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# Ceria-Water-Reactions Studied by Liquid Cell TEM

**Muhammad Sajid Ali Asghar, Beverley Inkson, Günter Möbus**

Dept of Materials Science and Engineering, University of Sheffield, Sheffield, UK

[m.sajid@sheffield.ac.uk](mailto:m.sajid@sheffield.ac.uk), [g.moebus@sheffield.ac.uk](mailto:g.moebus@sheffield.ac.uk)

**Abstract.** Liquid cell TEM is demonstrated to be a highly suitable new technology to study chemical reactions of cerium oxide nanostructures in aqueous environment. Ceria nanoparticles are found to show a diversity of behaviour. At low beam intensity, particle hopping movements and particle attachment, including chain formation is observable. At high intensity, when the water is turned ultra-enriched in ions by radiolysis, we find (in order of observation) particle rounding and shrinkage, followed by complete dissolution, along with formation of new reaction phases, and finally gas bubble formation.

## 1. Introduction

The unique advantage of in-situ TEM with a liquid-cell specimen holder is the capability of observing nanostructured materials in the original wet state, as they would mostly be employed in service. In fact, the wet-chemical aqueous synthesis is the most wide-spread and most high-throughput technique of all nanoparticle synthesis approaches. Furthermore, a majority of the most successful applications of oxide nanoparticles in consumer or industrial applications is in aqueous phase, including as examples, nanoceria polishing slurries, sunscreen lotions, combustion additives in transport fuels, wet-phase catalysis agents, environmental pollution cracking, and for chromium-replacement coatings on aluminium.

Standard dry TEM would have the disadvantage of missing intermediate phases in reaction studies (such as hydroxides unstable in air), but also cannot reveal the true aggregation behavior. Only liquid cell TEM of nanoparticle suspensions allows the observation of developments by continuous video recording. Often the radiolysis of water by intense electron beams is quoted as a limitation [1], as some reactions do not proceed as they would in neutral water. This work is however entirely based on using deliberate liquid cell irradiation of ceria suspensions as a study subject, and aims at emulating highly ion-enriched solutions and visualizing reactions under these extreme conditions.

## 2. Materials and Methods

Ceria nanoparticles are suspended in water and loaded into a liquid cell holder sandwiched between two Si-nitride membranes as described in [2] (model Protochips Poseidon P500 flow system used in static mode). TEMs chosen include JEM3010 LaB6 at 300kV and JEM2010F FEG with GIF at 200kV. Irradiation is then applied at variable levels with intensities adjusted to trigger the desirable reactions, see 3.1. Large changes to local water thickness means no universal dose rate threshold exists. Digital video recording allows for capture of sub-s frame rate, depending on binning, with mostly 6 frames/ s achieved in this work.

