

# Ordering of Liquid Crystals on Photocatalytic Titania Surfaces

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## Abstract:

We have fabricated thin films of titania by atomic layer deposition (ALD). We used the photocatalytic activity of the films to design liquid crystalline systems that can be triggered to undergo orientational transitions upon illumination. Polarization modulation-infrared reflection-adsorption spectroscopy (PMIRRAS) was used to provide evidence that the orientational transitions arise from photocatalytic generation of a carboxylic acid-containing species in the liquid crystal. This study reports the first design of liquid crystalline systems that respond to the photocatalytic activity of metal oxide films.

## Summary of Research:

We used the ALD process to fabricate titania ( $\text{TiO}_2$ ) thin films using tetrakis(dimethylamino)titanium (TDMATi) and water ( $\text{H}_2\text{O}$ ) as precursors and a deposition temperature of  $225^\circ\text{C}$ . After 60 cycles of deposition, we measured the ellipsometric thickness of the  $\text{TiO}_2$  films to be  $3.27 \pm 0.03$  nm (Woollam spectroscopic ellipsometer).  $\text{TiO}_2$  thin films were then annealed at  $500^\circ\text{C}$  for 15 h in air to obtain the anatase (101) phase of titania, as confirmed by X-ray diffraction analysis [1]. The films were also analyzed by X-ray photoelectron spectroscopy and the ratio of O to Ti was determined to be 2.04:1, consistent with the expected stoichiometry of titania [1].

The aim of our study was to couple photocatalytic reactions on the surface of titania with orientational transitions in liquid crystalline materials. Titania is a well-known photocatalyst with a wide band gap of 3.2 eV and is photoactive under UV illumination ( $<385$  nm). We characterized the orientations of the nematic LC 4-cyano-4'-pentylbiphenyl (5CB) (structure shown in Figure 1(a)) on  $\text{TiO}_2(101)$  by preparing micrometer-thin films of 5CB on  $\text{TiO}_2(101)$  and characterizing their optical appearance using polarized light microscopy. We discovered that the orientations of 5CB on  $\text{TiO}_2(101)$  are dependent on ambient relative humidity (RH) levels. At low humidity (0-20% RH) or under dry conditions, 5CB exhibits a homeotropic (perpendicular) orientation on  $\text{TiO}_2(101)$  (Figure 1(b), (d)) whereas upon increasing RH, 5CB tilts away from the surface normal to ultimately assume a planar (parallel) orientation

