

Final Report:

Photo-Directed Molecular Assembly of Multifunctional Inorganic Materials

Submitted by: B.G. Potter, Jr. (PI; Materials Science and Engineering Dept. (MSE), University of Arizona)

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Project Team: Kelly Simmons-Potter (co-PI; joint appointments in Electrical and Computer Engineering Dept. (ECE) and Optical Sciences (OSC), University of Arizona); J.D. Musgraves (MSE grad student); Z. Schneider (OSC grad student).

DOE Office of Science Program Managers: Dr. B. Gersten

Executive Summary:

Key results arising from the project are summarized. The photomediated molecular assembly strategy under investigation focused on the photoactivation of intermolecular linking processes between metal alkoxides (i.e. hydrolysis and condensation) to influence the evolution of bond topology and longer range structural development during solution-phase synthesis of metal oxides. Consistent with the overall project thrusts detailed in the initial proposal, research provided new insights into the intrinsic photoresponse and assembly of complex, heteroleptic Ti-based metal alkoxides possessing optically accessible ligand groups. Using a suite of electronic, vibrational, and nuclear spectroscopic probes, coupled with quantum chemical computation, the excitation wavelength and fluence dependence of molecular photoresponse and the nature of subsequent hydrolysis and condensation processes have been probed in pyridine-carbinol-based Ti-alkoxides with varied counter ligand groups. The counter ligand groups investigated provided a range of water stabilities, optical absorption energies, and photosensitivities. Of particular interest, $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ (where $\text{OPy} = \text{OC}_6\text{H}_6\text{N}$ and $\text{TAP} = \text{OC}_6\text{H}_2(\text{CH}_2\text{N}(\text{CH}_3)_2)_3$) was shown to be largely insensitive to hydrolysis in pyridine solutions, enabling the photocatalysis of hydrolysis and condensation to be effectively isolated from conventional (dark) reaction kinetics in dilute solutions due to the steric restrictions imposed by the tri-amino-phenoxy (TAP) ligand. Studies involving water-containing, pyridine-based alkoxide solutions, excited at energies resonant with the cyclic TAP ligand groups, have confirmed the photoinitiation of intermolecular bond formation at the TAP site, culminating in metal-oxygen-metal linkages. Moreover, control of solution water content allowed the manipulation of the resulting nanostructure in films photodeposited directly from solution. The latter results were extended to demonstrate the photopatterned deposition of a micro-scale physical relief structure of partially condensed oxide without the need for post-fabrication processing of a homogeneously deposited film.

Experimental efforts were integrated with density functional theory (DFT) computational modeling of the metal-alkoxide precursors in the study. Normal-mode analyses of energy-minimized unreacted alkoxide structures and anticipated reaction product species (e.g. hydrolyzed molecules, dimers) aided the interpretation of FTIR and Raman vibrational spectroscopic data, contributing insight into the reactions accessed and photoproducts formed. Time-dependent DFT (TD-DFT) computations on $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ enabled molecular excitation processes to be evaluated in the context of UV-vis spectroscopic studies of both solution and solid-state systems.

On a programmatic level, the project was an effective vehicle for the development of two successful collaborations involving complex metal alkoxide synthesis and structural confirmation (Dr. T.J. Boyle, Sandia National Laboratories) and quantum chemical modeling (Dr. R. Corrales, University of Arizona, formerly Pacific Northwest National Laboratory). The project resulted in the development of eight peer-reviewed publications/proceedings, 12 conference presentations, and one patent disclosure (photodeposition of patterned thin films).

Overview and Rationale:

The research involved the investigation of a new, optically directed molecular assembly methodology. The strategy integrates photoinduced structural modification with the rational design of complex metal alkoxide precursors to control the solution-based synthesis of metal oxides. Selective photo-activation of reaction points about the metal center are intended to influence the development of intermolecular bonds, the ensuing higher-order structure, and the associated material properties. With the overall goal to optically modify the reaction kinetics that result in intermolecular bonding (e.g. hydrolysis and condensation rates in sol-gel systems), ligand selection has been predicated on the opportunity to uniquely access the targeted ligand (via incident wavelength tuning) and the need to produce a photostructural state for the site that enhances chemical reactivity. It is also preferable to isolate conventional reaction processes from those catalyzed by photoexposure to allow clear examination of photostimulated phenomena and the eventual control of network evolution via optical excitation. To this end, a collection of heteroleptic, pyridine-carbinol-based, mononuclear Ti-alkoxide precursor molecules were examined (see Figure 1). These precursors exhibited a range of conventional hydrolysis kinetics dictated by the sterics and chemical nature of the counter ligand coordinating the metal center.

Photocatalyzed processes observed in irradiated solutions and solution-cast films of $(\text{OPy})_2\text{Ti}(\text{4MP})_2$ and $(\text{OPy})_2\text{Ti}(\text{4AP})_2$ (where OPy = pyridine-carbinol ($\text{OC}_6\text{H}_6\text{N}$), 4MP = 4-mercaptophenoxide ($\text{OC}_6\text{H}_4\text{SH}$), 4AP = 4-aminophenoxide ($\text{OC}_6\text{H}_4\text{NH}_2$)) were compared with conventional reaction phenomena through the use of unirradiated control solutions. Further studies primarily focused on a structural analogue of these precursors (i.e. $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ (where TAP = tri-amino-phenoxide ($\text{OC}_6\text{H}_2(\text{CH}_2\text{N}(\text{CH}_3)_2)_3$)). This latter Ti-alkoxide exhibited even greater inhibition of

conventional (dark) hydrolysis and condensation reactions through increased steric constraints at the TAP ligand sites thus providing an enhanced opportunity to examine the influence of solution chemistry and optical excitation conditions on these reaction processes.

