FORMATION OF TITANIA USING A BIOMIMETIC-DERIVED METHOD

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ABSTRACT

In nature, organisms form intricate silica structures at ambient temperatures and pH. Numerous studies of these organisms have identified some biomimetic approaches for precipitating and templating silica. It has been theorized that these biomimetic approaches could precipitate metal oxides other than silica such as titania and alumina. These metal oxides are of interest as potential decontaminating substrates for the hydrolysis and oxidation of chemical agents. Recent studies have demonstrated the ability of polyamines to aid in the matrix-assisted precipitation of the anatase form of titanium dioxide. SEM and X-ray analysis results will be presented and the effects of varying polymer chain lengths and reaction conditions will be discussed.

INTRODUCTION

Nature has the ability of not only forming silica at ambient conditions, but also controlling the resulting morphology. This is in contrast to current industrial methods which contain some caustic materials and have limited control of morphology. In order to gain a better understanding of how nature precipitates and controls silica formation, a significant amount of research has been done on different organisms[4,6,9]. Two organisms have been extensively studied, the diatom and the sea sponge *Tethya aurentia*. Both organisms use proteins for the precipitation and control, but the action of each protein appears to be different.

The diatoms use a combination of the peptide silaffin and polyamines to precipitate the silica. By acting as Lewis bases, the silaffin and polyamines form acid/base complexes with silicic acid, to promote rapid hydrolysis and subsequent condensation as silica. Morphology control is achieved by varying the composition of the silaffin sequence and by varying the chain length of the polyamine[4, 6].

The sea sponge forms spicules using Silicatein, an enzymatic protein from the Cathepsin L subfamily. The Cathepsin L subfamily consists of lysosomal proteolytic enzymes which act as proteases. Silicatein, unlike other enzymes in the family, acts upon a small molecule, silicic acid, rather than proteins. Condensation of silica spontaneously commences once hydrolysis of silicic acid molecules has begun, but at a slower rate than with silaffin. The slower condensation rate is attributed to the low local concentration of hydrolyzed silicic acid molecules available at any given time, as the binding pocket of Silicatein can only bind one silicic acid molecule at a time. This contrasts the silaffins, which bind multiple silicic acid molecules simultaneously. This allows the hydrolyzed silicic acid molecules to condense more rapidly due to their close proximity.

Building upon previous knowledge, several alternative agents have been identified as potential biomimetic agents for precipitating silica[1,2,7,8]. These include block copolymers and small bimolecules, such as cysteamine and ethanolamine, which upon testing have shown success in precipitating silica. Analysis has suggested that these agents use a mechanism similar to the biological agent.

The objective of this study is to precipitate metal oxides using mimics similar to those mentioned above and to gain an understanding as to the specific parameters affecting this precipitation. This article presents and discusses early results from efforts to precipitate titania and alumina specifically.

PROCEDURES

Precipitation of Titania using the polyamines: The polyamines were obtained from various vendors and are listed below. For each reaction, 100µl of polyamine dissolved in 25mM Tris HCl (10% wt/vol) were mixed with 800µl of 25mM Tris HCl and 100µl Titanium (IV) bis-(ammonium lactate)-dihydroxide (TBALD) purchased from Sigma-Aldrich. The mixture was incubated at room temperature for 24 hr with mild agitation. Precipitates were collected via centrifugation and washed in MilliQ (MQ) water. Analysis of the precipitation was performed using scanning electron microscopy (Zeiss EVO 60 SEM, equipped with an EDAX Genesis EDS X-ray Detector). Tetraethyloxysilane (TEOS) was used as a positive control.