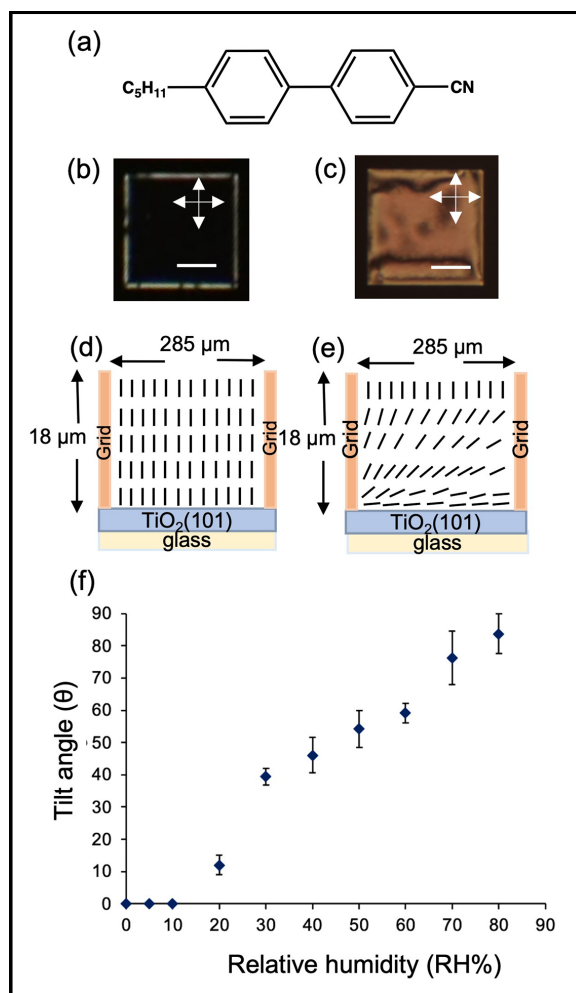


Figure 1: (a) Molecular structure of 4-cyano-4'-pentylbiphenyl (5CB). Optical micrographs (crossed polarizers) of 5CB hosted in copper grids on  $3.27 \pm 0.03$  nm-thick films of  $\text{TiO}_2(101)$  under dry nitrogen conditions (b) and under 80% RH air (c). Schematic illustrations of director profiles of (d) homeotropic and (e) planar orientations of 5CB at  $\text{TiO}_2(101)$ . (f) Plot of change in tilt angle of 5CB from surface normal on  $\text{TiO}_2(101)$  as a function of RH level. Scale bar: 100  $\mu\text{m}$ .

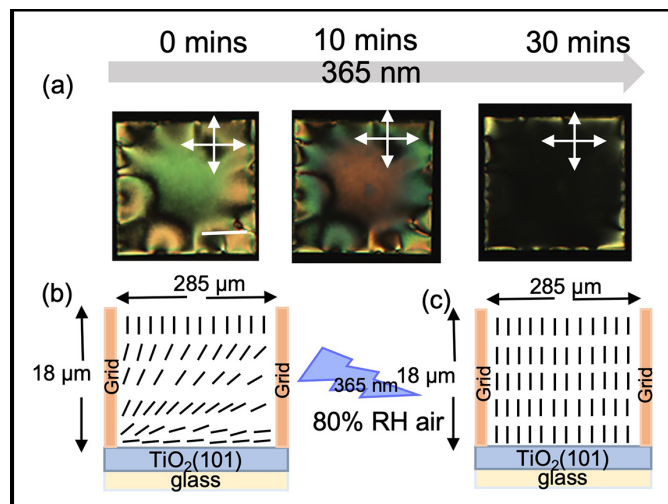


Figure 2: (a) Optical micrographs (crossed polarizers) of 5CB hosted in copper grids on  $3.27 \pm 0.03$  nm-thick films of  $\text{TiO}_2(101)$  under 80% RH air upon illumination by a UV lamp of wavelength 365 nm and intensity  $1.8 \text{ mW/cm}^2$  at time 0 mins, 10 mins, and 30 mins. Schematic illustrations of director profiles for (b) planar and (c) homeotropic orientations of 5CB on  $\text{TiO}_2(101)$ .

at 80% RH (Figure 1(c), (e), (f)). Prior studies have reported that water can adsorb to metal oxides such as titania under ambient humidity conditions and that the surface coverage of water is dependent on the humidity level [2]. Ongoing experiments are testing the hypothesis that increasing water coverage on  $\text{TiO}_2(101)$  weakens the binding of 5CB in the perpendicular mode and triggers an orientational transition.

To study the influence of the photocatalytic activity of  $\text{TiO}_2(101)$  on the orientations of nematic 5CB, we illuminated micrometer-thick films of 5CB on  $\text{TiO}_2(101)$  at a wavelength of 365 nm under 80% RH. Upon UV illumination, the optical appearance of the nematic 5CB film changed from bright to dark, indicating an orientational transition from planar to homeotropic as shown in Figure 2(a), (b). In contrast, no change in optical appearance was observed when a micrometer-thick film of 5CB supported on a photo-inactive silica surface was illuminated with UV light. Additional support for our conclusion that the orientational transition of 5CB observed on  $\text{TiO}_2(101)$  was driven by photocatalytic activity was obtained by using PMIRRAS measurements of nanometer-thin films of 8CB (a homolog of 5CB) supported on  $\text{TiO}_2(101)$  on platinum-coated Si wafers. Platinum films were e-beam deposited on Si wafers. Upon UV illumination, we measured a new peak in the IR spectrum corresponding to a C=O group ( $1688 \text{ cm}^{-1}$ ), consistent with photo-oxidation of 8CB to a carbonyl-containing compound as indicated in Figure 3 (a), (b). Mass-spectrometry confirmed that photo-oxidation of 5CB on  $\text{TiO}_2(101)$  forms the acid-containing molecule