Once reaction points about the metal center have been photoactivated, the subsequent intermolecular bond formation and overall assembly of molecular aggregates and extended structure is also anticipated to be influenced by the concentration and local dynamics of reactants in the system. Thus, a key aspect of the project was the evaluation of molecular photoresponse under a range

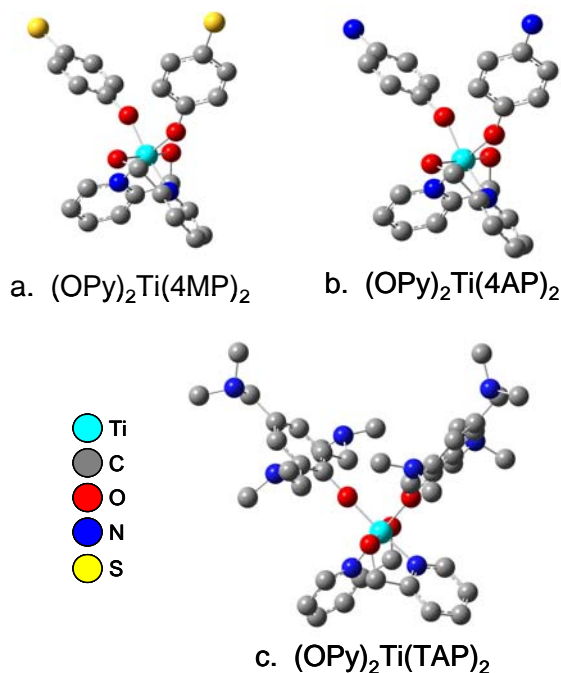


Figure 1: Heteroleptic Ti-alkoxide structures. Hydrogen atoms removed for increased clarity. (OPy= $\text{C}_6\text{H}_6\text{NO}$, 4AP= $\text{OC}_6\text{H}_4\text{NH}_2$ 4MP= $\text{OC}_6\text{H}_4\text{SH}$, TAP= $\text{OC}_6\text{H}_2(\text{CH}_2\text{N}(\text{CH}_3)_2)_3$).

of local structural/chemical environment conditions anticipated to influence these assembly phenomena, i.e. from dilute solutions to solid-state precursor material and with varied available water contents.

Finally, the photoinduced material assembly strategy, in concert with the use of micro-scale photopatterning, has the potential to effectively combine bottom-up and top-down multilength scale structural control in a single processing methodology. In this context, project findings involving optically-induced material formation on substrates in contact with metal alkoxide solutions provided an opportunity to demonstrate photopatterned film deposition in these systems directly from solution.

The research effort pursued a science-based understanding of photomediated material assembly throughout the solution-phase synthesis process, a widely used and versatile method for the synthesis of multifunctional oxides and molecular hybrid materials. Experimental efforts were supported by computational evaluation of precursor molecular systems and anticipated electronic excited states and photoinduced reaction products.

Project Achievements:

Given the overall project goals described above, research efforts involved the investigation of local, intramolecular photostructural processes in the context of ensuing intermolecular reactions and molecular aggregate assembly. Given the coupled nature of these phenomena, spectroscopic analysis of photoinduced modification of solution and solid-state species (i.e. photoproducts) were examined with varied excitation photon energies and under varied environmental and reaction conditions (local atmosphere, solution chemistry) to help better understand the excitation process and its ramifications on the ensuing, photocatalyzed reaction and material evolution. Taken in concert with DFT modeling, an interpretation of optically mediated modifications in these systems was developed. Serendipitous results in the course of these studies have also resulted in new opportunities for the direct deposition of thin film relief structures directly from solution and the potential impact of films produced in this manner to play a role, for example, in the design of nanostructured electrical junctions, charge transport phases and dielectric interlayers in novel photovoltaic and microelectronic devices.

As mentioned, the project focused on mononuclear, Ti-alkoxide precursor structures possessing different degrees of stability to hydrolysis (Figure 1). Results obtained during their examination are summarized below.

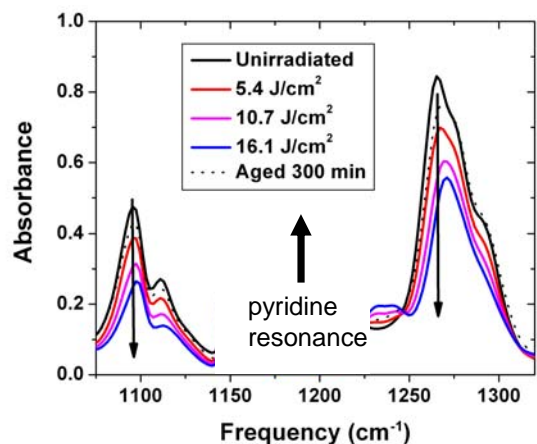


Figure 2: FTIR absorption spectrum of 0.48 M $(\text{OPy})_2\text{Ti}(\text{4MP})_2$ solution (in pyridine) as a function of total accumulated UV-fluence at $\lambda = 337.1$ nm. A large solvent-related resonance feature (location indicated) has been removed for clarity. The response of an unexposed control sample (denoted “aged”) also provided.

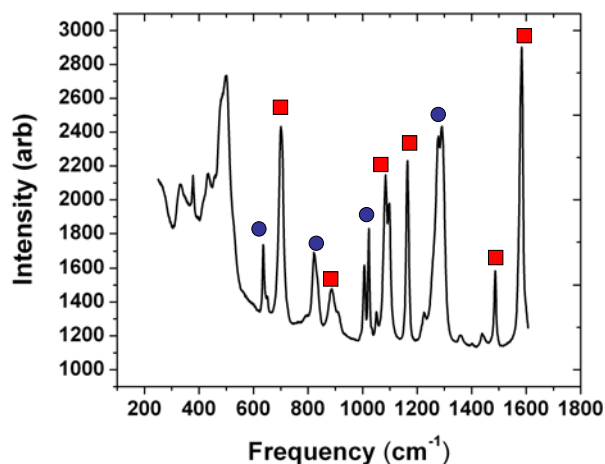


Figure 3: Raman spectrum obtained from $(\text{OPy})_2\text{Ti}(\text{4MP})_2$ solution cast film. Red square denotes 4MP localized vibrational mode; blue circle denotes vibrational mode associated with the OPy moiety.

