

# UV-induced Wettability Change of Teflon-modified ZnO Nanorod Arrays on LiNbO<sub>3</sub> Substrate

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**Abstract**—Aligned ZnO nanorod arrays films were grown on LiNbO<sub>3</sub> substrates by aqueous growth, and subsequently rendered superhydrophobic with RF sputtered coated Teflon. The as-prepared surface exhibits superhydrophobicity with a water contact angle (CA) of 154.5°. After 2 hours of UV irradiation on the surface, the surface wettability was approaching hydrophilic state; CA was measured to be 113°. This study provides insights into the methodology of a low cost, efficient technique that has great potential for preparing nanostructured surface with tunable wettability [1].

**Keywords**—ZnO; nanorod; superhydrophobicity; wettability; UV irradiation

## I. Introduction

Wettability is one of the most important properties of solid surfaces, which is mostly governed by the surface free energy as well as the geometric structure of the surface [2]. Tunable wettability has a wide range of applications; examples cited in literature include, fluid microchips and micro-reactors, it is crucial to have the ability to prepare surfaces with high contrast of wettability for water on the same kind of substrates [3]. Superhydrophobic surfaces are usually developed with a combination of a rough surfaces coupled with low surface energies, on which the latter is commonly achieved by coating materials with fluoroalkanesilane [2]. Feng et al in 2004 reported a reversible transition from superhydrophobicity to superhydrophilicity on aligned ZnO nanorod films induced by UV light [5]. Following this achievement, other nanostructured metal oxides with tunable wettability induced upon irradiation of UV light were studied [6-8]. However, the UV-induced decline of hydrophobicity on Teflon-modified ZnO nanostructured surface has not been reported.

## II. Experiments and Discussion

For the preparation of ZnO nanorod growth, the LiNbO<sub>3</sub> substrate was RF sputter coated with a 1.2 μm ZnO seed layer as seen in Figure 1. Such a seed layer improves the uniformity and orientation of ZnO nanostructured arrays and facilitates their growth. Nanostructured arrays of ZnO were grown in a sealed reaction vessel via the hydrothermal decomposition of 10 mM of HMT / zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) solutions as described by L. Vayssieres [9]. In this process, reaction vessel was placed inside an oven for 20 hrs at 80°C. After which the substrates were extricated and washed with DI water to remove any residual zinc salts and dried in a stream of N<sub>2</sub>.

The ZnO nanostructure coverage and morphology was observed by FEI Nova nanoSEM. ZnO nanorods grown on LiNbO<sub>3</sub> substrates exhibit uniform growth that occurs at a high density as seen in Figure 2. LiNbO<sub>3</sub> substrate bound nanorods have a large variation in width ranging between approx 125 nm to 200 nm as can be seen in Figure 3. This width variation plays an important role in roughing the surface.

