

Bioinspired mineralisation: macromolecule mediated synthesis of amorphous germania structures

Siddharth V. Patwardhan¹, Stephen J. Clarson*

Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

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We humbly dedicate this investigation to our good friend, colleague and mentor Professor James E. Mark on the occasion of his 70th birthday.

Abstract

The unique optical properties of germanium dioxide or germania (GeO_2), and in particular when compared with other glasses such as silicate glasses, have attracted the attention of scientists and made germania based materials highly suitable for optoelectronic applications. Germanium is known to resemble silicon in some of its chemical properties (in vitro) and biochemical properties (in vivo). The recent findings on the importance of the role of the (bio)macromolecules in (bio)mineralisation has led us to investigate the role of synthetic macromolecules in facilitating the formation of germania particles for the first time. One novelty is that the process described herein was carried out under ambient conditions and at neutral pH. The macromolecules used were poly (allylamine hydrochloride) (PAH) and poly-L-lysine (PLL), and it should be noted that both are cationically charged at neutral pH. Either germanium (IV) ethoxide or germanium (IV) isopropoxide were used as the germania precursors. The products were characterised by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD). Well-defined spherical germania particles were seen by electron microscopy and they were shown to be amorphous by XRD. In addition, based on Energy Dispersive Spectroscopy (EDS) observations, it was proposed that the facilitating macromolecules may be incorporated into the germania. Furthermore, when the reaction mixture was subjected to external shear, the formation of elongated rod-like germania structures was successfully achieved. It is proposed that the macromolecules act as catalyst/scaffold/template in a similar fashion to that described in the literature for the formation of (bio)silica as facilitated by (bio)macromolecules. This novel process is of importance for both the design of new materials based on germania and also silica-germania hybrids. These materials have a variety of potential commercial applications, an example being their use in optical fibre technologies. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Biomimetic synthesis; Biomineralisation; Waveguides

1. Introduction

The superior optical properties of germanium dioxide or germania (GeO_2) when compared to those of other glasses, such as silicate glasses, have attracted the attention of scientists and engineers for applications in fibre optics, waveguides, optoelectronic devices [1,2] and complementary metal-oxide semiconductors (CMOS) [3]. Germania glasses have higher refractive index values (typically between 1.6 and 1.65) without any dopants, whereas the

refractive index of typical silica glasses are around 1.45 [2]. Germanium dioxide is an attractive optical material due to its high transmittance over a wide spectral range (0.28–5 μm) and, in particular, in the near IR region, when compared with silicate glasses. In addition, germania has minimum optical losses at longer wavelengths when compared with quartz waveguides (10^{-1} – 10^{-3} dB/km for GeO_2 ; 0.2 dB/km for SiO_2). A detailed comparison of germania and silicate glasses has been presented by Margaryan and Piliavin [1]. Considering the importance of GeO_2 and its potential applications as discussed above, it is of importance to develop new synthetic and processing methods for germanium based materials. Germanium alkoxides typically undergo polymerisation via hydrolysis and condensation reactions similar to those seen in the case of alkoxysilanes (see Fig. 1). Typically, germania is produced by the high temperature oxidation of germanium tetrachloride (GeCl_4) giving crystalline GeO_2 [4]. The high

* Corresponding author. Tel.: +1 513 556 5430; fax: +1 513 556 3473.
E-mail address: stephen.clarson@uc.edu (S.J. Clarson).

¹ Present address: Interdisciplinary Biomedical Research Centre, School of Biomedical and Natural Sciences, Nottingham Trent University, Nottingham NG11 8NS, UK.

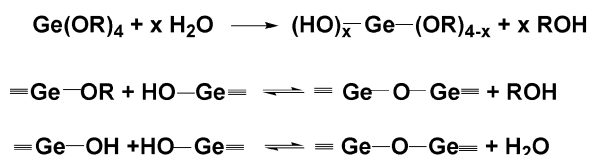


Fig. 1. Typical hydrolysis and condensation reactions of germanium alkoxide leading to the formation of germania.

temperature synthesis of crystalline germania whiskers has been also demonstrated previously [5].