$(\text{OPy})_2\text{Ti}(\text{4MP})_2$: Early work in the project focused on controlled atmospheric environment studies of $(\text{OPy})_2\text{Ti}(\text{4MP})_2$ (= Ti-4MP) in both solutions and solution-cast (dried) films. These materials were irradiated at energies resonant with an intrinsic ligand-to-metal charge transfer band observed in the UV-vis absorption of the films ($\lambda_{\text{ex}} = 337.1$ nm) [1]. Both FTIR analysis of the solution and micro-Raman analysis of the films clearly indicated a preferential disruption of the 4MP ligand over that of the bidentate OPy ligand upon UV-exposure. Figure 2 depicts two IR-active vibrational resonances associated with in-plane 4MP vibrational modes after UV-exposure. A clear reduction in intensity, distinct from that observed in an unexposed sample is observed. Moreover, Raman data in the solid-state samples shows a similar behavior, with the added advantage of a more thorough evaluation of OPy and 4MP resonances free from solvent interference effects (Figure 3). Ligand-specific vibrational modes were confirmed via normal mode analysis of energy minimized molecular confirmations obtained using DFT modeling. Photoexposure of the films under two different atmospheric compositions (air with 40 % relative humidity (RH) and dry Ar) revealed a marked increase in the magnitude of Raman peak area changes, associated with the 4MP ligand,

when films were irradiated under the air atmosphere. This effect is interpreted in terms of the hydrolysis of the 4MP ligand excited-state conformation upon photoexcitation. This interpretation is supported by the development of a weak Raman band at approximately 810 cm^{-1} consistent with a Ti-OH vibration. Evaluation of control films (no photoexposure but under air and also with controlled addition of water to solution) further

confirmed the influence of hydrolysis on the spectral signature of the 4MP ligands. Thus, resonant excitation of the charge transfer process in the molecule appears to accelerate (photocatalyzes) the conventional hydrolysis reaction at the 4MP site. The inherent chemistry of the ligand groups present serves to enhance a ligand-specific preferential reactivity under photoexposure.

(OPy)₂Ti(TAP)₂: The conventional hydrolysis rates of the 4MP-containing precursors precluded a more detailed examination of photoinduced reactions (hence the use of relative humidity as a means to introduce water of reaction into these systems without causing rapid precipitation). As with the other molecules examined in the project to-date, the pyridine-carbinol (OPy) ligands present in these molecules are bidentate in nature, coordinating the central metal atom through oxygen and nitrogen bridging bonds. Replacement of the monodentate 4MP by another phenoxide moiety modified by three amino groups (in contrast to the single sulfur in the 4MP ligand) produced the tri-amino phenoxide (TAP) ligand (see Figure 1). The increased steric bulk of tri-amino-phenoxide (TAP), and the amino functionality of the TAP ligand were intended to strongly inhibit conventional hydrolysis of the alkoxide in the pyridine-based solutions examined. This allowed photoinitiated processes to be examined independent of competing conventional (dark) reactions, particularly under conditions where these kinetics would dominate the evolution of the solutions of more reactive precursors.

Studies addressing the photoresponse of (OPy)₂Ti(TAP)₂ (= Ti-TAP) solution and solid-state samples thus served as the primary focus for subsequent work. The excitation-wavelength dependence of optically induced electronic state and vibrational structure changes in anhydrous and water-containing Ti-TAP solutions was examined in

an effort to more fully understand the excitation mechanisms involved and the influence of solution chemistry on the photoinduced behavior observed. Efforts were also extended to an examination of photoinduced hydrolysis and condensation in solid-state films of the pure alkoxide under dry and moist inert-gas atmospheres.

Spectroscopic studies have confirmed the presence of hydrolysis and condensation products in suspended particulate and deposited film phases produced upon UV-exposure of water-containing Ti-TAP pyridine solutions, providing confirmation of a key goal of the

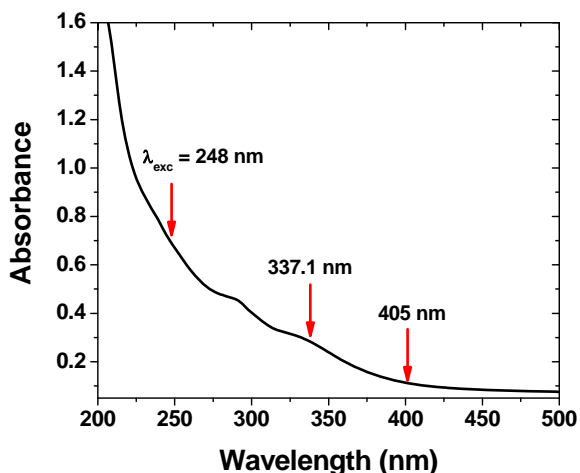


Figure 4: UV-vis absorption spectrum of a spin-coated (OPy)₂Ti(TAP)₂ thin film. Excitation wavelengths used in the solution- and solid-state-precursor photoresponse studies are indicated.

overall research effort, i.e. the photoinduced assembly of metal-oxygen-metal linkages in the development of a solution-synthesized metal oxide. These results also led to the discovery of a novel photoprocessing capability for these Ti-alkoxides: the photopatterned deposition of partially condensed oxide directly from solution. This film photodeposition strategy provided an alternative thin-film synthesis approach to dip- and spin-coating and was under examination to elucidate the underlying deposition

mechanisms and the microstructure of the resulting material and to explore its potential for the direct photopatterning of metal oxides (direct fabrication). Good agreement between the transition energy results of time-dependent DFT (TD-DFT) modeling and UV-vis absorption spectroscopy of $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ allowed a more complete

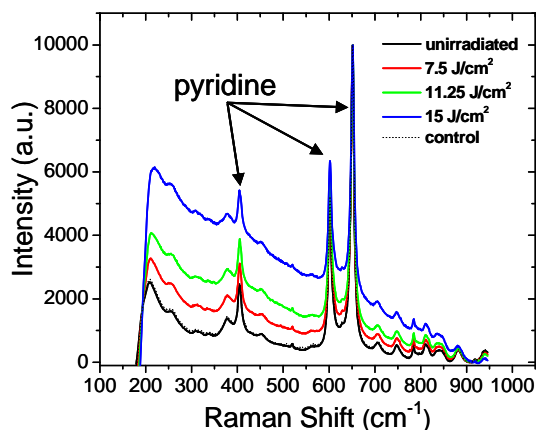


Figure 5: Representative Raman spectra collected from the stock(aq) $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ solutions described in the text upon UV-exposure at $\lambda = 248$. High intensity pyridine resonances (visible in all spectra) are indicated.