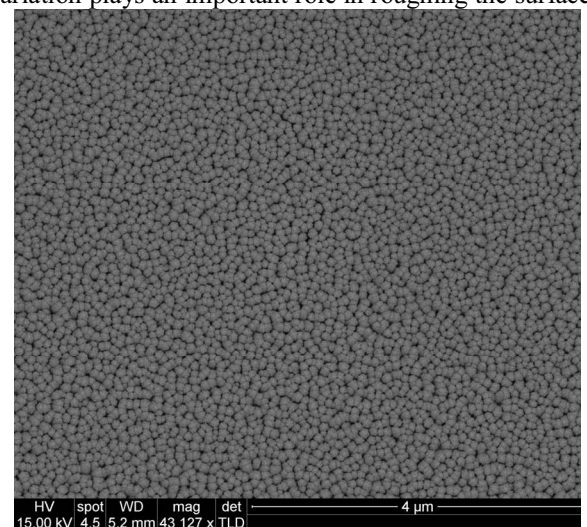


Figure 1 - ZnO seed layer on LiNbO<sub>3</sub>

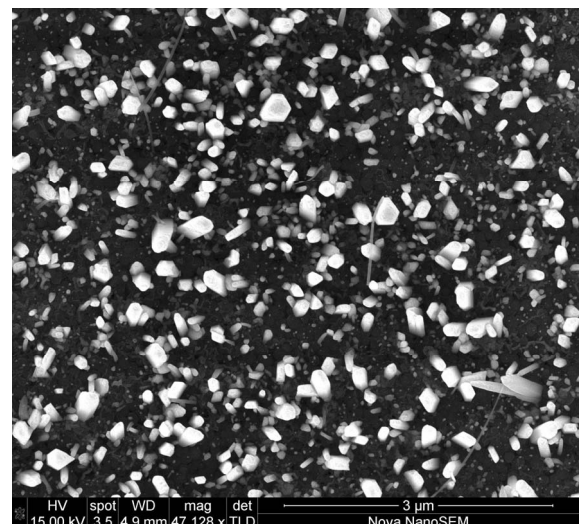


Figure 2 - ZnO nanorod growth on LiNbO<sub>3</sub> substrate

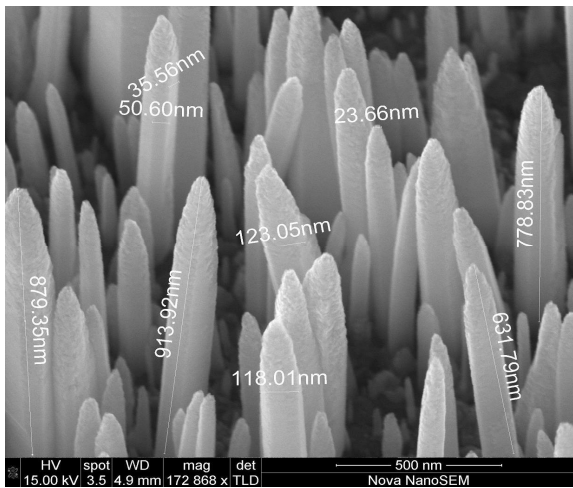


Figure 3 - ZnO nanorod view at high magnification, 35° rotation

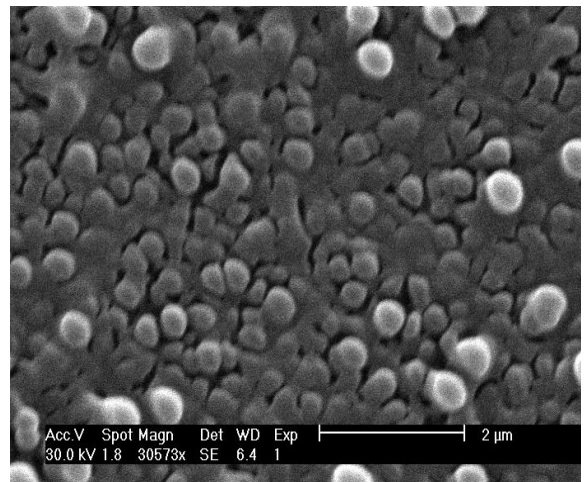


Figure 5 - surface morphology of Teflon-modified ZnO nanorod arrays

A water droplet was placed onto the prepared surface, it was observed that the droplet quickly spreads away, and leaving a water contact angle less than 5° (Figure 4). This strongly indicates that ZnO nanorod arrays exhibits superhydrophilicity. According to Wenzel's model which hypothesizes that the liquid completely penetrates into the troughs of the surface texture, surface roughness enhances not only hydrophobic but also hydrophilic properties [11]. That is on a flat homogenous surface, if the contact angle is less than 90°, roughness will make the surface even more hydrophilic; if greater than 90°, roughness will enhance the hydrophobicity [13]. In this case, the CA on flat surface of ZnO single crystal is only 31° (much smaller than 90°) [10], the surface roughness provided by the aligned ZnO nanorod structure reduces the CA further, and introduces superhydrophilicity on the surface.

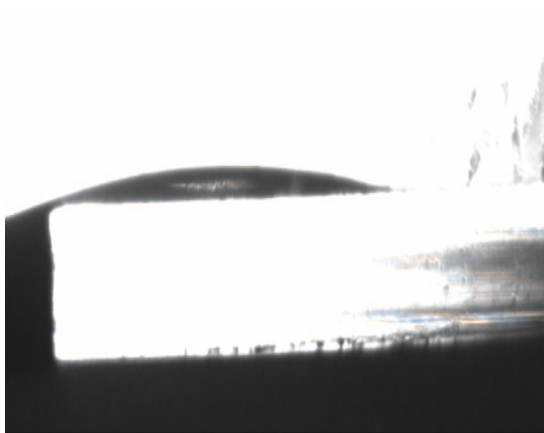


Figure 4 - shape of water droplet on plain ZnO nanorod surface.

In order to render the surface hydrophobic Teflon was used, as it is a well-known water repelling material due to its very low surface free energy [3]. The ZnO nanorod arrays are RF sputtered with a Teflon target, at 80 W for 20 minutes. This produces a 50-80 nm thick of Teflon layer on top of the ZnO nanorod arrays. As shown in Figure 5 and 6, the original ZnO morphology is well covered by Teflon.

