In-situ nucleation of silicon particles using environmental transmission electron microscopy

Dr Lucian Roiban[1], Dr. Cynthia Cibaka-Ndaya[2], Dr. Kevin O'Connor[3], M. Emmanuel Opeyemi Idowu[2], Professor Jonhatan G.-C. Veinot[3], Dr. Glenna L. Drisko[2]
[1]INSA Lyon, Université Claude Bernard Lyon 1, CNRS, MATEIS, UMR5510, Villeurbanne, France, [2]ICMCB, UMR 5026, CNRS, Univ. Bordeaux, Bordeaux INP, Pessac F-33600, France, [3]Department of Chemistry, The University of Alberta, Edmonton, Canada

Background incl. aims

Silicon (Si) particles are excellent candidates for the development of optical metamaterials with high scattering efficiency for applications in anti-counterfeiting, nonlinear nanophotonics and enhanced Raman scattering. An optimized synthesis method that allows the fabrication of Si nanoparticles with resonant properties that depend on their size, crystallinity and density would open the way to the large-scale production of such so-called metamaterials. Today, one of the most promising synthesis methods is the thermal disproportionation of hydrogen silsesquioxane (HSQ), which produces resonant silicon particles with the desired criteria. However, the disproportionation of HSQ occurs at very high temperatures and the particles produced are polydisperse in size, requiring a separation process to obtain a monodisperse particle.

In this work, the nucleation and growth of Si particles from the thermal disproportionation of HSQ and the formation of silicon nanoparticles with diameters up to 70 nm were investigated. Advanced in situ environmental transmission electron microscopy (ETEM) was used to directly observe the formation of Si particles from HSQ to resonant particles at high temperature under 20 mbar of gas pressure.

Methods

In situ experiments were performed using a FEI ETEM Titan 80-300 environmental microscope operating at 300 kV equipped with a OneView camera from Gatan. HSQ grains were crushed in a mortar and then dispersed in 2-propanol, a drop of the highly dilute dispersion was placed on a Si_3N_4 chip compatible with DENSsolutions Wildfire sample holder then dried. The experiments were performed under a gas pressure of around 20 mbar. The gas employed was argon or a mixture of N_2 - H_2 (95%-5%). The temperature was raised from RT to 800 °C at a rate of 10 °C/sec with about 2 min of plateau every 100 °C. From 850 °C to 1300 °C, the temperature was increased by step of 50 °C, at a rate of 10 °C/sec with plateaus of about 20 min – 1h at 900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C in order to record images and videos of the nucleation and growth processes. Cooling of the sample to RT was carried out by step of 100 °C at a rate of -10 °C/sec.

Results

As expected, the thermal decomposition of HSQ was found to begin at temperatures above 1000°C. Once the Si crystalline nuclei are formed, two main growth processes are observed, including particle-particle coalescence and, more surprisingly, particle displacement through the matrix, leaving traces through the HSQ matrix due to interfacial chemical reactions. At 1000°C, small particle nuclei of about 1 nm are visible, then with increasing temperature to 1200°C, particles of 7-11 nm are observed. Then these particles begin to coalesce, indicating high mobility within the system, and the particles formed have a larger projected diameter (Figure 1a).

The second growth mechanism observed shows that the particles move through the sample by changing shape and growing up to 70-80 nm (Figure 1b). They show a liquid-like behavior, are very mobile and change shape rapidly. This liquid-like behavior below the typical melting point of silicon is attributed to a beam effect lowering the melting point during in-situ observation.

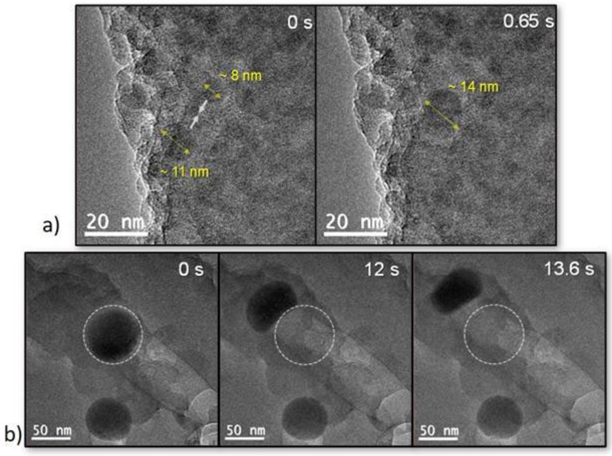
The in-situ experiments were complemented by in-situ XRD measurements up to 1200 °C, demonstrating a solid-state growth mode below the melting point of Si. [1,2]

Conclusion

This study was conducted under extreme conditions using an ETEM under 20 mbars of gas and at 1300°C and helped to illuminate the growth mechanism of Si nanoparticles from a silicon rich oxide precursor. It was found that crystalline Si domains grow easily in the solid state starting from 1000°C. For the first time, a highly malleable and mobile phase was observed in real time, suggesting an intermediate liquid-like behavior that facilitates particle growth. Growth processes by coalescing and moving within the matrix after the crystallization were identified. This study was complemented by an ex-situ investigation of the role of the reducing atmosphere in the disproportionation reaction.

Figure 1: Si particles formed after thermal decomposition of HSQ grew by two different mechanisms: a) Particles coalescence, the Si particles have high mobility at 1200°C and during the encounter they form larger nanoparticles. b) At 1300°C the particles have liquid like behavior with high mobility moving through the matrix while growing.

Graphic:



Keywords:

In-situ, HSQ hdisproportionation, Si synthesis

Reference:

[1] Cibaka et al. Chem. Mater. 2023, 35, 20, 8551–8560
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