The chemical characteristics of germanium and its resemblance to silicon have been reported previously and some of these properties are briefly described below. Germanium is found naturally at about 7 ppm typically in the form of germanium, zinc and silver ores [6]. Germania exists in four polymorphs [7]: hexagonal (α -GeO₂), tetragonal (β -GeO₂), cubic and amorphous germania. Germania is soluble in water at 0.447 g/100 g water in the form of germanic acid [8]. Germanium has also been proposed to be a micronutrient in various biological systems [9a]. The effects of germanium (Ge) for aquatic organisms [10] on the growth/biosilicification and the interactions of Ge with silicon (Si) have been studied in various living organisms such as diatoms [9a], sponges [9b,11–16], grasses (rice shoots) and rats [17]. It was concluded by various scientists that Ge affects (or even inhibits in some cases) the growth of these organisms by altering the process of biosilica deposition. For example, in sponges, the occurrence of irregular spines and/or ‘bulbs’ was seen [11–16] while in diatoms, the appearance of unusual organelles was observed in the presence of Ge [9b]. These effects of Ge on biosilicification were attributed to the specific Ge–Si interactions in different ways. It was proposed that germanic acid copolymerises with silicic acid during biomineralisation [9a]. In addition, Ge was found to cause renal failure in humans [18]. Thus, from a chemistry viewpoint, germanium may substitute for silicon

in various silicates. In Table 1 we have summarised comparison of some of the properties of Si and Ge oxides. The specific interactions of Ge with Si and/or interference of Ge in Si–protein associations can be seen as possible reasons for in vivo effects. We have previously hypothesised [19–21] that it would be interesting to investigate the interactions of Ge with various (bio)macromolecules (such as silicateins, silaffins, etc) that have been recently found to govern (bio)silicification in various in vivo and in vitro systems [20–48]. This can be carried out systematically by studying the activity of related (bio)macromolecules in various germanium media.

As a first step to address the aforesaid concerns, in this investigation we have discovered a new route for the rapid and controlled synthesis of amorphous germania (GeO₂) particles under conditions of ambient temperature and pressure, and at neutral pH. We have used either of two macromolecules—poly(allylamine hydrochloride), PAH and poly-L-lysine, PLL—to facilitate the synthesis of germania (GeO₂) particles under mild conditions with control over product morphologies.

Biomineralisation, which is an inspirational source for this synthesis, involves a series of complex processes, which lead to the formation of inorganic structures in biological systems. Such processes enable the formation of species-specific structures made of minerals in vivo through a combination of unique materials chemistry and biochemistry [9,49]. It has been shown that biomineralisation may be mediated by various biomolecules such as proteins and polysaccharides [22–26,48]. Such studies have led to the discovery of a series of synthetic (bio)macromolecules (including polypeptides), which are cationically charged at neutral pH and capable of hydrogen bonding in solution, that were able to facilitate silicification under such mild conditions in vitro [20,27–47,50]. In particular, poly(allylamine hydrochloride), PAH and poly-L-lysine, PLL were found to facilitate the formation of silica structures. As the

Table 1
Comparison of some of the properties of silicon (silica) and germanium (germania)

Property	Si (SiO ₂)	Ge (GeO ₂)
Atomic radius (Å)	0.42	0.47
Refractive index [2]	1.45	1.6–1.65
Transmission [1]		0.28–5 μm; near IR
Optical losses (dB/km) [1]	~0.2	10 ⁻¹ –10 ⁻³
Occurrence [6,8,53]		
Ores	Silicates (Si + O = 78% of the earth's crust)	7 ppm as Ge, Zn and Ag salts
Aqueous soluble	1.5–5 mg/ml (total = 9.6 × 10 ¹² tonnes in the earth's oceans)	0.06 μg/L
Organisms	Structural component, micronutrient	Micronutrient
Chemical interactions [9,11–17]	Ge inhibits Si uptake and polymerisation in diatoms and sponges	
Chemistry	Both can (co)biomineralise from their respective monomers in vivo	
Relation with diseases in humans	Fibrosis upon inhalation	Renal failure upon oral ingestion [18]
Associated with DNA and RNA [9b]	24.2–489 ppm dry wt	0.3–5.3 ppm dry wt
Uptake [9b]	20–50 mg/day ^a	0.4–1.5 mg/day ^a