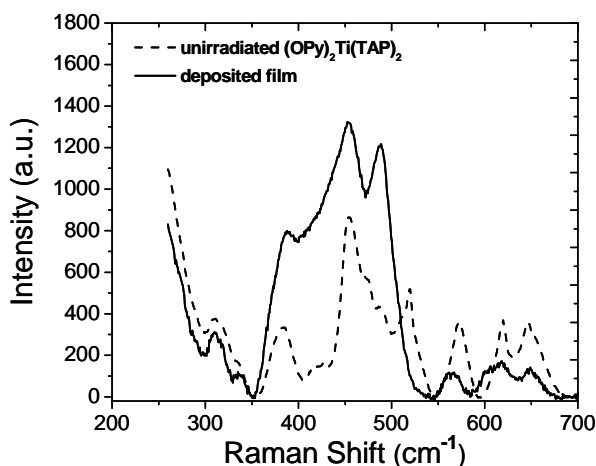


Figure 6: Raman spectra collected from photoproducts formed upon UV-irradiation (at $\lambda = 248$ nm) of the stock(aq) $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ solutions. Data obtained from the particulate residue and the deposited film described in the text are provided in a. and b., respectively.

transfer processes (337.1 nm, 405 nm (off-resonance)) typical of these Ti-alkoxide molecules [2,3].

Samples for UV-exposure and optical spectroscopic study were prepared by dissolution of $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ (106 mM) in anhydrous pyridine (1 mL typical specimen size) under standard inert atmosphere (Ar) conditions (referred to here as the “stock”

interpretation of the underlying electronic states involved in optical excitation of these experimental compounds for the first time. Analysis of excited state electron density distributions was expected to provide new insight into the underlying mechanisms leading the photocatalysis of hydrolysis and condensation at the ligand sites.

A more detailed description of results obtained for the Ti-TAP molecular system model follows:

a. Solution Systems: Photoinduced phenomena and structural investigations.

A study of photoresponse was pursued in both anhydrous and water-containing pyridine-based solutions. Further insight into the nature of photoexcitation (and its associated impact on the photostructural response of the molecular system) was obtained by optical exposure over a range of excitation wavelengths resonant with localized transitions of the cyclic ligand groups and charge-transfer transitions involving these ligands and the metal center. Figure 4 contains a representative absorption spectrum from a 50 nm thick film of unreacted $(\text{OPy})_2\text{Ti}(\text{TAP})_2$. Excitation was accomplished using pulsed laser (KrF excimer at 248 nm and nitrogen at 337.1 nm) and continuous-wave LED (405 nm) sources. These excitation wavelengths are indicated on Figure 4 showing their coincidence with absorption features associated with the cyclic ligands (248 nm) and charge

solution). Solution samples containing a 4:1 molar ratio of H₂O to Ti (designated “stock (aq)”) were also prepared by appropriate water addition to the 106 mM (OPy)₂Ti(TAP)₂ (anhydrous pyridine) stock solution. Both anhydrous (stock) and water-containing (stock (aq)) samples, that were not subsequently photoexposed, served as controls during the investigation. All solutions were contained within 1 cm (square cross-section) fused silica cuvettes during optical evaluation. Solutions were stirred on a magnetic stir plate (Teflon™-coated stir bar) during irradiation (control solutions were also stirred). This allowed more complete exposure of the solution volume, particularly during 248 nm and 337.1 nm excitation due to the high absorbance of the pyridine solvent and the (OPy)₂Ti(TAP)₂ species, respectively, at these wavelengths.

UV-irradiation at 248 nm produced significant modification of the Raman spectra of the water-containing solutions. Figure 5 contains the Stokes-scattered Raman spectra obtained as a function of cumulative UV-fluence at this wavelength. A dramatic increase in background signal was observed with UV-fluence for these stock (aq) solution samples. By contrast, no significant changes in background level were observed in similar samples which were irradiated at the other photon energies depicted in Figure 4 [4]. High-intensity pyridine resonances have also been identified in Figure 5. In contrast, no changes in the Raman spectra of control (unirradiated) solutions were observed under identical handling conditions. Dissimilarities in the solution responses at different wavelengths are associated with differences in the excitation processes accessed [4]. The presence of particulates was readily observed visually (increased cloudiness) in the 248 nm-excited samples that exhibited the enhanced Raman background. Photoinduced formation of this suspended solid phase in these hydrous

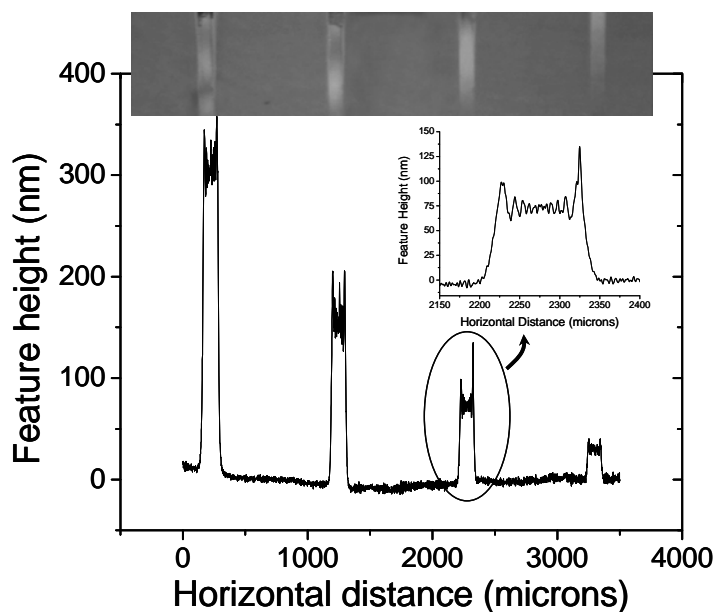


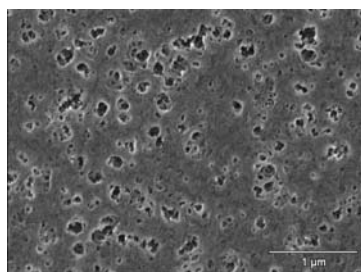
Figure 7: Stylus profilometer trace of a multiple-line, physical relief structure photodeposited onto a fused silica substrate. A plan-view optical micrograph (reflection) of the photopatterned features is also provided. The total UV-fluence used to produce each line in the pattern was (from left to right): 192, 96, 48, and 24 J/cm² at the 248 nm excitation wavelength. (The x-axis provides the scale for the optical micrograph.) A detailed view of near-field, Fresnel diffraction-produced topology is provided in the inset.

solutions was also accompanied by the deposition of an opaque, white material on the wall of the cuvette in a region corresponding to the UV-beam spatial extent.