Table 1 List of polyamines tested

Polyamine	**Avg. Molecular Weight**	**Manufacturer**
PAA-H-10C (poly allyl amine)	59,900Da	Nitto Boseki, LTD
Erkol@ M12 (vinyl alcohol/vinyl amine)	80-140 kDa	Erkol, S.A
Basocoll@ (vinyl amine and N-vinylformamide)	two MW fractions	BASF
Catiofast@ PR8106 (polyvinylamine-HCl)		BASF
Poly allylamine	70,000	Sigma-aldrich

Precipitation of Titania with Sephadex@ Resin: DEAE Sephadex@ A-50, Sephadex@ LH60, and Sephadex@ G-100 were swelled according to the manufacturer's directions in 25mM Tris pH 7.2. For each reaction 500µl of the sephadex was added to 500µl TBALD and incubated at room temperature for 24 hr with mild agitation. The sephadex was collected via centrifugation and washed with MQ water. The resin was analyzed using SEM and EDS.

Test to Precipitate Alumina using Polyamines: For each aluminum reagent, a 1M solution was prepared in 25mM Tris pH 7.2. For each reaction, 100µl of the aluminum reagent was dissolved in 800µl 25mM Tris-hydroxymethylaminomethane (Tris-HCL) pH 7.2 with 100µl polyallylamine (10% wt/vol). The reaction was allowed to incubate for 24 hr at room temperature with mild agitation. Aluminum reagents examined include aluminum acetate (Bayer Healthcare), aluminum acetate basic (EMD), aluminum lactate (ALFA AESAR), aluminum 2-ethylhexanoate (STREM Chemicals), aluminum nitrate (ALDRICH), and aluminum perchlorate (ALFA AESAR).

RESULTS

Polyamines were tested for their ability to precipitate titania from TBALD. Every polyamine tested precipitated the TBALD from solution. Scanning electron microscopy (SEM) and Energy Dispersive

Spectroscopy X-ray detector (EDS) analysis on SEM studs with carbon tape indicated the precipitations are plate-like and composed of titanium and oxygen (Figure 1). X-ray diffraction analysis indicates that the precipitate is amorphous with no indication of crystal structure. Varying the pH of the buffer from 6.0 to 8.0 did not change the morphology of the precipitate. Attempts to precipitate alumina using the polyamines proved unsuccessful.

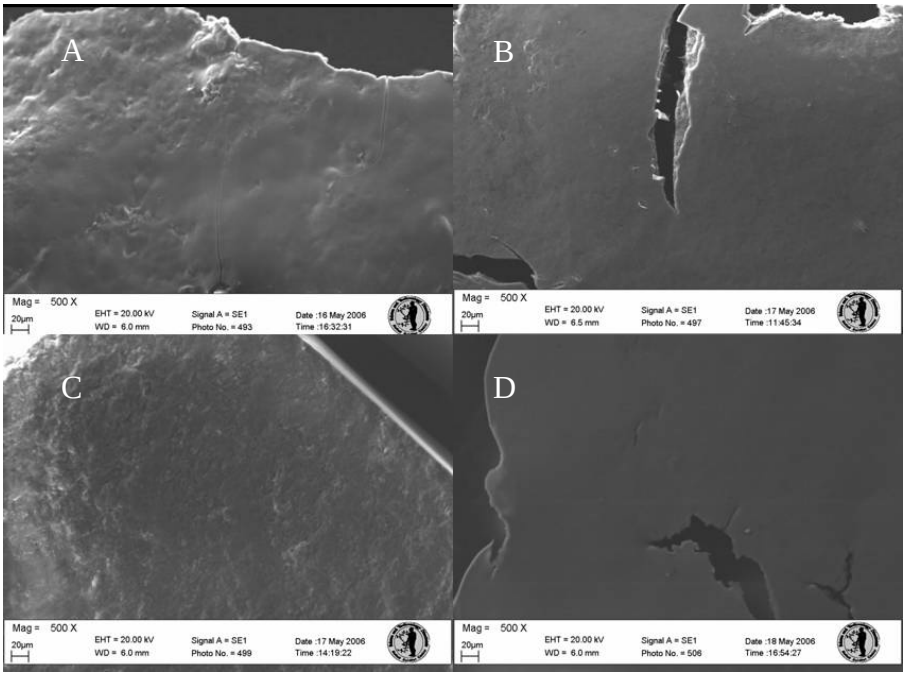

Figure 1. SEM images (500X) of titania precipitated with polyamines in Tris buffer pH 7.2. A) polyvinyl amine and poly N-vinylformamide, B) poly(ally amine) –H-10, C) poly (ally amine), D) polyvinylamine-HCl.

