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Photomodification of heteroleptic titanium-based, complex metal alkoxides

Z.V. Schneider^{a,*}, K. Simmons-Potter^a, T.J. Boyle^b^a University of Arizona, Optical Sciences, 1630 East University Boulevard, Tucson, AZ 85721-0104, United States^b Sandia National Laboratories, Advanced Materials Laboratory, Albuquerque, NM 87106, United States

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ABSTRACT

A heteroleptic titanium metal alkoxide $(\text{OPy})_2\text{Ti}(\text{4MP})_2$, where $\text{OPy} = \text{NC}_5\text{H}_4(\text{CH}_2\text{O})_2$ and $\text{4MP} = \text{OC}_6\text{H}_4(\text{SH})_4$, was investigated as a candidate precursor for the solution-based (sol-gel) synthesis of titanium oxide via the photoactivation of intermolecular linking reactions (e.g., hydrolysis/condensation). The evolution of the electronic structure of the solution-based molecule arising from conventional (dark) chemical reaction kinetics was compared with that of samples exposed to ultraviolet (UV) radiation at wavelengths of $\lambda = 337.1$ nm and 405 nm using UV-visible absorption spectroscopy. Photoinduced changes in the spectra were examined as a function of both the incident wavelength of exposure and the total fluence. Experimental results confirm the UV-induced modification of spectral absorption features, attributed to ligand-localized and charge transfer transitions accompanied by structural changes associated with hydrolysis and condensation. The photoenhancement of reaction kinetics in these processes was confirmed by the increased modification of the absorption features in the solution spectra, which saturated more rapidly under UV-illumination than under dark conditions. Similar saturation behaviors were observed for both the 337.1 nm and the 405 nm incident wavelengths with the same total deposited energy density indicating a relative insensitivity of the photoinduced response to excitation energy for the wavelengths and fluences studied.

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1. Introduction

The manipulation of the precursor's molecular structure is a crucial step in enabling future advances in nanotechnology. The ability to control the synthesis of nanostructured materials, through manipulation of bond formation kinetics and the geometry of molecular assembly, is of critical significance in the design of multi-length scale structures and their resultant associated properties. Of recent interest is the ability to photo-mediate these processes such that bond formation can be driven through controlled illumination. Prior research has demonstrated the potential for ultraviolet (UV)-irradiation in influencing molecular structures for a variety of different metal alkoxide gel films [1–7]. For example, metal alkoxides that have been chemically modified with β -diketones, exhibit a general reduction in the rates of hydrolysis and condensation reactions at these ligand sites [8,9]. Subsequent exposure of films generated from these precursors to UV light results in the decomposition of the chelate rings and the completion of network formation via condensation. This modification alters the solubility of the film in organic solvents [1–7]. Patterned optical exposure and subsequent chemical etching has been shown to enable the formation of surface relief structures in these films.

More importantly, it has been reported that both water and UV light were necessary to decompose the β -diketones ZnO gel films [7] and to enable the photopatterned deposition of physical relief structures directly from Ti-based alkoxide solutions [10,11] through a photoinduced hydrolysis process.

In the context of the present work, past research has shown that $(\text{OPy})_2\text{Ti}(\text{4MP})_2$ where $\text{OPy} = \text{NC}_5\text{H}_4(\text{CH}_2\text{O})_2$ and $\text{4MP} = \text{OC}_6\text{H}_4(\text{SH})_4$ (referred to as Ti-MP) in anhydrous solutions and in the unreacted solid state is very sensitive to environmental humidity which implies that changes in the molecular structure involves hydrolysis [12–14]. In fact, a photocatalyzed hydrolysis process was observed via vibrational spectroscopy in solutions of the titanium metal alkoxide Ti-MP [12,13]. Under appropriate illumination conditions, Raman spectroscopic analysis of this alkoxide also confirmed the preferential photostructural modification of the 4MP ligand over that of the OPy ligand. This disruption in the 4MP ligand was more pronounced when irradiating in a moist environment than under dry argon. Interestingly, the OPy ligand showed no distinguishable change, supporting an interpretation of the effect as associated with a photoinduced hydrolysis process at the 4MP ligand site [12].

In the present study, further investigations of electronic structural changes in solution-based Ti-MP were pursued. The UV-induced and conventional reactions present in solutions based on this alkoxide were examined via UV-visible spectroscopy studies. Given the identification of resonance features in the UV-visible

* Corresponding author.

E-mail address: ZVS@email.arizona.edu (Z.V. Schneider).

spectra of these molecules with transitions involving specific structural moieties, this probe provided additional insight into the nature of photoinduced changes in local atomic structure resulting in linking reactions at the onset of material formation. The photoresponse was examined as a function of total fluence of the optical exposure and saturation behavior was monitored for different excitation wavelengths of interest.

2. Experimental procedure

2.1. Precursor preparation

The heteroleptic titanium metal alkoxide Ti–MP was synthesized according to literature preparatory routes [14]. In general, $\text{Ti}(\text{OCHMe}_2)_4$ was reacted with two equivalents of H–OPy to form $(\text{OPy})_2\text{Ti}(\text{OCHMe}_2)_2$, which upon isolation was further reacted with two equivalents of H–4MP in pyridine to yield Ti–MP.