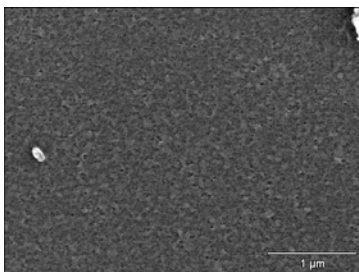
Micro-Raman investigation of the solid-phase photoproducts (i.e. the suspended particulate in solution and the deposited film on the cuvette wall) was used to evaluate the impact of UV-exposure on the molecular structure of (OPy)₂Ti(TAP)₂. Raman examination of photoproducted suspended particulate and deposited film materials (dried under Ar for 36 hours) confirmed the presence of both hydrolysis (Ti-OH stretching vibrational modes) and condensation (Ti-O-Ti stretching modes) products. Figure 6, for example, contains a representative

Raman spectrum obtained from the deposited film material exhibiting a broad increase in Raman scattering intensity in the UV-deposited film between 400 to 450 cm^{-1} , which has been assigned to the development of Ti-O-Ti bridging structures [5]. Sharper vibrational resonances, assigned to the original OPy and TAP ligands, present in both the particulate residue and deposited film, indicate the incomplete reaction of the organic ligand groups and their retention in the dried, photoprocessed material. Further analysis of these spectra indicated a greater tendency for disruption of the TAP ligand group upon photoexcitation.

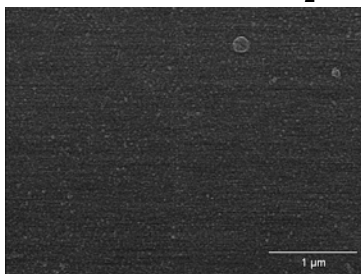
b. Direct Photodeposition from Solution: The results of a more controlled demonstration of UV-induced film deposition is provided in Figure 7, showing the formation of patterned lines obtained by photoexposure through an aluminum shadow mask. In this case, approximately 0.1 mL of stock (aq) solution was placed on a fused silica microscope slide and covered with another silica slide in contact with the solution. UV-exposure (at 248 nm) through the upper slide resulted in film deposition on the surface of the upper slide in contact with the solution. The shadow mask was shifted laterally between sequential exposures, resulting in the development of an array of lines approximately 120 microns wide. The total UV-fluence at each line was increased, from 24 J/cm^2 to 192 J/cm^2 , moving from right to left in Figure 7. A subsequent wash in pyridine after UV exposure removed excess, unreacted material. A patterned physical relief structure was thus produced without post-exposure chemical etching. Moreover, stylus profilometry (Figure 7) indicated a nearly linear dependence of film thickness on UV-fluence within the fluence range examined. Thicknesses were found to vary from 30 to 310 nm for the 24 J/cm^2 and 192 J/cm^2 exposures, respectively [4]. Closer



1:1 $\text{H}_2\text{O}:\text{Ti}$, 10 J/cm^2



4:1 $\text{H}_2\text{O}:\text{Ti}$, 10 J/cm^2



8:1 $\text{H}_2\text{O}:\text{Ti}$, 10 J/cm^2

Figure 8: SEM micrographs (plan view) of partially condensed thin films photodeposited from $(\text{OPy})_2\text{Ti}(\text{TAP})_2$: pyridine solutions containing varied water:Ti stoichiometries (provided below each image). Optical exposure in all cases occurred at $\lambda = 248 \text{ nm}$ for a total accumulated fluence of 10 J/cm^2 .

examination of the profilometer trace in Figure 7 (see inset), in fact, reveals surface topographic structure on the top of the deposited lines whose cross-sectional profile is consistent with the near-field Fresnel, single-slit diffraction pattern anticipated with the photopatterning geometry used [6].

Excitation

Wavelength Effects:

Subsequent studies of this photodeposition phenomena were also carried out to provide further insight into the mechanisms involved in film formation and nanostructure development. An excitation wavelength-dependent study at the

same photon energies used in the initial study of photoproducts revealed that, again, only 248 nm wavelength light was sufficient to produce measurable thin film formation. Resonant with the transitions involving the cyclic groups present in the molecule, the photon energy is also resonant with similar cyclic moieties associated with the solvent (pyridine). The large absorption strength of these resonances produces a very limited penetration depth into the solution, likely the reason for film development at the near surface region of the incident container wall. Moreover, the sensitivity of film formation to excitation energy in this range tends to support the indirect excitation of the Ti-TAP molecule by solvent-to-solute energy transfer [4,7].

Solution Chemistry Effects: Insight into the effect of solution chemistry on the evolution of structure subsequent to optical excitation and intermolecular linking reactions was provided through an examination of films photodeposited from solutions with water to alkoxide ratios of 1:1, 4:1, and 8:1 ($\text{H}_2\text{O}:\text{Ti}$), producing conditions ranging from insufficient to surplus water for complete hydrolysis of the metal center. Figure 8 contains electron micrographs of the photodeposited materials obtained after 10 J/cm² optical fluence at 248 nm. Clearly, a greater porosity is observed in the 1:1 material while a more dense material is produced for the 8:1 solution stoichiometry likely indicative of the degree of network formation affected by the extent of hydrolysis possible with each water content [8]. These results confirm the importance of both optical and conventional process controls in the development of extended oxide network structures via photoinitiated sol-gel chemistry.