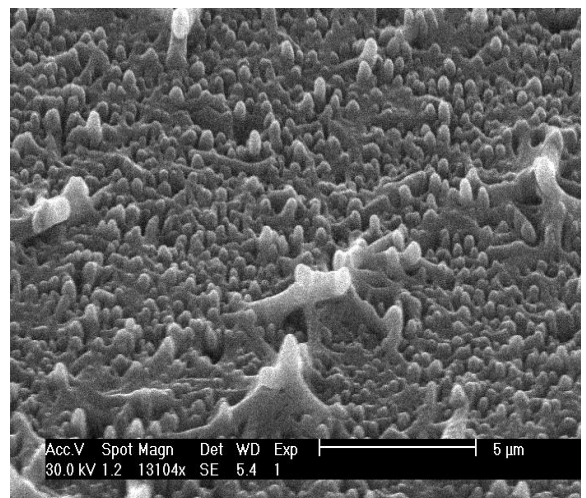


Figure 6 - surface morphology of Teflon-modified ZnO nanorod arrays, 15° rotation

On a plain ZnO seed layer that is coated with Teflon, water contact angles were measured to be 110° as seen in Figure 7, but 154.5° on Teflon coated ZnO nanorod surface as seen in Figure 8.

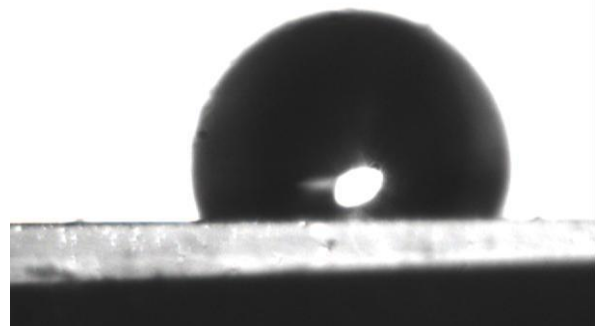


Figure 7 - Shape of water droplet on Teflon-modified ZnO seed layer

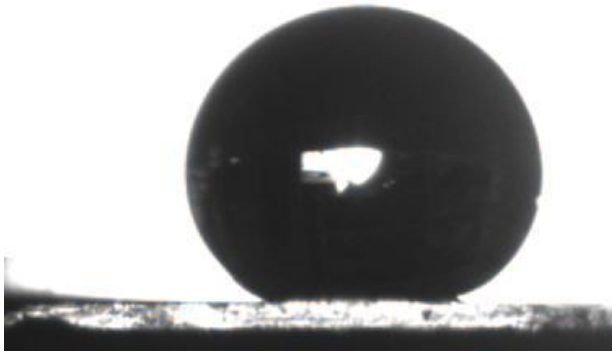


Figure 8 - shape of water droplet on Teflon-modified ZnO nanorod surface

The difference in these two contact angles is ascribed to the difference of the roughness ratios on the respective surfaces. For a flat smooth and chemically homogeneous solid surface, the CA of a liquid droplet is defined by Young's equation [11]:

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

where  $\theta$  is the CA and  $\sigma$  is the surface free energy. The indices represent the different interfaces: solid-vapor ( $sv$ ), solid-liquid ( $sl$ ), and liquid-vapor ( $lv$ ). The wetting properties of the nanostructures, nevertheless, are different from the smooth films, which are described by Eqn. 1. In Cassie-Baxter's model which assumes the water droplet sits on top of the composite structure [12], the Young's equation is modified as:

$$\cos \theta_w = \gamma \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (2)$$

where  $\theta_w$  is the CA predicted by Cassie-Baxter's theory, and a roughness factor  $\gamma$  is the ratio of the actual and the projected areas. With respect to the plain RF sputtered ZnO (shown in Fig. 7), the roughness factor is slightly bigger than 1 which is the roughness of a perfectly smooth ZnO surface. Conversely, the roughness factor of surface such as the ZnO nanorods (shown in Fig. 8), has an  $r$  which is much larger than one. Thus, the increase in surface roughness due to the nanostructure results in a significantly larger CA compared to one on the smoother surface.

After UV irradiation for 2 hours, the CA of the water droplet on the Teflon-modified ZnO nanorod arrays decreased, and it was measured to be around  $113^\circ$ . Reversibility was slow as after 7 days of storing the sample in a dark environment, a CA was re-measured to be approximately  $154^\circ$ .