^a Information obtained from: http://www.gettingwell.com/drug_info/nmdrugprofiles/nutsupdrugs/sil_0235.shtml, <http://www.tjclarkinc.com/minerals>.

solution chemistry of Ge resembles the solution chemistry of Si, herein we have investigated the macromolecule mediated synthesis of amorphous GeO₂ particles in order to provide a new synthetic strategy for this important material. It is hoped that this study and others that are in progress may also enable us to understand Ge–(bio)macromolecule interactions [51,52].

2. Experimental

2.1. Chemical reagents

Tetraethoxygermane or germanium (IV) ethoxide (TEOG) and tetra(iso-propoxy)germane or germanium (IV) isopropoxide (T-i-POG), 97%, were used as germania precursors, and were purchased from Sigma-Aldrich (Cat. 339180 and 447641, respectively). The macromolecules used were poly(allylamine hydrochloride), PAH, (Molecular Weight = 15,000 g/mol) and poly-L-lysine hydrochloride (Molecular Weight = 22,100 g/mol) were also purchased from Sigma-Aldrich (Cat. 283223 and P2658, respectively). The buffer used was a potassium phosphate buffer, pH 7.0 (Fisher, Cat. SB 108–500). Deionised ultra filtered (DIUF) water (Fisher, Cat. W2-4) was used for washing the centrifuged samples. All reagents were used as received without any further purification.

2.2. Germania synthesis

A typical reaction mixture contained 80 μ L of the buffer, 20 μ L of the solution of the respective macromolecule of the desired concentration in the buffer and 2–5 μ L of the respective germania precursor. All the reactions were carried out at 20 °C, atmospheric pressure and neutral pH. All the reactants were measured and were shaken well to thoroughly mix in each case. As soon as, the germania precursor was added, a white precipitate was observed. In the case of shear experiments, the reaction mixture was vigorously stirred using a stir bar during the course of the reaction. It should be noted that in the control experiment in the absence of any macromolecule, no well-defined precipitation was observed.

After the desired reaction time, the samples were centrifuged at 13,400 rpm for 3 min. The supernatant was removed and the precipitate was then re-dispersed in the DIUF water. This washing of samples was repeated three times to remove the free polymer and thus ensure that the reaction had been terminated. This solution was diluted further and 2–4 drops of this solution were placed on aluminium sample holder for Scanning Electron Microscopy analysis in each case. The solution was then left to dry on the sample holders under ambient conditions overnight.

2.3. Sample characterisation

2.3.1. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

A palladium–gold alloy was vacuum evaporated onto the dried samples. They were then investigated using a Hitachi S-4000 Field Emission Scanning Electron Microscope at the Advanced Materials Characterization Center, Department of Materials Science and Engineering, University of Cincinnati. EDS analysis was performed using an OXFORD ISIS system attached to the SEM.

2.3.2. X-ray diffraction analysis (XRD)

Germania powder was prepared in a similar way as described in the earlier section. The dried powder was mounted on adhesive tape and was then scanned using a Philips X'pert Diffractometer.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The formation of spherical germania particles was observed by SEM when PAH was used with either of the two precursors (see Fig. 2). In the case of PLL mediated synthesis, small amounts of germania were precipitated and were not studied further at this time. In the absence of any macromolecule no well-defined precipitation was observed. These observations were seen for both the germania precursor systems (TEOG and T-i-POG). The sizes of the spherical particles formed in the case of PAH mediated synthesis were in the range: ca. 400 nm, ca. 1 μ m and ca. 3 μ m. As seen from Fig. 2(d), well dispersed germania particles were observed and very little agglomeration was seen. The role of PAH in the germania formation is proposed to involve the organisation of the macromolecule in solution followed by nucleation, catalysis and/or scaffolding of germania structures leading to phase separation. When the reaction mixture was perturbed by stirring during the reaction, formation of elongated particles was observed (see Fig. 3). These results are comparable to our previous studies on the formation of spheres and elongated silica structures with and without external shear [21,36]. We have reported elsewhere that poly(allylamine hydrochloride), PAH and poly-L-lysine, PLL were each able to facilitate the formation of well defined novel silica structures from various silica precursors at neutral pH and we believe that similar mechanism(s) may also apply in the case of germania synthesis as reported herein [21,36]. Formation of highly anisotropic rod-like morphologies is thought to be due to the perturbation of the orientation or self-assembled structures adopted by the macromolecules in solution, which is then followed by the nucleation and growth of germania.

