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Titania Condensation by a Bio-Inspired Synthetic Block Copolymer

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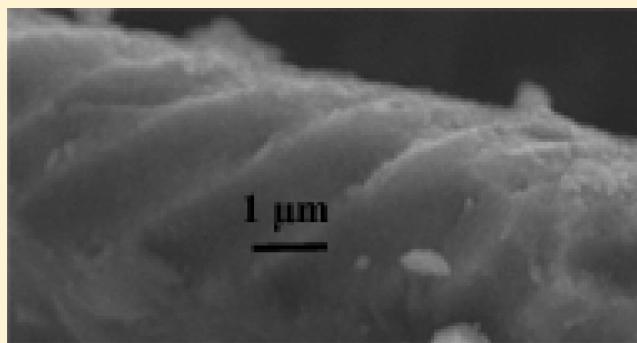
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Supporting Information

ABSTRACT: Silicatein α , an enzyme found at the center of silica spicules in marine sponges, is known to play a role in silica condensation from seawater. It has also been shown to catalyze the formation of silica from various silica precursors such as tetraethyl orthosilicate (TEOS). Inspired by the finding that the serine-26 and histidine-165 amino acids in the enzyme are required for silica formation from TEOS, we synthesized poly(hydroxylated isoprene-*b*-2-vinylpyridine) block copolymers to mimic these amino acid residues. Here, we present the results of our investigation utilizing this biomimetic polymer to condense titania from titanium isopropoxide (TiP). Our silicatein α mimic is shown to condense titania at neutral pH and room temperature and is compared to material produced by standard sol–gel methods. Heats of crystallization are observed to be 72% lower for the titania made from the mimic polymer, and indistinct X-ray diffraction peaks, even after heating well above the crystallization temperature, suggest a higher degree of titania condensation with the silicatein α mimic. Results from thermogravimetric analysis show that the mimic formed titania initially contains ~15 wt % polymer and that the surface area increases from less than 5 to greater than 110 m²/g when heated to 400 °C. Titania made from the silicatein α mimic also shows a higher catalytic activity than does commercial Degussa P25 TiO₂ for the photodegradation of N-nitrosodimethylamine (NDMA), degrading 73% of the NDMA in two hours as compared to 62% with Degussa P25. The biomimetic system presented here offers the promise of an environmentally friendlier method of titania production and will enable applications requiring neutral pH and low temperatures, such as titania composite synthesis, surface coating, or catalyst design.

KEYWORDS: biomimetic, titania, block copolymer, catalysis, template



1. INTRODUCTION

In order to understand the molecular mechanism of biosilicification, Shimizu et al. studied *Tethya aurantia*, a marine sponge found off the coast of Santa Barbara, and characterized the proteins occluded in its biologically silicified structure.¹ Of the three proteins isolated, silicatein α was the most abundant. Cha et al. were then able to successfully condense silica from precursors such as tetraethylorthosilicate (TEOS) and phenyltriethoxysilane using the isolated silicatein α as a catalyst.² Site directed mutagenesis indicated that the serine-26 and histidine-165 residues in silicatein α were necessary for the catalysis of silica formation,^{2,3} and based on this information, we synthesized a block copolymer, poly(hydroxylated isoprene-*b*-2-vinylpyridine), that mimics the serine and histidine residues in silicatein α , as illustrated in Figure 1, and successfully catalyzed silica formation using this synthetic block copolymer.⁴ Highly condensed silica was formed with silicatein α mimic and the rate of hydrolysis of TEOS was shown to be higher than that of acid or base catalyzed silica condensation.⁴ These results demonstrated the neutral pH and room temperature synthesis of silica catalyzed by our biomimetic block copolymer.

Although silica formation has been the focus of our previous studies, ceramics such as titania can also be formed from alkoxide precursors. The conventional method of titania synthesis is by a sol–gel process involving the use of titania precursors in low or high pH in order to control hydrolysis and condensation rates.⁵ For titania precursors at neutral pH, the hydrolysis rate constant is 10^{-3} M⁻¹ s⁻¹, while the condensation rate constant is 30 M⁻¹ s⁻¹.⁶ This means that at neutral pH, condensation is significantly faster than hydrolysis and titania will tend to condense nearly as soon as it is hydrolyzed. In order to form structured titania, it is necessary to hydrolyze the titania precursor and shape it before condensation. At low pH, the hydrolysis rate constant increases and the condensation rate constant decreases, resulting in the formation of a stable sol phase that can be molded into different shapes and heated to slowly drive condensation and form a gel phase.^{5,7} In biological systems, however, hydrolysis and condensation of ceramics takes place at near neutral pH and ambient temperature.^{3,8}

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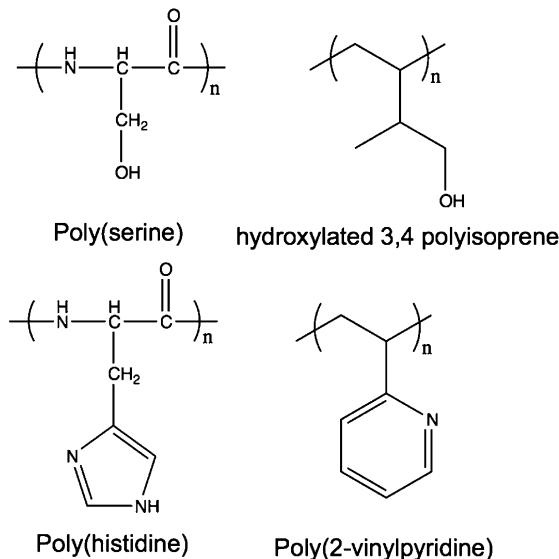


Figure 1. Structural comparison between the amino acid residues shown to be necessary for TEOS catalysis in silicatein α and the pendant groups of the synthetic block copolymer mimic.

