the patterned hydrothermal synthesis of TiO_2 for hydrophilic area because its hydrophilicity can be ensured by photocatalytic activity with UV irradiation. Hydrothermal synthesis on a fluoride-doped tin oxide (FTO) substrate produces an array of TiO_2 vertical rods. By masking the hydrothermal synthesis with star-like patterned photomasks, TiO_2 rods were successfully synthesized leaving hydrophobic star-like areas. A star-like pattern has four tapers to gather the spread thin oil film to make a droplet. After observing the morphology of the structure, oil droplet repelling performance was examined. It was found that the sliding angle of oil droplet in water drastically decreased with the help of patterned structure. The effect of UV irradiation dose on the repelling performance was also made clear.

Hydrothermal synthesis, wettability pattern, water/oil, droplet, repellent

1. Introduction

Anti-adhesive or self-cleaning surfaces are often required not only in industry but in daily life. Contact angle of a liquid droplet is determined as the equilibrium of interfacial tensions at the boundaries between liquid, solid, and ambient substance such as air. By applying hydrophilic/hydrophobic pattern on a surface, contact angle of a droplet becomes not unique but variant depending on the location. Using these patterns, spread oil could be gathered and self-cleaning function was demonstrated [1]. However, its functional life was limited because the wettability changed with time.

Titanium dioxide (TiO_2) has stable super-hydrophilicity after ultraviolet (UV) irradiation due to photocatalytic activity [2]. Hydrothermal synthesis can produce an array of TiO_2 rods on a fluoride-doped tin oxide (FTO) substrate [3, 4]. However, its patterning has not been tried due to high process temperature.

This study aims to produce patterned array of TiO_2 rods with hydrothermal synthesis and evaluate the repelling characteristic of oil droplet in water. Future applications are also discussed.

2. Principle

Figure 1 shows the change in oil droplet contact angles showing the effect of environment and the principle of droplet repelling. The upper photographs show the oil droplets in water. The contact angle on a hydrophilic surface becomes large while that on hydrophobic surface is small due to the change in interfacial tension balance [1]. The lower figure shows cross-section of oil droplet stretched across the wettability boundary together with the force vectors representing interfacial tensions at the boundaries. It can be found that the oil droplet moves from hydrophobic area to hydrophilic one due to a driving force caused by the imbalance of tensions, which is the principle of repelling.

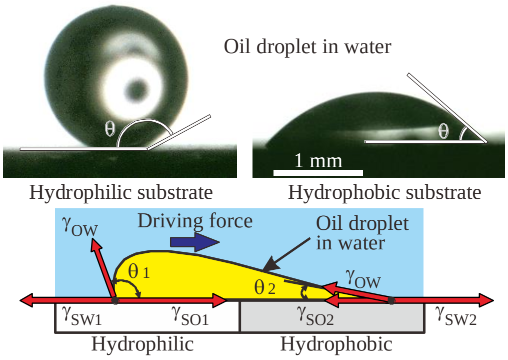

Figure 1. Principle of droplet repelling in case of oil droplet in water

3. Preparation of wettability-patterned samples

Figure 2 shows the preparation of wettability pattern to enhance the driving forces together with its principle. Key is the tapered wettability to produce repelling forces as shown in lower right in the figure. Widely spread oil changes to high-contact angle droplet with the help of the driving force. With the increase in contact angle, the circumference of contact becomes shorter and eventually the droplet will float into water due to the density difference. Typical design is regularly placed star-like pattern that combines four tapers as shown in the figure.

The pattern was produced by photolithography and the remained photoresist was used as a mask for subsequent hydrothermal synthesis. After hydrothermal synthesis, vertical rod array of TiO_2 can be obtained as the results of epitaxial crystal growth on an FTO substrate that has similar lattice constant (0.474 nm) with TiO_2 (0.458 nm). Typical size of the star-like pattern was 0.25 mm in width with 0.5 mm pitch. The hydrothermal synthesis conditions are shown in Table 1. The reaction temperature was set at 150 ^oC. The rod length increased with the reaction time, and typically, it was set at 4 hours based on preliminary experiments.

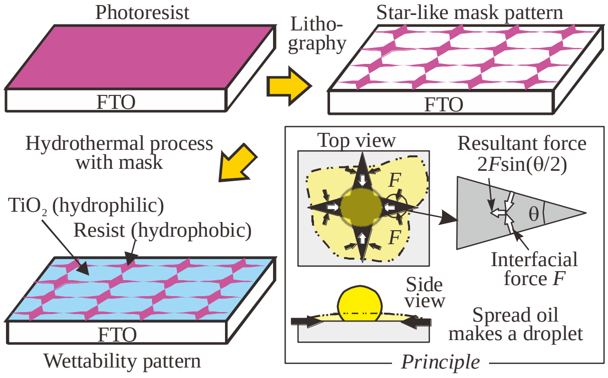

Figure 2. Enhancement of repelling force with wettability pattern

Table 1 Experimental conditions

Substrate	FTO glass, 10 mm×12.5 mm	
Photoresist	OFPR-8000 (Tokyo Ohka)	
Contents of source solution	H_2O	30 mL
	HCl	30 mL
	$TiCl_4$	1.0 mL
Reaction condition	Temperature	150 ºC
	Time	2-12 h