Thermal Annealing: Thermal treatment of these photodeposited films has also been pursued to evaluate the retention of nano and microstructural features while

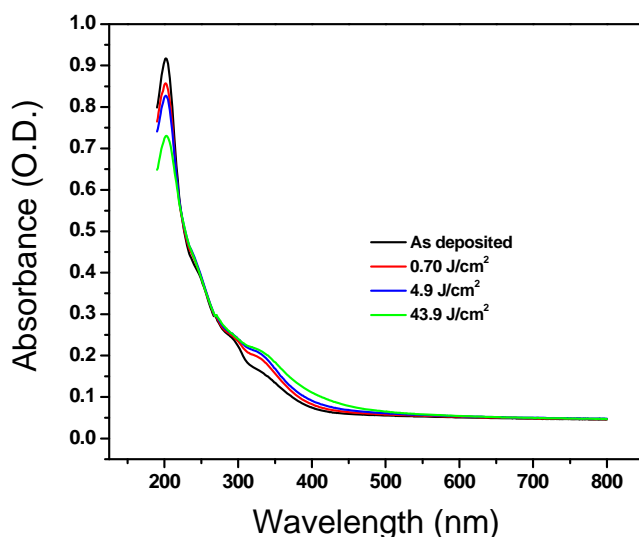


Figure 9: Representative UV-vis absorption spectrum taken from a spin-coated $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ thin film irradiated at 248 nm.

ensuring conversion of the partially condensed matrix (containing remnant organic ligand groups and fragments (as confirmed by Raman spectroscopy) to a fully oxidized phase. Early studies of controlled atmosphere firings (isochronal and isothermal anneals) indicate that oxidation of the films is possible with limited consolidation of the amorphous network (SEM, ellipsometry, surface profilometry analysis) [8].

Optimization of the thermal processing in the context of providing photodefinable TiO_2 substrates for cellular

scaffolding and as a nanostructured junction component in 3rd generation photovoltaic device structures should be promising.

c. Solid-state systems: photoinduced phenomena and electronic structure

As mentioned earlier, an examination of the photoresponse of Ti-TAP in solid-state systems (spin- and solution-cast films) has also been pursued. Representative results of UV-induced UV-vis absorption modification in spun films under an Ar atmosphere (relative humidity < 10%) are provided in Figure 9. A general increase in near-UV absorption over the 300-400 nm range was observed after 248 nm irradiation. This absorption increase was accompanied by a decrease in absorbance at a peak centered at approximately 200 nm. Changes in absorption in these ranges may be

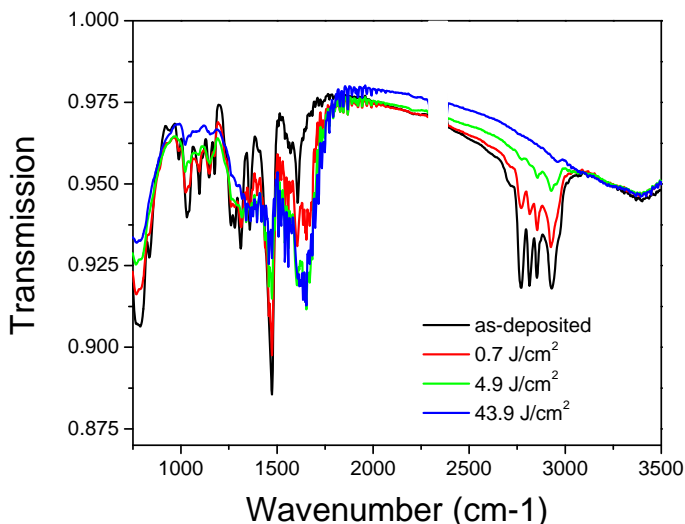


Figure 10: Representative FTIR spectra from solid-state Ti-TAP precursor films irradiated at $\lambda = 248$ nm showing reduction in sharper resonances associated with OPy and TAP ligands (see bands about 1100, 1590, and 2800 cm^{-1}).

indicative of ligand disruption influencing the energetics and/or character of ligand-to-metal charge transfer transitions in the 300-350 nm band. Similar effects, observed in the Ti-TAP solutions discussed above (observable only in the 300 – 350 nm band due to pyridine absorption), indicate that the phenomenon is intrinsic to the molecule. These changes in UV-Vis absorption are accompanied by an ellipsometrically verified increase in refractive index ($\lambda = 632.8$ nm) from 1.585 to 1.64 (± 0.002) and a net decrease in film thickness

from 770 nm to 530 nm (± 20 nm). The corresponding vibrational spectra (Figure 10) show that these modifications in electronic structure and physical dimension are associated with the disruption of ligand groups, indicated by a reduction in absorption strength at OPy and TAP-based resonances (confirmed by DFT normal mode analysis, see below) across the spectral range examined.

d. Quantum Chemical Modeling.

Density Functional Theory (DFT) energy minimization and subsequent normal mode analyses of the resulting molecular conformations served as a means to obtain insight into the anticipated vibrational structure of the Ti-alkoxides under study. DFT was performed using a commercially available computational engine (Gaussian 03). Molecular geometry optimization was conducted using the B3LYP hybrid functional and a 6-31G* basis set. Following optimization, frequency calculations were conducted, again using the B3LYP functional and the 6-31G* basis set. These results enabled the interpretation of Raman and infrared spectroscopic signatures of these compounds and the assignment of peaks in these measurements to ligands and their associated modes of vibration. Computations involving the unreacted $(\text{OPy})_2\text{Ti}(\text{TAP})_2$ molecular structure were extended to investigate prototypical hydrolysis and condensation products,

including the effects of partial hydrolysis at the TAP or OPy site and the formation of a Ti-O-Ti bridging bond in a dimer structure. While these computations represented only approximations to actual structures and molecular interactions in the experimental systems under study (limited by the model complexity, computational resources, and time available), normal mode analysis of these model structures do provide support for band assignments in the photoproduct spectra, including the association of the 3280 cm^{-1} band, observed in the photoproduct Raman spectrum to the photoinduced formation of Ti-OH. Other ongoing single-molecule computations were designed to provide further insight into experimental findings. These efforts include the evaluation of the incomplete removal of the cyclic ligand groups (leading to linear chain alkoxide fragments) and the investigation of solvation environment effects (polar vs. nonpolar solvents) as a means