Although titanium is more electropositive than silicon and thus has a much faster rate of hydrolysis and condensation,⁶ the general reaction mechanism by which silica and titania precursors hydrolyze and condense in synthetic systems is similar.^{9–12} In this report, we present the results of our studies utilizing a synthetic biomimetic polymer catalyst for the production of highly condensed and catalytically active titania.

There have been several previous reports of the synthesis of titania at neutral pH and room temperature using natural proteins rather than synthetic polymers. Jiang et al. condensed titania at room temperature and neutral pH using the highly basic natural protein protamine.¹³ The authors described the titania formation as occurring by way of the negatively charged titanium(IV) bis(ammonium lactato) dihydroxide (TiBALDH) precursor adsorbing on the positively charged globular protamine followed by the amine mediated condensation. Another example is the use of recombinant silaffins to condense titania from TiBALDH precursor at room temperature.^{14,15} Finally, natural silicatein α filaments, extracted from *Tethya aurantia*, have been used by Sumerel et al. to condense titania at room temperature and neutral pH to form titania from TiBALD.^{16,17}

In the work reported here, our entirely synthetic silicatein α mimic is used to form titania. We describe differences in the structure and reactivity of the titania formed by the mimic polymer with titania made by a more traditional sol–gel method. To compare the catalytic activity of titanias, we employed the well-known photodegradation reaction of N-Nitrosodimethylamine (NDMA).¹⁸ NDMA can be formed during the chlorination of wastewater and is thus a serious human health concern.¹⁹ It can be degraded by UV light, and this process is often catalyzed by titania.²⁰ Our objective is to test the photocatalytic activity of titania prepared from our silicatein α mimic using NDMA as a model contaminant and compare its performance with commercial TiO_2 and platinized titania samples.

2. EXPERIMENTAL DETAILS

2.1. Materials. Isoprene (Acros Organics, stabilized, 99+%) and cyclohexane (Fisher Chemical, certified ACS grade) were dried over sec-butyl lithium and 1,1-diphenylethylene (DPE). The 2-vinylpyridine monomer (Acros Organics, stabilized, 97%) was dried over calcium hydride and distilled into a glass ampule under high vacuum. The initiator, sec-butyl lithium (1.3 M solution in cyclohexane, Acros Organics), was placed in a glass manifold consisting of six ampules, evacuated, and backfilled with dry cyclohexane. The ampules were then removed from the manifold with an oxygen/methane torch, and the concentration of initiator was determined by sacrificing two ampules for a double titration. Isoprene was dried overnight over sec-butyl lithium at -78°C , followed by distillation and ampulization. For hydroxylation of the isoprene block, 9-borabicyclo[3.3.1]nonane (9-BBN) (0.5 M solution in THF, Aldrich), sodium hydroxide (Fisher Chemical) and hydrogen peroxide (35 wt % solution in water, Acros Organics) were used as received and THF (Fisher Chemical, histological grade) was dried over sodium/benzophenone and distilled. For titania synthesis, THF and titanium(IV) iso-propoxide (TiP) (Strem Chemicals, 98%) were used as received. NDMA (Sigma-Aldrich, analytical-grade) and deuterated (*d*6) NDMA (Cambridge Isotope Laboratories, Inc., 98%) were used as received.

2.2. Titania Synthesis. The synthesis of hydroxylated poly(isoprene-*b*-2-vinylpyridine) has been previously reported,^{4,21,22} and characterization data is included in Supporting Information (SI). For titania condensation experiments, all chemicals were used as received. Reaction mixtures were made with a 1:2:14 mass ratio of polymer mimic/TiP/THF. First, the silicatein α mimic was weighed and dissolved in THF. The solution was stirred overnight followed by the addition of TiP. The mixture was then stirred for an additional 1 h. After sitting for 3–4 days, the reaction mixtures gelled. The gel was air-dried and ground into powder for further characterization. This sample made in the presence of the mimic polymer was designated as “Titania M” and calcined Titania M sample was designated as “Titania MA”. Titania was also condensed by adding TiP to water (Titania W), THF (Titania T), and THF+water (Titania TW). Table 1 summarizes

Table 1. Composition of Solutions Used to Condense Titania

	water	THF + water	THF + mimic	THF
THF	NA ^a	8.5 mL	8.6 mL	8.6 mL
water	8.5 mL	0.2 mL	NA	NA
silicatein- α mimic	NA	NA	540 mg	NA
TiP	1520 mg	1510 mg	1610 mg	1540 mg

^aNA = not added.

the solution compositions. The resulting precipitates were separated by centrifugation and dried in a vacuum oven at 60°C for 12 h. As a control experiment, reaction mixtures were made with polymers other than our mimic, including polyisoprene, hydroxylated polyisoprene, poly(2-vinylpyridine) (P2VP), Pluronics F-127, and polyethyleneimine (PEI).