4. Results of hydrothermal synthesis

Upper part of Fig. 3 shows the observation results of scanning electron microscopy (SEM). It can be seen from the upper left photo that star-like patterns were obtained as intended. Detailed observation on the upper right reveals that array of nano-rods was produced where the photoresist did not cover. Smooth area beside the rods was photoresist. After the process of high temperature and pressure in the solution, the resist layer remained without any damage though the top surface became rough in sub-μm. The rods aligned normal to the FTO substrate showing the directional crystal growth as already discussed [4], though at the edge of the pattern the rods did not align but inclined.

The lower part of the figure shows the results of confocal microscopy. It was found that the star-like pattern has sharp edge profile. From the cross-sectional profile shown at the bottom, the height of the rods over the photoresist was measured as about 3.4 μm and the variation of the height was measured about 0.5 μm.

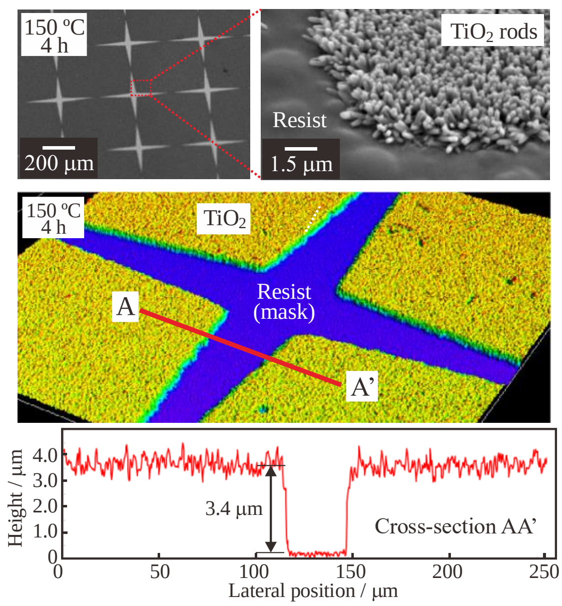

Figure 3. Results of SEM and confocal microscope observation

5. Evaluation of oil repelling performance

Sliding angle of oil droplet in water was measured to evaluate the repelling performance. Measurement was carried out upside-down in water because the oil droplet easily floats due to density difference. Figure 4 shows the snapshots when applying inclination to the substrate at constant speed. It can be seen that oil droplet had large contact angle in water and it started to move at small inclination angle as 8.4 deg. Then, the droplet floated up into the water in a short time. Before this experiment, the surface showed super-hydrophilicity after long time UV irradiation or sufficient dose.

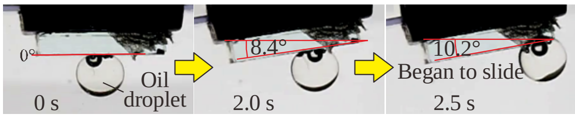

Figure 4. Sliding angle measurement of oil droplet in water

Figure 5 shows the effect of UV irradiation time or dose on the sliding angles of oil droplet in water, which shows the effect of photocatalytic activity on repelling performance. Sliding angle was defined as the critical angle that the droplet starts to move as shown in Fig. 4.

Before UV irradiation, the droplet did not float up into water but stayed on the surface. After UV irradiation of 30 min at the power of 40 mW/cm² the sliding angle decreased drastically, then decreased further with the increase in the irradiation time. It was found that one-hour irradiation is necessary to obtain small sliding angle as 10 degrees in this case.

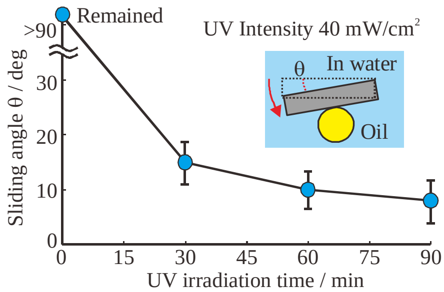

Figure 5. Effect of UV irradiation time on sliding angle of oil droplet

6. Discussion

Applying the same principle, repelling of water droplet in air is also possible. Insects that live near seaside, *Ligia exotica*, have similar water transfer mechanism on their legs. Such water transfer system can be also valuable for industrial products such as micro-fluidic devices or micro-total analysis systems (μTAS). It is necessary to establish a comprehensive design methodology that can adapt to various combination of liquids, surface conditions, and ambient substances.

7. Conclusions

Hydrophilic/hydrophobic pattern was obtained using patterned hydrothermal synthesis of TiO_2 nano-rods. After UV irradiation, the sliding angle of oil droplet in water decreased drastically. Optimization of pattern design is one the future works including its exploitation.

References

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