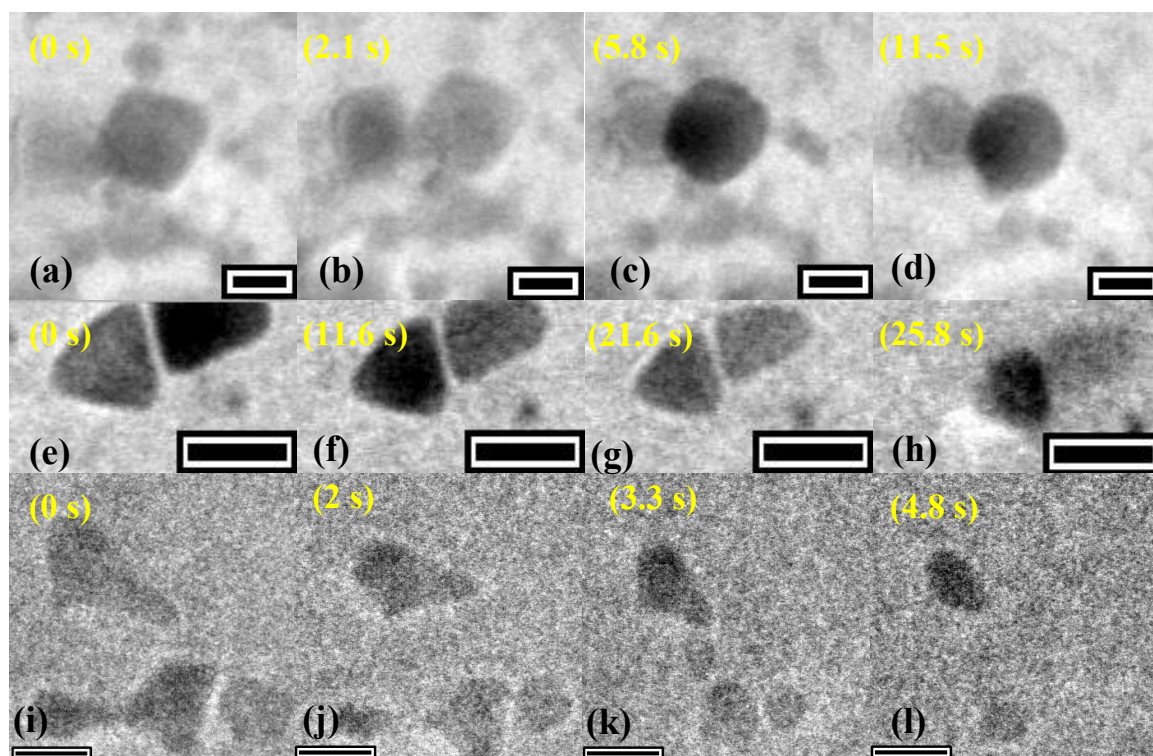


### 3. Results and discussion

Here we observe the behavior of ceria nano particles in water as a function of electron beam irradiation, which causes radiolysis and dissociation of molecule. For more details see [2, 3].

#### 3.1. Corrosion/dissolution

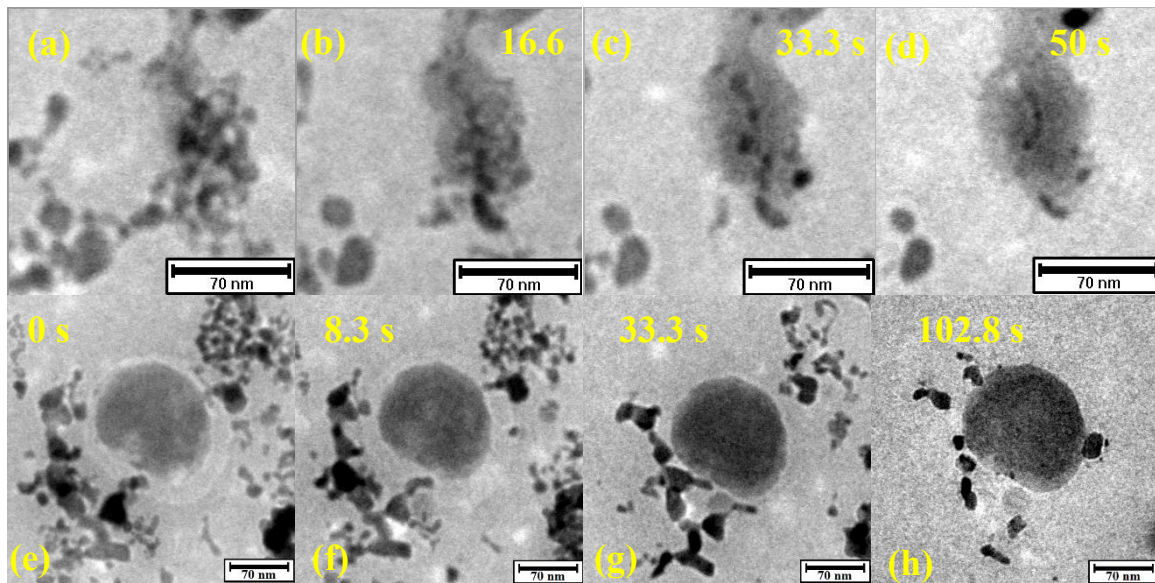
Figure 1, row 1, illustrates the onset of dissolution of ceria nanoparticles, which can be tracked and quantified to reveal a monotonous volume loss. However, the dissolution rate (volume loss normalized to momentary surface area) is not constant and appears to accelerate [2]. Figure 1, rows 1 and 2, emphasizes the shape transformation from octahedral to spherical preceding the dissolution in many cases, confirming that corner atoms suffer faster dissolution rates than flat-faced atoms.