For the synthesis of titania using a sol–gel method,^{23–25} 5 mL of TiP was added to 25 mL of ethanol and cooled to 4°C in an ice bath. In a separate flask, 0.5 mL of deionized water and 0.5 mL of 0.1 N HCl was added to 25 mL of ethanol and cooled to 4°C in an ice bath. The water–HCl reaction mixture was then added slowly to the TiP–ethanol mixture. After complete addition, the mixture was allowed to warm to room temperature with constant stirring. After 2 h, the reaction mixture was warmed to evaporate ethanol. The white precipitate was collected and dried under vacuum for 2 days and designated as “Titania SG”. Calcined Titania SG sample is designated as “Titania SGA”.

2.3. Thermal Analysis. Thermogravimetric analysis (TGA) was performed using a TA TGAQ500-0188 unit. The samples (10 to 15 mg) were loaded into platinum pans and heated from 50 to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen flow of 40 mL/min.

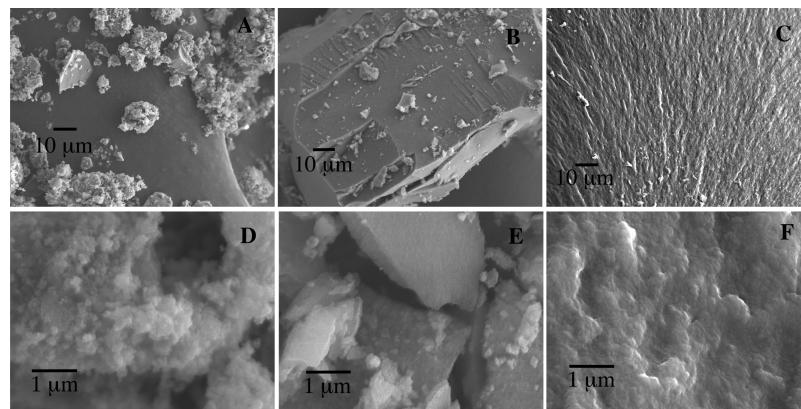


Figure 2. Representative FESEM images of titania condensed in (A) water showing small particles aggregated to form a precipitate (Titania W), (B) THF + water (2.3 wt % water) showing large monoliths mixed with small particle aggregates (Titania TW), and (C) THF + mimic (no added water) showing material that exists as a continuous rough surface (Titania M). In systems with only THF, no solid titania is formed and thus no image is included in the figure. Images D, E, and F show high resolution images of Titania W, Titania TW, and Titania M, respectively.

Differential scanning calorimetry (DSC) analysis of Titania M and Titania SG were done with a TA DSCQ100-0219 instrument with 5 to 10 mg of sample sealed in an aluminum pan and heated from room temperature to 600 °C.

2.4. Electron Microscopy. For scanning electron microscopy (SEM) analysis, dried titania samples were adhered to a SEM stub using carbon tape. Samples were then coated with gold/palladium using a Polaron Instruments SEM coating unit E5100 for 30 s to form approximately 1 nm thick coatings on the samples. Images were taken on a JEOL 6335F field emission (FE)SEM instrument operating at 10 kV accelerating voltage and a 15 mm working distance. Energy dispersive X-ray spectroscopy (EDXS) was run using a Thermo Noran System Six EDXS instrument attached to the FESEM. Point and shoot type EDXS analysis was conducted to determine the chemical nature of the feature of interest. FESEM and EDXS analyses of titania samples condensed in all reaction mixtures were obtained.

Transmission electron microscopy (TEM) was preformed with titania dispersed in methanol by ultrasonication for 30 min. This dispersion was drop cast on a 400 mesh TEM grid coated with a 3 nm thick carbon layer and allowed to dry. The images were obtained with a FEI Tecnai T12 S/TEM at 120 kV. Electron diffraction spectra of the crystalline titania samples were also obtained.

2.5. Surface Area Analysis. Brunauer–Emmett–Teller (BET) surface area analysis was conducted on an ASAP 2010 Micromeritics instrument and multipoint measurements were carried out at 77 K with nitrogen. Before analysis, the samples were degassed at 120 °C for 1 h.

2.6. X-ray Diffraction (XRD). An XDS 2000 Scintag diffractometer was used to record the XRD patterns of Titania M and Titania SG. Graphite monochromatic copper radiation ($\text{Cu K}\alpha$) was operated at 40 kV and 40 mA. A 2θ range of 5° to 70° was scanned at the rate of 2°/min. To investigate the effects of temperature on the surface area and crystallinity, Titania M and Titania SG samples were heated to 100 °C for 2 h and then cooled in a closed container. This was followed by BET surface area analysis and then by XRD measurement. The same samples were subsequently heated to 200 °C for 2 h, and the XRD and BET analyses were repeated. Data was collected up to 600 °C.