2.2. Solution preparation

Ti–MP is sensitive to moisture in the air and therefore samples were prepared and stored under inert atmosphere, glove box conditions and precautions to minimize air exposure were taken when handling this precursor. Crystalline solids were readily dissolved in anhydrous pyridine and stirred in scintillation vials under dry argon to yield an orange-hued, transparent solution. The mixture was then divided into two samples: (a) control solutions and (b) UV-irradiation solutions (identified as ‘UV-irradiated’ throughout this manuscript). Both these samples were handled under identical conditions throughout the experiment. In addition, prior to use, all glassware was purged with dry argon to minimize contamination with residual water. Despite these measures to minimize air and water exposure, the synthesized solutions were found to contain trace amounts of water from the solvents (99.0% anhydrous pyridine for UV-visible studies and 99.5% deuterated pyridine for nuclear magnetic resonance (NMR) spectroscopy studies, discussed below).

Solutions for UV-visible examination were prepared by dissolving 10 mg of powdered Ti–MP precursor into 6 mL of anhydrous pyridine, resulting in a solution concentration of 3.3 mM. Ti–MP is known to have a high absorption coefficient in the UV [12–14], hence this low concentration was chosen in order to maintain an absorbance (optical density) of the solution below 3.0, the practical sensitivity limit of the UV-visible instrument. After dissolving Ti–MP in pyridine, the solutions were sealed in 15 mm diameter, 2 mL borosilicate vials. Vial material was chosen to provide high transparency at the excitation wavelengths (>85% transmittance 300–700 nm).

2.3. Optical exposure and UV-visible spectroscopy

The samples prepared above were illuminated with two different ultraviolet (UV) light sources to examine the wavelength dependence of the photoresponse of Ti–MP on the saturation behavior in the absorption spectra. A collimated pulsed nitrogen laser ($\lambda = 337.1$ nm, ~ 8 ns pulse width, 10 Hz repetition rate, 1.05 mJ/pulse) and a 405 nm LED (5.25 mW of continuous-wave output, ± 10 nm) were used in this study to illuminate the samples. The UV-irradiated samples and the control samples were placed on the same magnetic stir plate and stirred during optical exposure. However, the control samples were optically isolated using an aluminum foil covering over the vial to prevent any exposure to stray light. The 405 nm LED (Roithner LaserTechnik) was operated through a constant current source at 21.2 mA.

After the UV exposure, both the control and irradiated samples were placed into the glove box under dry argon and approximately

0.2 mL of solution was extracted from each sample with a syringe and transferred to 1 mm fused quartz UV-visible spectroscopy cells for optical absorption measurements. Optical absorption spectroscopy was performed using a Perkin Elmer Lambda 950 spectrometer (instrument error <1%) over the wavelength range 300–600 nm. A background spectrum of pure pyridine was collected under identical conditions and the resultant spectrum was subtracted from all sample spectra to isolate only the response of the alkoxide. Three types of samples were characterized using the UV-visible spectrometer: UV-irradiated samples, control samples, and aged samples. All of the UV-irradiated samples were stirred continuously during the UV exposure. The control samples were prepared identically to the UV-irradiated samples and received identical handling (including stirring) as the UV-irradiated samples, save for optical exposure, as described above. The aged samples were placed in the glove box under dry argon with the cap sealed and with aluminum foil covering the vial to prevent further exposure to light; no stirring was performed on these particular samples.

2.4. NMR sample preparation

NMR spectroscopy was performed on solutions of Ti–MP in pyridine- d_5 (0.112 M), in order to affirm the conformation of the molecular structure. This concentration allowed for an appropriate signal-to-noise ratio to identify the various peaks within the NMR spectra. A standard 5 mm diameter, 8 in. Wilmad 507-PP NMR tube was used with parafilm wrapped around the cap to produce an airtight seal. Solution-based NMR spectroscopy was performed on these precursor molecules using a Bruker DRX-500, 5 mm dual probe. For the ^1H (500.1 MHz) and ^{13}C (125.8 MHz) spectra 16 and 1024 scans, respectively were used. The total amount of time to acquire ^1H and ^{13}C spectra for both the UV-irradiated and control sample, including transportation to the NMR facility as well as UV exposure, was 8 h.

3. Results

3.1. Structural confirmation: solution NMR

^1H and ^{13}C NMR (pyridine- d_5) spectra were collected for both the UV-irradiated and unirradiated samples. The ^{13}C NMR spectrum of Ti–MP is shown in Fig. 1. The nuclei positions were labeled and correlated with peak positions in the NMR spectra. These peak positions were identified by acquiring and analyzing both one-dimensional (^1H and ^{13}C) and two-dimensional (HSQC and HMBC) spectra. Database information on ligand identities and their corresponding nuclei resonance locations were used as a first approximation to correctly identify these peak locations with nuclei positions. The three large peaks are associated with the resonance of the pyridine solvent. The unlabeled peaks most likely are attributable to NMR signals arising from decomposed moieties of the molecule or residual ligand. Further, the OPy ligand can exhibit both chelated and unchelated formations that can also account for some of the unidentified peaks [14]. Overall, the NMR spectrum confirms the conformation of the molecule. As previously mentioned, NMR sample preparation and data acquisition elapsed times were approximately 8 h.

3.2. Optical absorbance and UV-irradiation effects

Fig. 2 depicts optical absorption spectra of 3.3 mM as-prepared solutions of Ti–MP in anhydrous pyridine as well as the effect of 337.1 nm UV-irradiation on the optical absorbance of the solutions. The impact of the optical irradiation can be seen in the overall de-

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