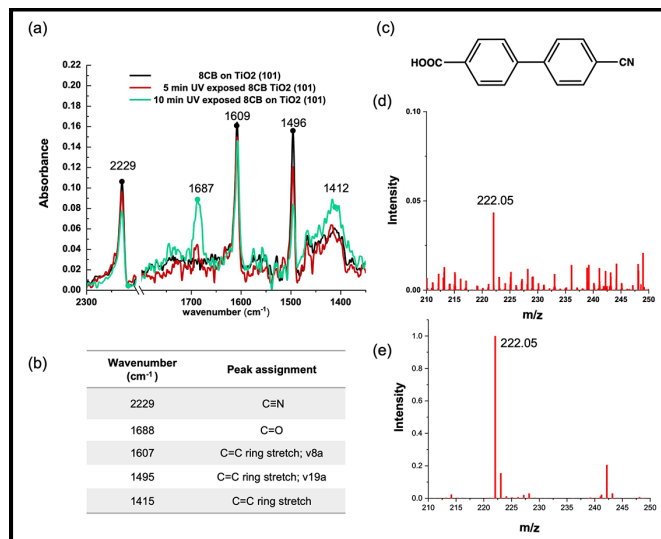


Figure 3: (a) PMIRRAS spectra of nanometer-thick layers of 8CB on  $\text{TiO}_2(101)$  (black), exposed to 365 nm UV illumination for 5 mins (red) and 10 mins (green). (b) Vibrational frequency ( $\text{cm}^{-1}$ ) assignments for peaks in (a)  $\nu$  represents stretching, and  $\beta$  represents in-plane bending. (c) Molecular structure of 4'-cyanobiphenyl-4-carboxylic acid (CBCA). Electrospray ionization-mass spectra plot of (d)  $25 \mu\text{M}$  5CB reacted under 365 nm UV illumination on  $\text{TiO}_2(101)$  (e)  $5 \mu\text{M}$  CBCA in methanol collected in negative ionization mode.

4'-cyanobiphenyl-4-carboxylic acid (CBCA) (structure shown in Figure 3(c)) as indicated in Figure 3(d), (e).

Prior studies have revealed that carboxylic acid-containing molecules bind strongly to titania in the perpendicular mode [1]. This prior result provides support for our conclusion that the photocatalytic activity of  $\text{TiO}_2(101)$  can generate a carboxylic acid-containing compound within a nematic film of 5CB and thus trigger homeotropic anchoring of the LC mixture. This result provides the first evidence that photocatalytic transformations on titania can be coupled to orientational transitions in LCs.

Current work in this project is focused on understanding how the ligand environment created by a LC can modify the catalytic activity of titania.

## References:

- [1] Nanqi Bao, Jake I. Gold, Jonathan K. Sheavly, James J. Schauer, Victor M. Zavala, Reid C. Van Lehn, Manos Mavrikakis, and Nicholas L. Abbott, Ordering Transitions of Liquid Crystals Triggered by Metal Oxide-catalyzed Reactions of Sulfur Oxide Species. *J. Am. Chem. Soc.* 2022, 144, 36, 16378-16388. <https://pubs.acs.org/doi/full/10.1021/jacs.2c03424>
- [2] A. L. Goodman, E. T. Bernard, and V. H. Grassian, Spectroscopic Study of Nitric Acid and Water Adsorption on Oxide Particles: Enhanced Nitric Acid Uptake Kinetics in the Presence of Adsorbed Water. *J. Phys. Chem. A* 2001, 105, 6443-6457. <https://pubs.acs.org/doi/abs/10.1021/jp0037221>