2.7. X-ray Photoelectron Spectroscopy. XPS analysis of annealed samples of Titania M and Titania SG were analyzed with a Phi Multiprobe Model 2S–120 instrument. The titania samples were adhered to a sample holder using carbon tape. The binding energies (and hence, bonding states) of the titanium and oxygen atoms of each sample were determined by examination of the intensity, shape, and energy of the Ti 2p and O1s peak, respectively.

2.8. UV–Vis Diffuse Reflectance Spectroscopy (DRS). Titania samples were diluted 10 times with barium sulfate. The powder was ground and packed into a sample holder to create a smooth surface.

DRS data was acquired on a Shimadzu UV-2450 UV–vis spectrophotometer with a DRS accessory. The reflectance data was then transformed into Kubelka–Munk absorption.

2.9. NDMA Photocatalytic Degradation. Standard 10⁶ mM solutions of NDMA in deionized water were prepared. In 200 mL of this solution, 100 mg of Titania MA was dispersed. This was treated for 30 min in a sonication bath to disperse the catalyst particles. The dispersion was then aerated for another 30 min to achieve adsorption–desorption equilibrium. The reaction mixture, in a quartz container, was then exposed to UV light (sixteen 15 W UV–C lamps emitting monochromatic light at 254 nm). A sample (~5 mL) was taken at various time intervals during the 3 h experiment. The dispersed titania was separated from these samples by centrifugation and a UV–vis spectrum of the clear solution was obtained on a Shimadzu UV-2450 UV–vis spectrophotometer. In order to establish a calibration plot, UV–vis spectra for a range of known concentrations of NDMA were obtained and the absorbance of each concentration at 250 nm was plotted against concentration. The concentrations of unknown samples were determined using this calibration plot. For comparison with Titania M, the same experiments were run with samples of Degussa P-25 and platinized titania synthesized according to a literature procedure.²⁶ Experiments were also done without any titania catalyst. All experiments were repeated 3 times.

Additionally, the photocatalytic degradation of NDMA with Titania M was preformed with and without UV light. A 100 mg portion of Titania M was dispersed in 100 mL of 10⁵ mM NDMA solution. The solution was sonicated and aerated as described in the preceding paragraph. In the absence of UV light, the solution was kept in an oil bath at 50 °C to simulate the heat generated during photodegradation. Samples were taken at various time intervals during the experiment. After separating the titania particles, 0.8 mL of 125 μM deuterated NDMA solution in water was added to 1.2 mL of treated NDMA and analyzed by the Direct Analysis in Real Time–Mass Spectroscopy (DART-MS) technique. A series of solutions containing 50 μM deuterated NDMA and known concentrations of NDMA (unlabeled) were analyzed in DART-MS as calibration standards. The ratio of intensities of labeled and unlabeled NDMA solutions were plotted against the NDMA concentration, and this plot was used to determine the concentration of unknown samples.

3. RESULTS AND DISCUSSION

3.1. Electron Microscopy. Increasing the concentration of water in the system increases the rate of hydrolysis. If the hydrolysis rate is fast, condensation starts from multiple points growing simultaneously, resulting in the formation of highly ramified, low-fractal dimension structures.⁵ Figure 2A, showing Titania W (titania condensed by adding TiP to water),

illustrates such a condition by SEM. The powdered sample is shown to consist of small particles, generally less than 1 μm in diameter, with some aggregation leading to particles as large as 10 μm .

As the hydrolysis rate is slowed by decreasing the concentration of water, the particle size increases and the number of particles decreases. Figure 2B shows an FESEM image of Titania TW (titania condensed by adding TiP to a THF and water mixture with 2.3 vol % of water). The sample consists of particles roughly 10 μm in size, with several up to 100 μm in size. These particles are much larger than those formed in the Figure 2A water reaction. This is due to condensation from fewer nucleation sites, a situation resulting from a lower concentration of hydrolyzed titania molecules.

As the concentration of hydrolyzed species is lowered even further, hydrolyzed species tend to react with growing condensate rather than with other monomeric hydrolyzed species, forming dense condensates with highly condensed structures.⁵ Some amount of water, however, is required for the hydrolysis to occur as evidenced by our finding that even after one month no precipitate forms when TiP is added to THF containing no added water. When TiP is added to a mimic polymer solution in THF containing no added water and allowed to stand for 3–4 days in a closed vial, a translucent gel is formed. Figure 2C shows the FESEM image of the dried gel (Titania M). Larger chunks of condensate 500 μm and bigger in size are observed in the mimic catalyzed reaction. EDXS analysis of all three titania samples (shown in SI 2, SI 3, and SI 4) confirms the presence of titanium and oxygen.

THF is a hygroscopic solvent, so it is expected that there will be some amount of water present. However, the described experiments are carried out at the same time using the same source of THF. Hence, the concentration of water dissolved in THF is nearly constant in these experiments and does not account for the observations. Further, the water present in THF is shown to not hydrolyze TiP without silicatein α mimic.

As a control, TiP is also added to THF solutions of Pluronics F-127, polyisoprene, hydroxylated polyisoprene, and P2VP. These solutions stay clear for over a month, showing no signs of condensation. As even the homopolymer blocks of the silicatein α mimic block copolymer do not condense titania on their own, the mechanism of titania formation is shown to be more than simple association of hydrolyzed species.^{4,27} These control experiments further support the hypothesis that silicatein α mimic catalyzes TiP hydrolysis.

