**Photo-Active Inorganic Films in Combination with Controllably Wetted Rough Polymeric Surfaces**

M. A. Frysali,[1,2,*] L. Papoutsakis,[1] G. Kenanakis,[1] and S. H. Anastasiadis[1,2]
[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece
[2] Department of Chemistry, University of Crete, Heraklion, Greece
* E-mail address of presenting author: lampap@iesl.forth.gr

Herein, we focus on surfaces with controlled, switchable wettability in response to one or more external stimuli.[1-3] Furthermore, the aim is to combine photo-active properties with responsive features in order to achieve an environmentally relevant surface, which exhibits controllable water adhesion characteristics as well. The development of artificial smart surfaces has gained the interest of the scientific community the last decades. There have been great efforts by researchers to understand and control the wettability of solid surfaces.[3] Various approaches have been utilized to produce hierarchically rough surfaces, which can reversibly switch from superhydrophobic to superhydrophilic.[1-3] On the other hand, ZnO and $TiO_2$ have been widely used as photocatalysts for degradation of organic dyes.[4] In general, the photocatalytic activity is related to size and surface area.[5] One dimensional nanostructures, such as nanowires and spikes, offer higher surface to volume ratio compared to catalytic coatings. In this work, our goal is to combine the photocatalalytic activity of the metal oxides with the control of the surface wettability.

Two parallel routes were followed. The one took advantage of a sol-gel/spin coating method on glass or silicon wafer substrates in order to develop ZnO nanowires. These formations emerge uniformly perpendicular to the surface, exhibiting a typical hexagonal wurtzite structure as was evidenced by XRD measurements and SEM micrographs. Afterwards, the carboxyl end-functionalized poly(2-vinylpyridine), *P2VPCOOH, w*as grafted-to the surface by spin coating onto glass or silicon surfaces following thermal annealing above the glass transition temperature ($T_g$).

The photocatalytic behavior of the combined surface was tested by utilizing FT-IR spectroscopy. Fig.1 presents the normalized integrated area vs. irradiation time curves for the degradation of stearic acid utilizing ZnO nanowires and a P2VPCOOH coating. It can be noted that the sample exhibited remarkable photocatalytic activity, by degrading 70% of stearic acid in 60 min of UV irradiation.

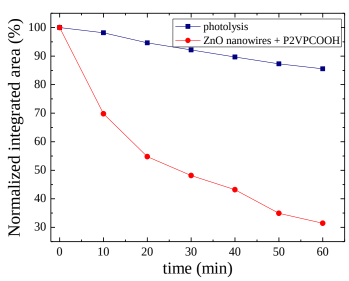


Fig. 1: *Normalized integrated area vs. irradiation time curves for ZnO nanowires and* a *P2VPCOOH coating.*

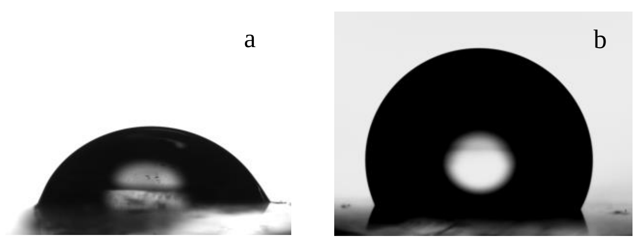


Fig. 2: *Images of water droplets onto* (a) *ZnO nanowires and (b) ZnO nanowires with* a *P2VPCOOH coating.*

The wettability of ZnO nanowires with and without polymer was also measured utilizing the sessile drop method. Wettability measurements (Fig. 2) show that the combination of the roughened surface with the polymer coating enhances the effect of hydrophobicity evidenced by the increase in contact angle from 64$^o$ to 115$^o$.

The second route made use of Ti:Sapphire femtosecond laser ($\lambda$=1026nm) under reactive gas ($SF_6$) atmosphere irradiation technique in order to create micro/nano scale roughness in a single-step process (Fig 3).

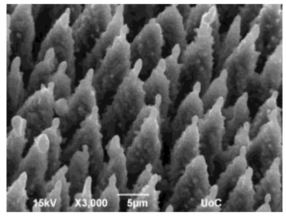


Fig. 3: *SEM image of the artificial silicon surface irradiated at a laser fluence of 2.13*J $cm^{-2}$.

After the coating of the patterned surfaces with ZnO seed layer, the decolorization of methylene blue (MB) was calculated by measuring the absorbance of the solution with UV-Vis spectroscopy. Fig. 4 represents the normalized integrated area vs. irradiation time for the patterned surface. According to this, the degradation of MB was about 40% following 60 min of irradiation.

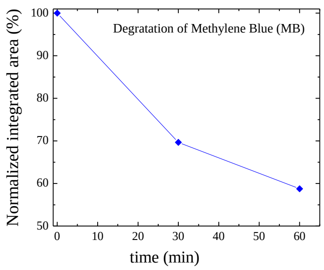


Fig.4: *Normalized integrated area vs. irradiation time curves for silicon microstructured surfaces with ZnO seed layer and P2VPCOOH coating.*

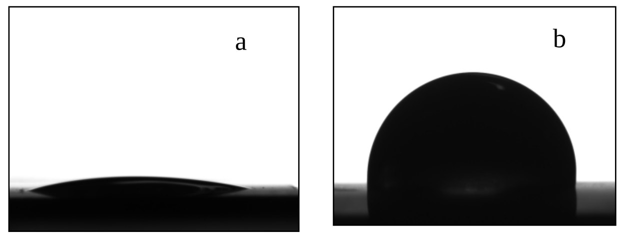


Fig. 5: *Images of water droplets onto (*a*)* a *silicon patterned surface with a ZnO seed layer (b)* a *silicon patterned surfaces with a ZnO seed layer and a P2VPCOOH coating.*

The wettability of the patterned surfaces with and without polymer was tested by contact angle measurements (CAM) (Fig 5).

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