DEAE Sephadex$^{@}$, Sephadex$^{@}$ LH60 and Sephadex$^{@}$ G-100 were exposed to TBALD. The DEAE Sephadex$^{@}$ resin formed a precipitate over the resin spheres which EDS analysis showed was composed of titanium and oxygen (Figure 2). The Sephadex$^{@}$ G-100 showed some precipitation of the TBALD while the Sephadex$^{@}$ LH60 had no precipitation (results not shown).

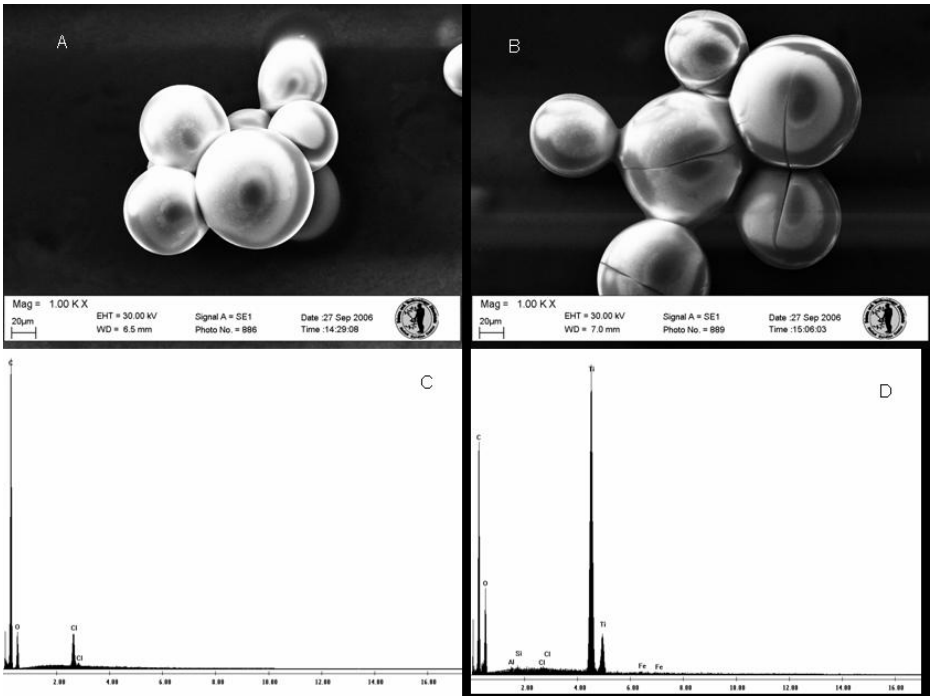

Figure 2. SEM images of DEAE Sephadex@ with and without exposure to TBALD at pH 7.2. A) DEAE resin with no TBALD exposure. B) DEAE Sephadex@ with TBALD exposure. C) EDS results for A D) EDS results for B

DISCUSSION

The polyamines precipitated the TBALD regardless of the polyamine type and pH. X-ray diffraction analysis indicated that the precipitate is amorphous. The EDS analysis shows that the precipitate is composed of titanium and oxygen. These results are similar to previous studies for precipitation of titania using Silicatein[10]. Although more experimentation must be performed to confirm this, the results and the literature suggest the precipitate is a form of TiO_x.

At the start of the study, the proposed mechanism for the precipitation of other metal oxides using polyamines was assumed to be the same as that for silica. This would have the amine group forming a weak bond with the metal and replacing any R group with an OH. Condensation would then proceed spontaneously to form the oxide. The results presented here support this assumption in part, but there are mechanistic differences between the precipitations of silica and titania.