Our results are much different than those of previous groups who utilized nitrogen-containing polymers in the production of titania. There have been reports of the use of P2VP containing block copolymers as a template for titania.^{28–30} Kumar et al. hydrolyzed titania precursors with the help of acid catalyst, while the purpose of P2VP was to form hydrophilic domains. The hydrolyzed TiP has affinity for P2VP, and these hydrophilic domains act as a template for the condensation of the already hydrolyzed titania.²⁸ Li et al. used hydrophilic domains of P2VP but with a different precursor (TiCl_4).²⁹ Shin et al. proposed the use nanoparticles formed by PS-*b*-P2VP in toluene as a template for titania, while still using a sol–gel method to form titania.³⁰ These accounts do not report or claim any catalytic effect of P2VP. The use of poly(ethylene imine) (PEI) for titania condensation has also been reported.^{31,32} However, the function of PEI beyond the adsorption of hydrolyzed TiP species was not discussed. We observe no condensation of titania with PEI even after one

month, suggesting that PEI is not catalytically active in our titania condensation system.

3.2. Thermal Analysis. Shown in Figure 3 are the results of TGA analysis of Titania M, Titania SG, and silicatein α mimic

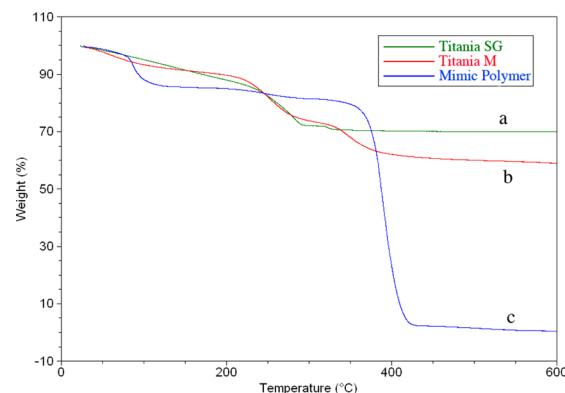


Figure 3. TGA plots of Titania SG, Titania M, and mimic polymer. The green line (a) is of Titania SG and shows slow water loss followed by a condensation event near 300 °C. The red line (b) is from Titania M and shows the loss of polymer near 350 °C. The blue line is mimic polymer alone and shows the polymer decomposing between 350 and 400 °C.

polymer. Both titania samples show similar weight loss profiles until approximately 350 °C, when the Titania M loses 10–15 wt % between 350 and 400 °C due to the decomposition of the polymer mimic. This is a significantly smaller amount of polymer than is found in the mimic synthesis of silica from TEOS,^{27,33} and the origin of this difference is a focus of current research. The TGA of the mimic polymer alone shows degradation of the polymer and the polymer associated with titania to be in the same temperature range. This suggests that mimic polymer is not strongly associated with the titania; otherwise, a change in degradation temperature would be expected. This result is also in agreement with the hypothesis that the mimic catalyzes hydrolysis and the hydrolyzed precursor diffuses some distance before condensing.

Results of DSC analysis for the two titania samples are shown in Figure 4. Titania SG shows an endotherm at 75 °C due to evaporation of residual solvents. A broad shoulder above 200 °C corresponds to evaporation of TiP. Titania M shows 3 endotherms with peak temperatures at 60, 250, and 350 °C. The first two endotherms are due to evaporation of residual solvent and unreacted TiP. The endotherm at 350 °C corresponds to degradation of polymer in the Titania M sample. In addition, Figure 4 shows that Titania SG crystallizes at 391 °C and Titania M crystallizes at 512 °C. Confirmed by XRD results, these crystallization temperatures correspond to the phase transformation from amorphous to anatase titania. Various values for this crystallization temperature appear in the literature,^{34,35} as the phase transformation depends on factors such as type of precursor, synthesis method, and catalyst used. In DSC scans of Titania SG, the presence of a small peak next to the large one at 403.7 °C is due to the crystallization of bulk material. The 121 °C difference in crystallization temperature of the Titania SG compared to the Titania M is significant and may be due to the higher degree of condensation in the Titania M sample requiring a higher temperature for atom rearrangement.

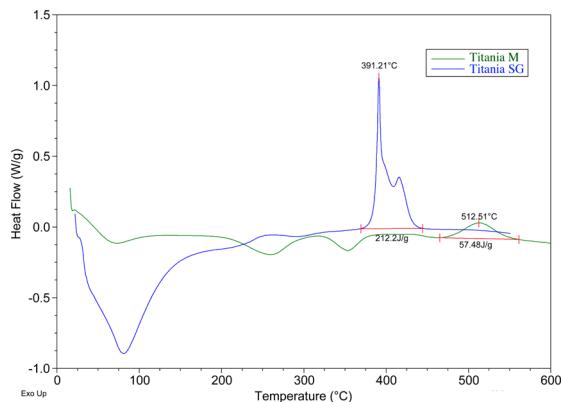


Figure 4. DSC curves for Titania SG and Titania M. The bottom green line is Titania SG and shows a bimodal transition with the first peak at 403.7 °C. This corresponds with the transition to the anatase crystal structure. The upper blue line is from the Titania M and shows a much latter transition to the anatase crystal structure, occurring at 512.5 °C. Additional peaks are also seen in the Titania M that are not observed in the Titania SG, and these correspond to the degradation of the mimic polymer.