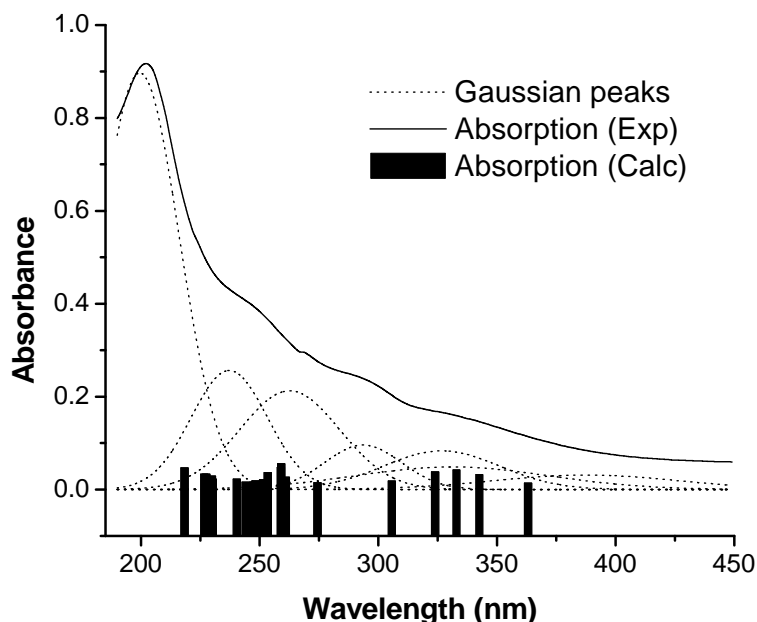


Figure 11: Representative experimental UV-vis absorption spectrum for a spin-coated solid-state Ti-TAP film showing the results of curve fitting with Gaussian components overlaid with the locations (bars) of transition energies computed using TD-DFT.

to understand differences in the tendency toward hydrolysis observed experimentally.

Through a collaboration with Dr. L.R. Corrales (UA), these DFT analyses were extended to involve time-dependent DFT (TD-DFT) studies of the energy minimized molecular conformations previous obtained and discussed above. In this case, electronic states were derived and utilized to estimate transition energies consistent with the excitation energies used in the photoirradiation process. In the TD-

DFT computation, energy-consistent relativistic effective core potentials (RECPs) developed by the Stuttgart group (Stuttgart RSC 1997 ECP) were used for the Ti(IV) center with the optimized valence basis sets supplemented by polarization functions. Standard 6-311+G* Gaussian basis functions were employed for the C, H, N, and O atoms. The vertical excitation energies and the oscillator strengths at the optimized ground state geometries were obtained by TD-DFT calculations implemented in NWChem 5.0 (a computational package accessed through the Environmental Molecular Sciences Laboratory (EMSL) at PNNL under a multi-investigator Computational Grand Challenge access grant). Good agreement between the transition energies of the computation and locations of absorption features in the experimental spectra were observed (Figure 11). Given the strong dependence on excitation photon energy of the molecular responses observed in the experimental studies, electron density mapping provides some of our first insight into the nature of states participating in the excitation

process. Analysis, for example, confirms the association of the lowest energy transition (HOMO-LUMO) with a ligand-to-metal charge transfer process from the TAP ligand to the Ti center (and the OPy ligand). Moreover, higher energy transitions in the 250 nm transition energy range are found to correspond to transitions involving electron density redistribution between the alkoxide oxygen p-orbitals and cyclic ligand groups providing early support for the unique role of these excitation energies in the photoinitiation of ligand disruption and bond destabilization [9].

e. Controlled Environment Dip-Coating: Capability Development

Consistent with project goals to integrate photoprocessing with standard thin film deposition as a means to influence material structural development during synthesis, a computer controlled dip-coating apparatus was assembled. Placed within a dedicated glove box, the system allowed early demonstration of photodeposition under inert atmospheres. Design and construction of an optical system allowed controlled delivery of photons at prescribed points above the solution surface during the dipping process.

Collaboration:

The program benefitted from an ongoing collaboration with Dr. T.J. Boyle, at Sandia National Laboratories, for complex precursor synthesis and structural characterization. As developments within the project motivated the need for alternative molecular characteristics, Dr. Boyle responded with precursor structures from his established library of compounds and synthesis procedures. The collaboration has resulted in co-authorship of the publications and presentations involving these research efforts. The relationship with Dr. L.R. Corrales in the area of quantum computational chemistry for the TD-DFT analysis described above was also developed. Access to computational resources at PNNL, through a funded multi-investigator Computational Grand Challenge project, enabled these computations that were used to explore ground-state electronic structure.

Project Budget:

The budget project period with terminated in January 31, 2009.

Conclusion:

Under the current project, significant progress was made in the investigation of an optically directed molecular assembly strategy in the context of the solution-synthesis of oxide materials. Studies of the intrinsic photoresponse of candidate Ti-alkoxide precursors were pursued in a collection of pyridine-carbinol-based compounds, culminating in the successful demonstration of the photoinitiated formation of a partially condensed Ti-O-Ti network from solutions of $(OPy)_2Ti(TAP)_2$. The enhanced steric constraints and chemical character of the tri-amino-phenoxide (TAP) ligand contributed to inhibit conventional hydrolysis in pyridine solution, enabling the study of photoinitiated hydrolysis and condensation in solution under a range of excitation wavelengths. These spectroscopic studies established the presence of hydrolysis and condensation photoproducts in suspended particulate and deposited film phases produced upon UV-exposure of water-containing solutions thus providing confirmation of a key facet of the

overall research effort, i.e. the photoinduced assembly of metal-oxygen-metal linking moieties in the development of a solution-synthesized metal oxide. Extension of these results enabled the photoinduced, patterned deposition of a partially condensed oxide film directly from solution and in the context of established thin film deposition techniques, i.e. dip coating.

Programmatically, the project enabled the development of a unique and effective collaborative research environment spanning disciplines (Materials Science, Chemistry, and Optical Sciences) and leveraging resources and expertise from the national laboratories (Sandia National Labs and Pacific Northwest National Lab) to address fundamental issues critical to the successful understanding of the materials and processes involved. The program has also served as an effective vehicle for nanoscience education, providing opportunities for extended student visits to Sandia National Laboratories (to assist in precursor synthesis and characterization) and participation in national conferences.

