

Stability of Silicon Dioxide in Liquid Phase TEM

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Recently developed liquid phase transmission electron microscopy (LP-TEM) holds great potential for the study of many important nanoscale processes, in particular the synthesis of nanostructures, such as heterogeneous catalysts. Their synthesis usually involves the formation of metal (oxide) nanoparticles on a high-surface area oxide support. However, one of the main experimental challenges for in situ observation of this process is the interaction of the electron beam with the liquid, in particular water, forming many highly reactive chemical species and radicals [1] and locally changing the liquid chemistry. Recently, it was found that this change in chemistry in water severely reduces the stability of amorphous silica [2], an important material for biomedical and catalytic applications. To date however, most studies in LP-TEM focus on metal nanoparticles, resulting in a limited understanding of oxide behavior under these conditions.

In this study, our goal was to improve the understanding of the degradation mechanisms of amorphous silica in LP-TEM and to develop a method that would prevent or at least mitigate degradation. To this end, we investigated under STEM conditions the influence of the solid silica structure and the influence of the liquid composition. The stability of the solid towards excitation and destabilization in LP-TEM is expected to depend on silica porosity and degree of hydroxylation, which can be altered easily by calcination at different temperatures [3]. The influence of the liquid is thought to primarily depend on the formation of reactive chemical species and radicals due to the electron beam, which can be altered by addition of solutes.

Stöber silica samples calcined at 400 °C, 600 °C, 800 °C or 1000 °C were fixed on the Si_xN_y window of an Si chip (Protochips Inc., NC, USA) by adding a 0.5 μL droplet of the sonicated dispersion of the respective oxide in isopropanol and allowing the liquid to evaporate. After assembly, the cell was operated in flow mode with a flow of 2 μL/min of either pure H₂O, H₂O with 1.7M acetone or 0.1M acetic acid. Experiments with silica at different calcination temperatures were performed on a Tecnai 20F (FEI, Netherlands), while experiments with altered liquid composition were performed on a Talos F200X (FEI, Netherlands). All experiments were performed in STEM mode with a screen current of 0.2 nA, a 9.5 μs/pixel dwell time and operated at 200 kV acceleration voltage.

Figure 1a shows the decrease in measured surface area before and after 20 minutes of continuous STEM irradiation in pure H₂O for the sample calcined at 800 °C. A significant deformation and shrinkage is observed, while this effect does not occur in either the absence of water or the absence of the electron beam. No statistically significant difference between the samples calcined at the four different temperatures could be found (Figure 1b), even though nitrogen physisorption shows a clear difference in pore volume and BET surface area.

It is also known from literature that the degree of both surface and internal hydroxylation differs greatly [3].

Representative TEM images from the experiments with the solutions containing acetone or acetic acid are shown in Figure 1c-d. Acetone was added because of its influence on the radical chemistry in water [4] and acetic acid for its buffering effect. Acetone showed a surprising and severely destabilizing effect on the silica particles (Figure 1c), while acetic acid seemed to significantly stabilize the particles (Figure 1d).

In conclusion, these results show that the stability of amorphous silica in liquid phase TEM is mainly influenced by liquid chemistry induced by the electron beam. Preliminary experiments also indicate that this stability can be altered by changing the liquid chemistry, although the mechanism of stabilization is not yet understood completely and additional experiments are required. However, this shows that by carefully considering radiation chemistry of liquids and its influence on solids, silica can be significantly stabilized, which would ultimately allow it to be studied in LP-TEM successfully without dominating influence of e-beam induced liquid chemistry.

References:

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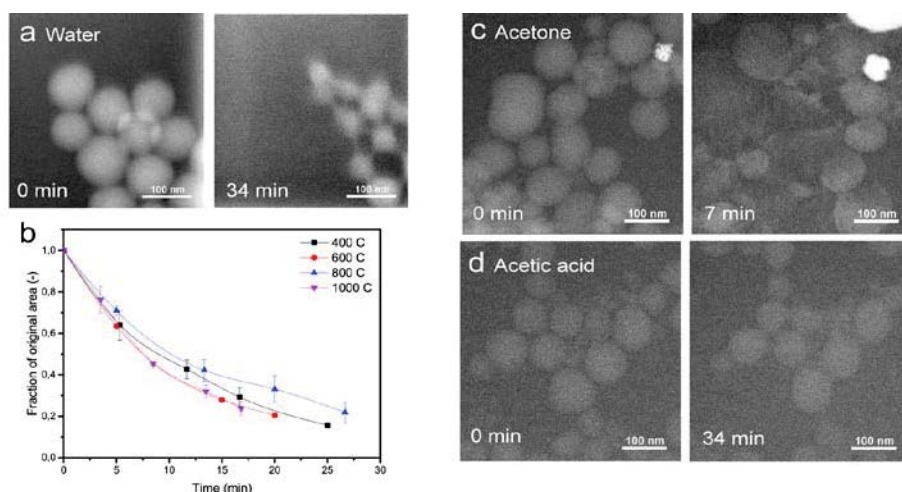


Figure 1. (a) Images of SiO₂ calcined at 800 °C before and after 34 min exposure to the scanning electron beam and water environment in LP-TEM. (b) Quantitative analysis of the decrease of surface area in LP-TEM for particles calcined at different temperatures. Images of SiO₂ particles before and after 7 min (c) and 34 min (d) exposure to the scanning electron beam, in a 1.7M acetone solution (c) and a 0.2M acetic acid solution (d) environment of LP-TEM.