A telling observation in our system is the difference in the heats of crystallization of the two titania samples. Since both samples lose weight during heating, the heats of crystallization are corrected and are found to be 87 J/g for Titania M and 312 J/g for Titania SG. Several explanations are possible, including the Titania M requiring less rearrangement for crystallization to occur. The small heat of crystallization of Titania M may also be due to the crystallization of only a small amount of material. In an attempt to resolve these possibilities, XRD is utilized.

3.3. X-ray Diffraction. In Figures 5 and 6 are shown the change in crystal structure as a function of temperature for

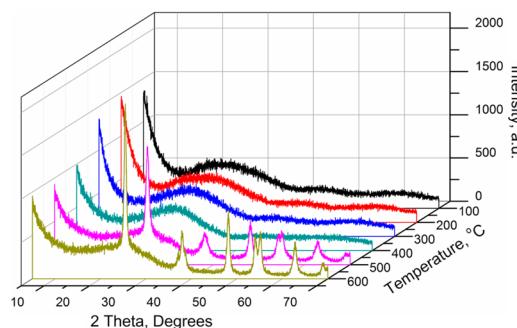


Figure 6. Temperature dependent XRD of Titania M. The transition from amorphous to anatase is observed to occur only after 500 °C, confirming the results from DSC. The peaks are seen to be broader than with the sol–gel material, even at higher temperatures.

In addition, these results help explain differences between the two titania samples in terms of degree of condensation and heat of crystallization. The XRD spectra of Titania SG at 400 °C consist of a few indistinct peaks as crystallization of bulk material has not yet occurred. At 500 °C, the spectra shows well resolved peaks that do not change much at 600 °C. Crystalline peaks for Titania M appear at 500 °C, since the crystallization has started before the peak crystallization temperature of 512 °C observed in the DSC data. These peaks are better resolved at 600 °C. Comparing the two titania samples, the XRD peaks of Titania SG are sharper and more distinct than that of Titania M. This suggests that less of the Titania M sample undergoes crystallization. A higher degree of condensation in the Titania M sample may account for both the higher temperature of crystallization (by 121 °C) as well as the lower heat of crystallization (by 72%) as compared to the sol–gel material.

3.4. Surface Area Analysis. To shed some light on the porosity of the formed titania as well as to further investigate the degree of condensation of the two titania samples, the BET surface area of both samples is analyzed as a function of annealing temperature and is presented in Figure 7. For Titania SG, the surface area decreases with increasing temperature. This is the expected behavior and has been observed by others.^{10,37} At temperatures below the crystallization temperature, the loss of surface area in the sol–gel material appears to result from further condensation. In the Titania M, however, an increase in surface area with increasing temperature is observed until the crystallization temperature is reached. This increase in surface area is due to the removal of polymer and indicates that the Titania M is, unlike the Titania SG, stable to further condensation at these temperatures. Based on the TGA scan in Figure 3, the silicatein α mimic polymer accounts for only 10 to 15% of the weight of the Titania M sample. The more than 100 fold increase in the surface area is likely explained by opening channels in the titania particle as the polymer is removed. The unique morphology and chemistry of the titania produced by the mimic is expected to have a significant effect on properties such as catalysis, and this is explored by comparison to other titania samples in photodegradation studies.

3.5. Transmission Electron Microscopy. TEM images of uncalcined and calcined Titania M samples are shown in Figure 8. The TEM images of uncalcined Titania M shows areas of lower contrast that are absent in images of calcined Titania M and uncalcined Titania SG. These regions are small, between 10 and 50 nm lateral dimension, and appear well dispersed in the sample. Due to the electron density contrast between polymer

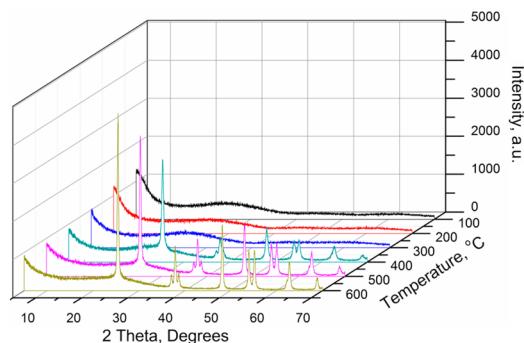


Figure 5. Temperature dependent XRD of Titania SG. The transition from amorphous to the anatase crystal structure is observed to occur at about 400 °C, with the peaks becoming sharper at higher temperatures.

Titania SG and Titania M. The two peaks in the DSC trace for the Titania SG are the result of two distinct crystallization events rather than condensation followed by crystallization. The XRD at 400 °C indicates the presence of crystalline material, suggesting that condensation occurs at a lower temperature. What appears likely is that the surface titania material is crystallized first, followed by the bulk material, giving the second crystallization peak at higher temperature.