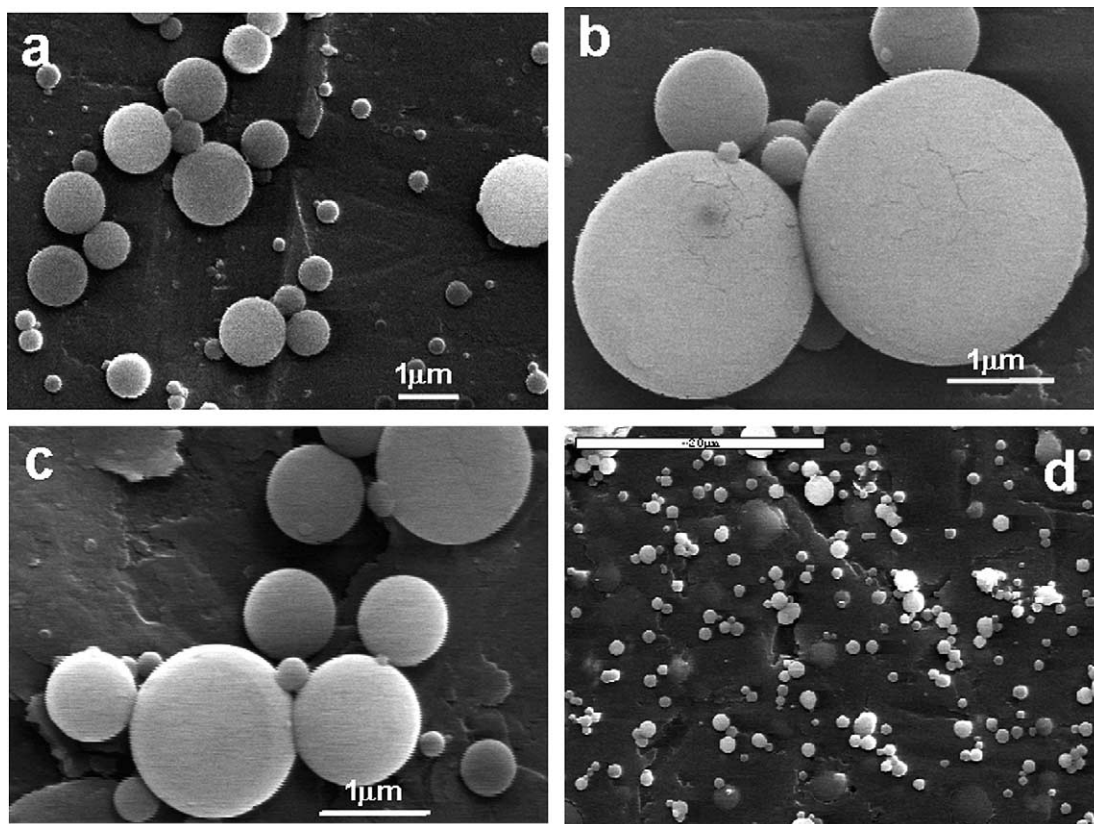


Fig. 2. Representative SEM micrographs of germania particles formed using PAH. (a)–(c) germania formed by mixing 2.85 μL TEOG with 20 μL of 50 mg/ml PAH in 80 μL buffer, (d) adding 4.27 μL T-i-POG with 20 μL of 50 mg/ml PAH in 80 μL buffer. Bar = 1 μm (a)–(c) and 20 μm (d).