Silica precipitated by polyamines forms as small nanospheres which encompass the polyamine[5]. Polyamine precipitates titania in a platelike manner, resulting in sheets of titania (Figure 1). This result occurs with all polyamines tested regardless of the pH. Sumerer had observed differences in the morphology for titania precipitated by Silicatein versus titania precipitated by a base-catalyst method[10]. He had offered that the templating effect of the Silicatein filaments smoothed out the titania while the untemplated base-catalyst titania were more random. Given that in this study both the polyamine precipitated silica and the titania are templated, some other factor besides templating must be influencing morphology differences. The chemical nature of the silica reagents versus the chemical nature of the TBALD may be a factor in morphology, but more research is necessary to determine this.

As previously described, polyamine acts as a mild base using the amine group to both bind the metal and catalyze the hydrolysis. To confirm the mechanism, three different Sephadex@ resins were utilized:

lipophilic Sephadex LH 60, a cationic resin with no amine groups; DEAE Sephadex, an anionic resin with amine groups; and Sephadex G-100, which is slightly anionic at pH 7.2 but has no amine groups. When exposed to the TBALD, the DEAE Sephadex and Sephadex G-100 resins were capable of precipitating the titania while the cationic sephadex LH-60 had no visible effect. The precipitation results of the slightly basic DEAE Sephadex and the slightly acidic Sephadex LH 60 were consistent with the above results, but the ability of the Sephadex G-100 to precipitate titania was surprising. Though it is mildly basic, there are no amine groups to bind the metal. An explanation may come from the hydroxyl groups found on the resin, which may have a similar ability to bind the metal and begin the hydrolysis. This suggests that any slightly basic surface with hydroxyl or amine ending may be capable of precipitation titania. Further testing will be performed to confirm this theory.

Attempts have been made to precipitate alumina using the polyamines. The most difficult hurdle has been finding water-soluble aluminum complexes. Most aluminum complexes are insoluble in water. Initial work was attempted with aluminum acetate and aluminum 2-ethylhexanoate. However, the solubility of these compounds was too low to adequately assess whether alumina could be precipitated from solution. Indeed, when tested with the polyamines, no precipitate was observed. Aluminum lactates and perchlorates are water soluble, and had been hoped to be good reagents, but when tested with polyamines, no precipitate was observed.

In the literature, gallium oxide has been precipitated using a Silicatein mimic[3]. The starting reagent was gallium nitrate which is water soluble. With this reaction, the nitrate group is hydrolyzed to form gallium hydroxide which condenses to gallium oxide. Since gallium is in the same group as aluminum, aluminum nitrate was tested with the polyamines. A precipitate formed quickly, but it dissolved within 30 min. Assuming that the aluminum followed the same mechanism as the gallium, the initial precipitation is probably $Al(OH)_3$ which is water insoluble. $Al(OH)_3$ is converted to $Al(OH)_4^-$ by basic solution[11]. Since the polyamine is acting as a mild base, it is suspected the polyamine first forms the insoluble $Al(OH)_3$, than further converts the complex to the water soluble and stable $Al(OH)_4^-$ complex.

CONCLUSION

These are only preliminary results, and though a precipitate was observed, analysis has failed to produce a positive ID. But the analysis results are consistent with those obtained for titania, suggesting the biomimetic approaches are capable of precipitating titania. The polyamine utilizes a mechanism for precipitating titania similar to that used for silica, where the polyamine acts as Lewis base binding then hydrolyzes the titanium complex to initiate titania precipitation. There are some mechanistic differences affecting morphology, but the primary mechanism is similar. Functionalized Sepadex beads acting as Lewis bases were demonstrated to be capable of precipitating titania. This supported the proposed mechanism.

Attempts to precipitate alumina demonstrated that the chemical nature of aluminum makes a biomimetic approach difficult. Though a precipitate can be formed using polyamines, it will eventually re-dissolve. It is proposed that the polyamine binds the aluminum complex to form the water insoluble complex $Al(OH)_3$. The polyamine, being basic in nature will further hydrolyzes the complex to $Al(OH)_4^-$ which is water soluble.

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