**Figure 1.** Octahedral ceria particles undergoing corner-ablation and rounding before dissolution (a-d and e-h); scale bar at 25nm. Final stages of dissolution of flat particles (i-l); scale bar at 10nm.

#### 3.2. Chemical Reaction Phases

Figure 2 illustrates some of the new phases observed to appear after prolonged irradiation of the nanoceria-water suspension. The new phases are clearly secondary reaction products forming as a result of the water becoming saturated in dissolved ions from either surface hydrolysis reactions (cerium ions, OH<sup>-</sup> ions) or also from ions formed directly from irradiation induced water splitting without involvement of cerium oxide. In many cases, the order of formation is complex, and new phases grow while initial dissolution or shrinkage of ceria is still in progress or even in early stages. A common phase observed (Figure 2) appears to be rather flat, roundish and of low mass-thickness contrast / low average atomic number. Its structure never shows any Bragg-scattering features and is certainly amorphous. In analogy to ex-situ literature [4] we identify these particles as amorphous Ce-hydroxide. Figure 2, top row, shows a case in which the amorphous phase grows, while the last of the crystalline raw particles are still dissolving. Another interesting special case, Figure 2, bottom row, is the formation of bright bands around new particles (Figure 2e), possibly a Ce-ion depletion zone. Otherwise the new phase is rather stable against radiative dissolution.

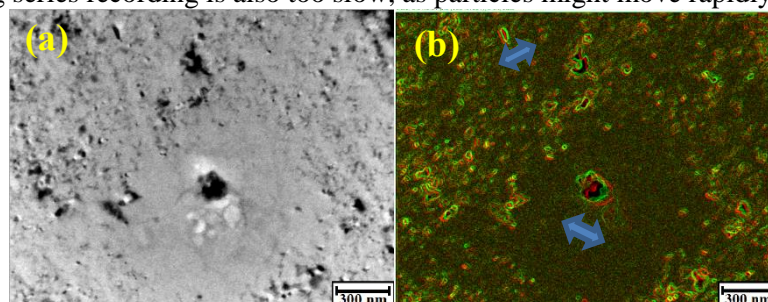


**Figure 2.** (a-d) New amorphous phase growing around ceria particles during later phases of dissolution. (e-h) amorphous phase initially surrounded by bright zone separating it from CNPs.

Further new phases observed [5] include the growth of crystalline high-aspect ratio needles during and alongside ceria dissolution, while another new phase after prolonged irradiation and dissolution appears roundish and of atomic number density similar to ceria. The final step in the sequence of experiments under deliberate high-intensity irradiation is the formation of a large number of nanosize bubbles. These gas bubbles of presumably [1] molecular hydrogen are of interest as in a ceria-water-suspension, two competing path-ways exist for  $H_2$ -production, (i) catalytic water splitting on ceria-surface active sites, and (ii) radiolytic direct water splitting anywhere in the liquid [6]. Our sequence of observations point to effect (ii) being dominant, while both might co-exist.

### 3.3. Exploring the 3D volume of liquid cell samples

More than any other kind of TEM specimens, liquid cell sandwich samples are intrinsically 3D, and a 3D reconstruction technique would be highly desirable. Standard tomography is not applicable, as tilt limits of the bulky holder, and more even self-shadowing of the deep Si-trough prevents high angular range series. Long series recording is also too slow, as particles might move rapidly.