These XRD results confirm that upon crystallization, both titania samples form the anatase crystal structure³⁶ (SI 5, SI 6, and SI 7 show the peak assignments and unit cell parameters).

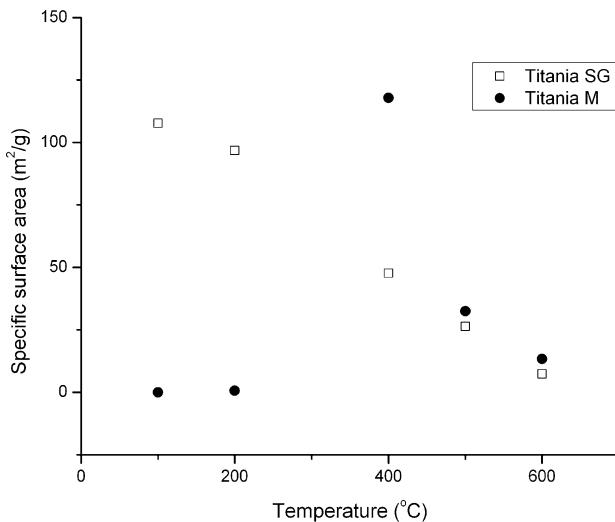


Figure 7. BET surface area of Titania SG and Titania M as a function of temperature. The red line, starting at $\sim 110 \text{ m}^2/\text{g}$, is of the Titania SG. As the temperature increases, further condensation of the titania leads to decreasing surface area. Titania M shows an increase of surface area with increasing temperature as the included polymer is burned out. Loss of surface area as a result of condensation is not seen. The onset of crystallization at even higher temperature leads to a loss of surface area.

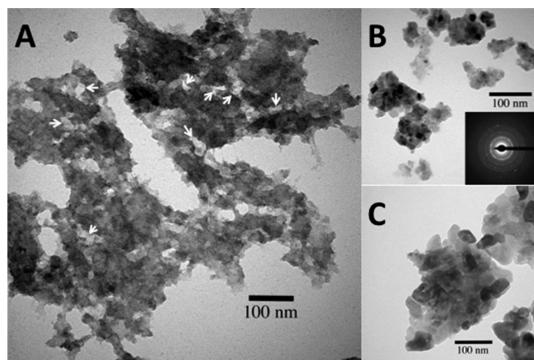


Figure 8. Representative TEM images of (A) uncalcined Titania M, (B) calcined Titania M, and (C) uncalcined Titania SG. Image A shows nanosized regions (marked by white arrows), possibly of mimic polymer. These domains are absent in images B and C. An electron diffraction image of calcined Titania M sample is shown in inset of image B.

and titania, we suspect these lighter regions are mimic polymer. Polymer would be absent in the calcined Titania M and sol-gel material.

3.6. X-ray Photoelectron Spectroscopy. XPS survey spectra for calcined samples of Titania M and Titania SG are shown in SI 9 and SI 10. Quantitative analysis of Titania M and Titania SG suggests the presence of more organic matter on the surface of Titania SG than on Titania M. High resolution XPS analysis of calcined samples of Titania M and Titania SG are shown in SI 11. After deconvolution, the spectra for Ti 2p 3/2 and 1/2 orbitals show single peaks at 458.7 and 464.3 eV for both titania samples. This indicates that the titanium is in the +4 oxidation state for both titania samples.¹⁶

3.7. UV-Vis Diffuse Reflectance Spectroscopy. K-M absorbance against wavelength data (shown in SI 12) shows that the Titania M sample absorbs in the visible region due to the presence of polymer. However, after calcination, this broad

absorbance disappears due to burning off of the polymer. The modified Kubelka-Munk (K-M) absorbance [$(\text{K}-\text{M}^*\text{hv})^{1/2}$] against energy for raw and calcined samples of Titania SG and Titania M is shown in Figure 9, and the indirect band gap

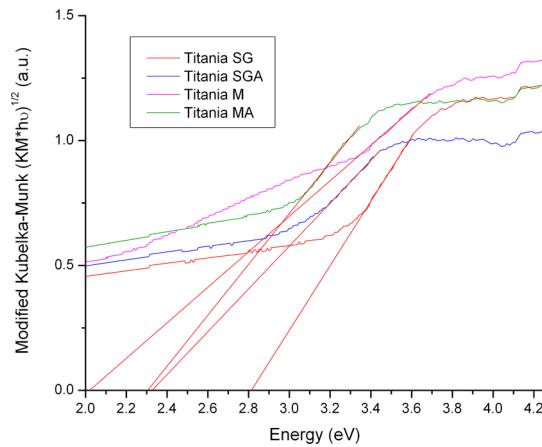


Figure 9. Modified Kubelka-Munk [$(\text{K}-\text{M}^*\text{hv})^{1/2}$] plotted against energy (eV) for uncalcined and calcined samples of Titania M and Titania SG for estimation of indirect band gap energy.

energies of the titania samples can be estimated from this plot.³⁸ The x -intercept of the extrapolation of the linear part of the modified K-M absorbance gives a good estimation of indirect band gap energy.^{39,40} Upon calcination, the indirect band gap energy of the Titania SG decreases from 2.81 to 2.33 eV. However, in the case of Titania M, it increases from 2.02 to 2.31 eV. This change in trend can also be attributed to the removal of polymer after calcination.