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Publications and Presentations Arising from the Project:

Publications:

1. "Nanostructure Development in Photodeposited Ti-oxide Thin Films: Effect of Solution Chemistry and Thermal Annealing," J.D. Musgraves, B.G. Potter, Jr. and T.J. Boyle, *J. Mater. Res.* **24**, 3372 (2009).
2. "Intrinsic Electronic Transitions of the Absorption Spectrum of (OPy)₂Ti(TAP)₂: Implications Towards Photo-initiated Structural Modifications," C.R. De Silva, J.D. Musgraves, Z. Schneider, B.G. Potter, Jr., T. J. Boyle, K. Simmons-Potter, L. René Corrales, *J. Chem. Phys. A* **113**, 5598 (2009).
3. "Photomodification of Heteroleptic Titanium-Based, Complex Metal Alkoxides," Z. V. Schneider, K. Simmons-Potter and T. J. Boyle, *J. Non-cryst. Solids* (2009).
4. "Photoinduced Deposition of Nanostructured Thin Films by UV-exposure of Heteroleptic, Ti-Alkoxide Solutions," J.D. Musgrave, B.G. Potter, Jr., and T.J. Boyle, *Mater. Res. Soc., Symp. Proc.*, San Francisco, CA, (2008).
5. "Photo-initiation of Intermolecular Bonding and Oxide Deposition in Ti-based Alkoxide Solutions," B.G. Potter, Jr., J.D. Musgraves, and T.J. Boyle, *J. Non-cryst. Sol.* **354**, 2017 (2008).
6. "Direct Fabrication of Physical Relief Structures via Patterned Photodeposition of a Titanium Alkoxide Solution," J.D. Musgraves, B.G. Potter, Jr., and T.J. Boyle, *Opt. Lett.* **33** (12) (2008).
7. "Photo-Induced Structural Changes in Titanium Alkoxides for Directing Molecular Assembly," J. David Musgraves, B.G. Potter, Jr., R. Sewell, and T.J. Boyle, in *Self Assembly of Nanostructures Aided by Ion- or Photon-Beam Irradiation—Fundamentals and Applications*, edited by R. Kalyanaraman, U. Valbusa, Z. Zhang (Mater. Res. Soc. Symp. Proc. 960E, Warrendale, PA, 2007) 0960-N05-03.
8. "Preferential Photostructural Modification of Heteroleptic Titanium Alkoxides for Molecular Assembly," J.D. Musgraves, B.G. Potter, Jr., R. Sewell, and T.J. Boyle, *J. Mater. Res.* **22**, 1694 (2007).

Presentations:

1. "Photoinitiated molecular assembly and thin film formation in Ti-alkoxide systems," J.D. Musgraves, Z. Schneider, K. Simmons-Potter, B.G. Potter, Jr. and T.J. Boyle, *Materials Research Society 2008 Fall Meeting*, Boston, MA.
2. "Photo-induced Film Deposition from Heteroleptic Titanium Alkoxide Solutions," J.D. Musgraves, B.G. Potter, Jr., and T.J. Boyle, presented at the *Glass and Optical Materials Division of the American Ceramic Society Spring Meeting*, Tucson, AZ, May 19-22, 2008.
3. "Photo-induced Manipulation of Titanium Metal Alkoxides," Z. Schneider, K. Simmons-Potter, and T.J. Boyle, presented at the *Glass and Optical Materials Division of the American Ceramic Society Spring Meeting*, Tucson, AZ, May 19-22, 2008.
4. "Theoretical Insight into Photostructural Modifications of Heteroleptic Ti-alkoxides for Molecular Assembly," C.R. De Silva, J.D. Musgraves, Z. Schneider, B.G. Potter, Jr., T. J. Boyle, K. Simmons-Potter, L. René Corrales, presented at the *Glass and Optical Materials Division of the American Ceramic Society Spring Meeting*, Tucson, AZ, May 19-22, 2008.

5. "Cellular Adhesion and Response to Thermally Modified, Sol-Gel Derived TiO₂ Thin Films," M. Coe, D. DeRosa, J. Blaine, J.D. Musgraves, M. Leick, F.L. Montiel, B.G. Potter, Jr., and M. Riley, presented at the Glass and Optical Materials Division of the American Ceramic Society Spring Meeting, Tucson, AZ, May 19-22, 2008.
6. "Photoinduced Deposition of Nanostructured Thin Films by UV-exposure of Heteroleptic, Ti-Alkoxide Solutions," J.D. Musgraves, B.G. Potter, Jr., and T.J. Boyle, presented at the Materials Research Society Spring Meeting, March, 2008, San Francisco, CA.
7. "Photo-directed Molecular Assembly of Metal Oxides," B.G. Potter, Jr., K. Simmons-Potter, J.D. Musgraves, and Z. Scheider, to be presented at the Fundamental Synthesis Research Challenges for 21st Century Materials DOE/BES Contractor Workshop, Baltimore, MD, July, 2007.
8. "Photo-Induced Molecular Structure Modifications in Metal Alkoxides for Directed Assembly in Inorganic Thin Films," J.D. Musgraves, B.G. Potter, L.R. Corrales, R. Sewell, T.J. Boyle, presented at the Joint University Conference on Glass/ Spring Division Meeting of the Glass and Optical Materials Division of the American Ceramic Society, Rochester, NY, May, 2007.
9. "UV-Induced Modification of Titanium-Based, Complex Metal Alkoxides," Z. V. Schneider, K. Simmons-Potter, and N. E. Jacobsen, R. Sewell and T. J. Boyle, presented at the Joint University Conference on Glass/ Spring Division Meeting of the Glass and Optical Materials Division, of the American Ceramic Society, Rochester, NY, May, 2007. Note: Awarded *second place* in the student poster presentation competition.
10. "Controlled Synthesis and Structure Modifications in Metal Alkoxides for Directed Assembly in Inorganic Thin Films," Robin M. Sewell, Timothy J. Boyle, Leigh Anna M. Ottley, Harry D. Pratt III, B.G. Potter, Jr., J. David Musgraves, presented at the Spring ACS Meeting, Chicago, IL, March, 2007
11. "Photo-Induced Structural Changes in Titanium Alkoxides for Directing Molecular Assembly," J. David Musgraves, J. Blaine, B.G. Potter, Jr., R. Sewell, T.J. Boyle. L.R. Corrales, presented at the Materials Research Society Fall Meeting, Boston, MA, December, 2006.
12. "Photo-Directed Molecular Assembly in Inorganic Thin-Films," J. David Musgraves, J. Blaine, B.G. Potter, Jr., R. Sewell, T.J. Boyle, presented at the Glass and Optical Materials Division of the American Ceramic Society Spring Meeting, Greenville, SC, May, 2006.

Patent Disclosure:

1. "Direct photodeposition of patterned metal-oxide and molecular hybrid thin films from photosensitive alkoxide solutions," B.G. Potter, Jr., K. Simmons-Potter, J.D. Musgraves, submitted March, 2008.