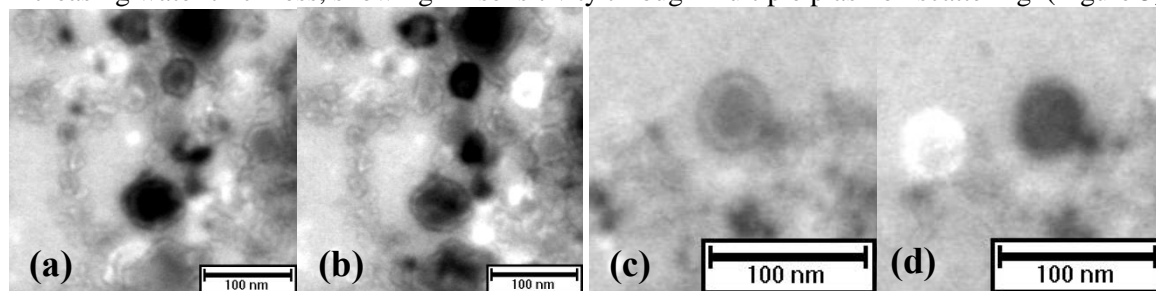
**Figure 3.** Raw image and superposition image from tilt-wobbler video recording showing two differing particle displacement directions (see arrows) and amplitudes.

(i) We propose in Figure 3 the acquisition of a video-sequence of nanoparticles suspended in water with the beam-tilt wobbler running at maximum speed. Particles attached to the top and bottom membrane clearly separate by their oscillation width and direction. Any  $\Delta z$ -height of floating particles can be extrapolated from their  $\Delta xy$  separation. An undisturbed video can still be recovered by selecting frames at one beam tilt only.

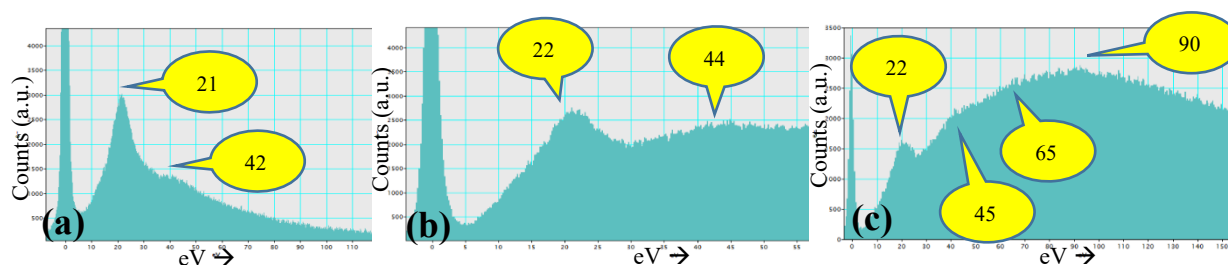


(ii) Another option is to evaluate Fresnel-fringe appearance around particles in vertical motion and calibrate the changes via a z-series of images manually lifted out of focus. (Figure 4)

(iii) While above methods (i,ii) result in the combined separation of the two membranes by water and gas bubbles, recording the EELS plasmon range signal from water [7] would give exclusive access to the water thickness only, as illustrated by a recording of spectra in different sample areas of increasing water thickness, showing  $\Delta z$  sensitivity through multiple plasmon scattering (Figure 5).



**Figure 4.** Pairs of particles showing jumping/tilting behaviour via Fresnel fringe changes.



**Figure 5.** Low loss EELS of water at 3 thicknesses. Labels: single to 4-fold plasmon peaks (in eV).

#### 4. Conclusions

The details of multiple reaction pathways, including dissolution of raw ceria nanoparticles and growth of secondary phases, with life video-recording of the nanoscale morphology development, are presented. The diversity of observations confirms that liquid-cell TEM in deliberately highly irradiated water should not be discarded as artificial, but be considered a highly useful testing methodology. Radiolysed water can be seen as an accelerated testing tool, allowing to research reactions which would run orders of magnitude slower (and being unobservable on the nanoscale) in laboratory wet-chemical setup. We also suggest that the quantification via time-resolved measurements of particle geometry data adds new precision to corrosion/reaction studies, which at the macroscale often suffer from invisible nanoscale surface roughness. Testing of multiple materials should also lead to faster classification of durability relative to one-another, as the rank-order would not shuffle, even if the radiolytic corrosion process is more complex than standard acid-leaching experiments.

The irradiation chemistry of aqueous ceria in particular gains importance due to the material being used or proposed as cell-protection agent during radiotherapy, irradiation-enhanced photochemical pollutant cracking in environmental waste-waters, and finally for  $\text{CeO}_2$  as  $\text{UO}_2$ -simulant in nuclear materials testing, whether for nuclear fuels in service, or for long term immobilisation.

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