3.8. NDMA Photocatalytic Degradation. The percentage of NDMA degraded in UV light using three different titania catalysts is shown in Figure 10. A control without any catalyst is also shown. NDMA degrades in UV light in the presence of water due to the formation of hydroxyl radicals and forms less toxic methylamine (MA), along with smaller quantities of dimethylamine (DMA), nitrate, nitrite, and ammonium species.¹⁹ However, this process is slow and is thus often

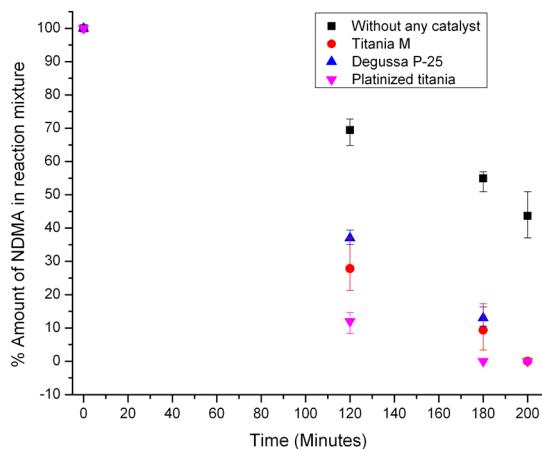


Figure 10. Photocatalytic degradation of NDMA without any catalyst and with Titania M, Degussa P-25 titania, and platinized titania. The higher reactivity of the Titania M as compared to the commercial sample suggests the lower crystallinity of the Titania M does not adversely affect its catalytic activity.

catalyzed by titania.²⁰ In this study, Titania M degraded 73% of NDMA, while commercial Degussa P-25 titania and platinized titania degraded 62% and 88%, respectively, in the initial 120 min time interval. The catalytic activity of platinized titania was clearly enhanced due to presence of platinum on the titania surface.

There are several properties that affect the photocatalytic activity of titania including crystal structure, morphology, surface area, and porosity. The Titania M is shown to possess a higher degree of condensation than Titania SG and $13.35\text{ m}^2/\text{g}$ surface area. The titania samples used for comparison in the catalyst tests are platinized titania and commercial Degussa P25 sample. XRD spectra of the two control samples are shown in the SI 13 and SI 14. Degussa P25 has a higher surface area and a higher degree of crystallinity than Titania M. Thus, the better photodegradation results of Titania M compared to Degussa P25, as shown in Figure 10, suggest that the degree of crystallization does not necessarily correlate with the catalytic activity of the titania.

To be sure that NDMA is not being removed from the solution by adsorption on the Titania M surface rather than by degradation, a photocatalytic degradation experiment with and without UV light is performed. If adsorption is significant enough to extract such a high concentration of NDMA from solution, the same results should be observed in the absence of UV light. Lower concentrations of NDMA are used for this experiment so that even a small amount of adsorption will be observable. A more sensitive technique (DART-MS) is used to analyze the samples taken at various time intervals to rule out the possibility that degradation products are contributing to the peak of NDMA in the UV-vis spectrum. The plot in SI 15 shows that there is no significant adsorption of NDMA on Titania M surfaces. The 10^5 mM NDMA solution degrades within 5 min upon exposure to the UV light in the presence of Titania M. The concentration stays the same in the absence of UV light. Heat produced by UV radiation does not seem to have a significant effect on degradation of NDMA, as samples not exposed to UV are kept in an oil bath at 50°C .

4. CONCLUSION

Comparison of titania synthesized using mimic polymer (Titania M) with those prepared using the conventional sol-gel method (Titania SG) indicates structural differences in the materials formed. This is demonstrated by differences in the XRD spectra at increasing temperatures and the increase of surface area to $\sim 110\text{ m}^2/\text{g}$ for the Titania M and decrease in surface area for the Titania SG to $\sim 50\text{ m}^2/\text{g}$ when each is heated to 400°C . The phase transitions of the two materials are also very different, with the Titania M showing a 51.2 J/g transition at 512°C and the Titania SG showing a bimodal transition of 213.9 J/g starting at 403.7°C . TGA results indicate that the Titania M is composed of roughly 15% polymer prior to heating above the polymer decomposition temperature, while the Titania SG shows no such weight loss at that temperature. Photodegradation studies of the Titania M show an increase of catalytic activity as compared to a standard commercial titania catalyst, with the commercial material degrading 62% of the NDMA over a two hour period compared with 73% degradation with the Titania M.

In the study presented here, we have demonstrated the use of a block copolymer that mimics the natural enzyme silicatein α for the condensation of titania. The controlled condensation of titania is achieved at near neutral pH and ambient temperature,

and as the hydrolysis is separate from the condensation step, the rate of each can be separately controlled. This biomimetic system offers the promise of an environmentally friendlier method of titania production and will enable applications requiring neutral pH and low temperatures, such as titania composite synthesis or catalyst design.

■ ASSOCIATED CONTENT

S Supporting Information

EDX and XPS spectra, XRD data, BET surface area, and Kubelka-Munk absorbance versus wavelength plot for titania samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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