3.2. Energy dispersive spectroscopy (EDS)

Fig. 4 shows a representative EDS spectrum for germania synthesised using germanium (IV) isopropoxide and PAH as described above. The sharp peaks at 1.2, 9.8 and 11 keV correspond to germanium as indicated in the figure. In addition, sharp peaks for oxygen may indicate the formation of germania. Peaks for carbon and chlorine may be due to the presence of PAH in the product. The phosphorus peaks appear from the buffer. The sample holders were made of aluminium, hence the aluminium peak. The EDS facility did not have ability to detect the presence of nitrogen at this time. The germania powder was scanned in the Phillips

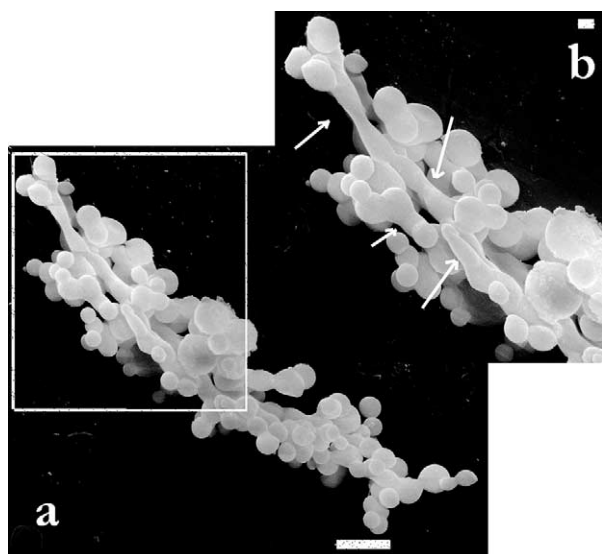


Fig. 3. Representative SEM micrographs of germania formed upon stirring. Germania formed by mixing 2 μL T-i-POG with 20 μL of 50 mg/ml PAH in 80 μL buffer. Highlighted area in (a) is presented at higher magnification in (b). Scale bar (a) 5 μm and (b) 1 μm . Arrowheads indicate the elongated structures.

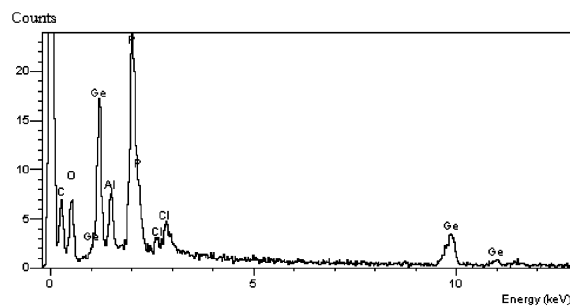


Fig. 4. Representative EDS spectrum of germania particles formed using PAH and T-i-POG.

X'pert Diffractometer. Due to the absence of any peaks in the XRD data (data not shown), it was concluded that the product does not have any crystallinity and thus the germania produced by this novel route was found to be amorphous.

We have described above the outstanding optical properties of the germania and germanate glasses, and we believe that, the results presented herein, which were obtained under mild synthetic conditions, will help in the design of novel materials based on germania and silica–germania hybrids. We have also described the interference of Ge in biosilicification. Moreover, the results presented herein may enable us to design new experiments in order to investigate Ge–(bio)macromolecule interactions. Currently, we are working on germania synthesis facilitated by various polymers, polypeptides and proteins. Furthermore, it is clear from these results that the interactions of charged macromolecules and nanoparticles may not be simply restricted to a particular system but may be rather generic. Further investigations pertaining to this hypothesis on the role(s) of macromolecules in the synthesis of related minerals such as zirconia, alumina and titania are currently also being undertaken in our laboratories.

4. Conclusions

A bioinspired synthetic strategy for preparing well defined amorphous germania micro-particles under ambient conditions and at neutral pH was successfully developed. This synthesis was facilitated by cationically charged synthetic macromolecules. It is proposed that the macromolecules act as a catalyst/scaffold/template for the particulate germania formation in a similar fashion to that described in the literature for silica formation as facilitated by a variety of cationically charged macromolecules [53]. Perturbation of the system gave novel elongated germania structures which could be invaluable in applications where anisotropic materials properties are desired. The materials synthesised by this bioinspired approach may be suitable for potential application in optical fibres and related optoelectronic applications.

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