As illustrated in Figure 10, even though the Teflon layer is not conformal on top of the ZnO nanorods, together with the

nanostructure, its surface energy is low enough to stop water droplet from filling up the gaps. But UV irradiation generates electron-hole pairs in the ZnO nanorod, with some of the holes reacting with lattice oxygen to form surface oxygen vacancies. Later, water and oxygen may compete to adsorb on them on the areas which are not covered by Teflon. However, the defective sites are kinetically more favorable for hydroxyl adsorption than oxygen from air. As a result, the surface hydrophilicity is improved [5].

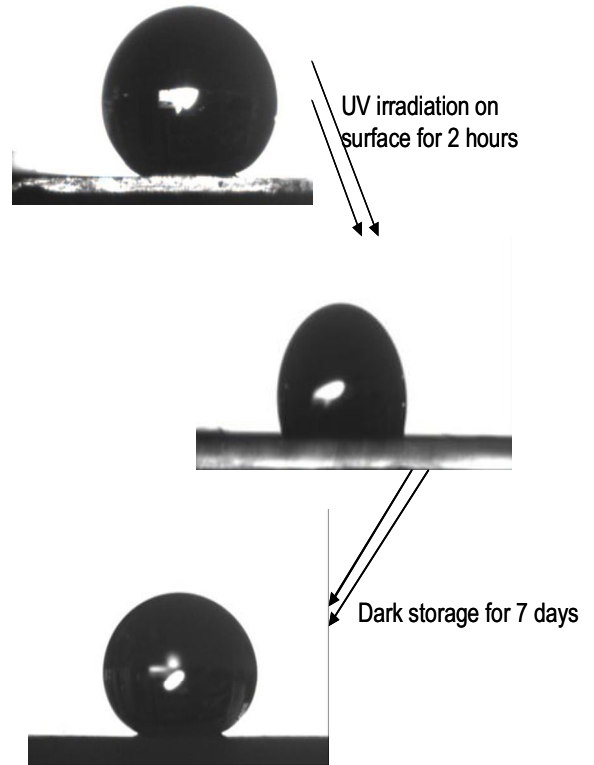


Figure 9 - shape of water droplet before and after UV irradiation, as well as after dark storage.



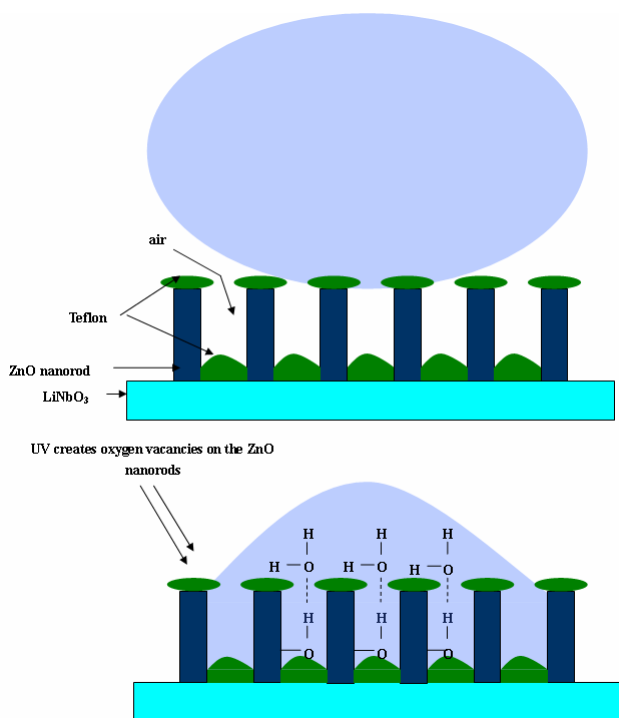


Figure 10 - mechanism of wettability change on Teflon coated ZnO nanorod surface

### III. Conclusion and Future Development

In summary, a highly oriented single-crystalline ZnO nanorod arrays has been prepared by an aqueous hydrothermal method, such surfaces are then RF sputtered with Teflon to obtain superhydrophobicity. This fabrication is simple, low cost, and efficient. Additionally, it has been experimentally demonstrated that, the wettability on Teflon-modified ZnO nanorod arrays is a function of UV irradiation.

Further research is underway to improve the response time of wettability change by using a combination of UV light and electric potential. Also the recovery times can be shortened by placing the sample in an oxygen rich environment at high temperature. Furthermore, better photo-sensitive materials such as TiO<sub>2</sub> and WO<sub>3</sub> are being studied to complement this study.

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