In-situ irradiation of cerium precursors in TEM to study nanocrystal formation

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Abstract
Three of the most commonly used precursor chemicals for wet-chemical nano-ceria synthesis are examined by means of direct dry electron irradiation in TEM. Transformation reactions of micron-size carbonate, chloride, and nitrate grains into nanocrystallites (internal or external) are recorded in situ. Progress of possible redox-changes of cerium is tracked by EELS. We find a straight local oxidation reaction for carbonates, but external nanorod formation by condensation in the case of chlorides, while nitrates show a multi-stage complex redox behaviour.

1. Introduction
Cerium-oxide, i.e. ceria, is one of the most important rare earth metal oxides, due to its chemical properties, e.g. absorption and release of oxygen and change in oxidation state (Ce³⁺ / Ce⁴⁺). Ceria nanoparticle (CNP) synthesis has been extensively studied via ex-situ chemical methods like low temperature (e.g. sol-gel) chemical precipitation, or hydrothermal/ high temperature chemical reaction, etc. Furthermore, ceria NPs have various applications in the fields of energy, catalysis, biomedical science, automotive, and environmental science. The most common laboratory process for ceria NP fabrication includes wet-chemical precipitation synthesis from dissolved precursors, such as cerium nitrate, cerium chloride or cerium carbonate. This process, triggered e.g. by NaOH, is flexible and can be tuned towards nanorod or cube formation and often includes metastable intermediate morphologies or phases. It is therefore interesting to examine dry transformations of the same precursor chemicals triggered by electron irradiation instead of forced hydrolysis, as this allows live in-situ observation. This latter technique continues on earlier studies of metal nanoparticle fabrication by irradiating Metalhalides [1-3], or on the Ca-carbonate to lime transformation in TEM [4].

2. Materials and Methods
We have used three hydrated precursors of cerium, including cerium carbonate hydrate (CCH), cerium chloride heptahydrate (CCl), and cerium nitrate hexahydrate (CNH); all from Sigma Aldrich, UK. For in-situ electron irradiation we have used TEMs JEM 3010 with a thermionic LaB6 electron gun and JEM 2010-F with field emission gun respectively. The JEM 3010 microscope allows the irradiation of materials with higher total current and higher accelerating voltage at 300 keV. The JEM2010-F, allows for finely focused electron irradiation as well as chemical analysis via energy dispersive x-ray spectroscopy (Oxford Instruments EDXS), and electron energy loss spectroscopy (EELS, Gatan GIF). We have used manual mortar and pestle to grind the raw powders. All micron-sized fragments...
are initially TEM-homogeneous, all appear amorphous and all three materials should initially share a Ce$^{\text{III}}$ oxidation state. Support films of holy carbon are used except for carbonates where silicon nitride thin films are preferred.

3. Results and Discussion

The results of dry irradiation of the three examined raw precursor powders of cerium chloride / cerium carbonate / cerium nitrate show different behaviour. For instance the electron irradiation of Ce carbonate hydrate is most predictable and reproducible at both voltages: The original phase develops internal sub-5nm nano-crystals by nucleation and growth (Figure 1). The entire impact region (beam imprint) shows clearly as a speckled and darker (higher average Z) zone. EELS tracking confirms that Ce$^{\text{III}}$ converts to Ce$^{\text{IV}}$ and the HRTEM of the nucleated nanocrystals is compatible with crystalline fluorite CeO$_2$, while the carbon peak rapidly shrinks (suspended on Si-nitride thin film).

![Figure 1](image1.png)

Figure 1: Electron irradiation of cerium carbonate: (a) before irradiation; (b) after 2min irradiation; (c) after 25min irradiation with crystallites encircled (JEM 2010F at 200kV).

The electron irradiation of cerium carbonate at 300 keV for two minutes shows a distinct impact region with formation of pores next to Bragg scattering new crystallites (Figure 2).

![Figure 2](image2.png)

Figure 2: CeCO$_3$ particle (a) before and (b) after ~ 2 min of electron beam irradiation and (c) higher magnification image of the irradiated region from (b). JEM TEM 3010 at 300 keV.

Contrary, the cerium chloride hepta hydrate is found to respond much faster to irradiation but also more delocalised. Rather than internally precipitating, a vast number of fresh free-standing nanostructures are immediately formed on the adjacent carbon-support film or nanorods are growing out of the precursor grain as show in Figure 3. This is equivalent to an evaporation-condensation mechanism reported for Ag and metal-halides earlier [2, 3]. However, EELS confirms that Cl still persists in the new particles, which can be round or rod shaped, see Figure 3. Lattice fringe
measurements on different particles match either CeCl₃ or CeO₂, however, EELS analysis is predominantly Ce³⁺.

**Figure 3:** Two examples of irradiation of cerium chloride precursor: Nano-rods and some nanoparticles freshly formed on carbon film outside the precursor material (200kV)

Finally, the results of electron irradiation of cerium chloride at 300keV show the beam intensity to influence the shape of new condensation particles: moderate intensity leads to irregular shaped nanoparticles (Figure 4a-b) while high intensity leads to spherical nanoparticles (Figure 4d-e), possibly rounded through ripening by secondary irradiation and quasi-melting.

**Figure 4:** Irradiation of cerium chloride precursor: a) freshly formed irregular shape nanoparticles, c) roundish nanoparticles near a precursor fragment (higher intensity than (a)); (b, d) are magnified views of (a,c). All at 300kV.

Results of Cerium nitrate hexa hydrate superficially resemble the case of carbonate with similar appearance of beam impact zone and de-homogenisation. Figure 5 shows progress of transformation from amorphous state to nanocrystalline state, starting with a small presence of crystals, probably from imaging irradiation. However, EELS analysis failed to confirm simple nitrite to oxide conversion, as we find mainly Ce⁴⁺ converting to Ce³⁺, opposite to expectation.

We point to the great variety of redox behaviour found. Simple reductions of dry compound powders by electron beams are well established, such as for halide salts (e.g. AgCl to Ag [3]). Also constancy of valence has been found for the case of Ca-carbonate to lime [4]. Here we find a rare case of oxidation of cerium ions (unusual for TEM irradiation which normally involves reduction) for our selection of Ce-carbonate. In this case EELS results and HRTEM-spacings both match formation of fluorite CeO₂ phase as final stage.
Figure 5: Irradiation of Ce-nitrate precursor after deliberate focused irradiation with nano-crystallites forming (a) with FFT-pattern (b) matching CeO$_2$ phase.

For the Ce-chloride case, no redox reaction is confirmed, as the final crystalline particles and rods have all Ce, O, and Cl as elements, as evidenced by EELS, and Ce is in Ce$^{III}$ state. This indicates that chloride rods and ceria particles might both form in parallel. Unlike any other precursor, the reaction progresses outside the original fragment, alike to the known delocal “evaporation/condensation” mechanism, known for other halides. However, no Ce-metal is found here. The unusual nitrate case with its redox-process appearing “inverted” from the carbonate case, might involve fast initial oxidation (before start of EELS monitoring) to CeO$_2$ followed by secondary beam-induced reduction to CeO$_{2-x}$, known to exist for this material, and for many other oxides [5].

4. Conclusion
Direct electron irradiation of dry precursor compound chemicals has a great potential to reveal insight into redox reactions, and is far too valuable to be labelled as unwanted “irradiation damage”. Results are relevant for comparison with either laboratory-based wet-chemical redox change methods, but also with novel liquid-cell TEM based in situ methods (M S A Asghar et al., see elsewhere these proceedings).

References
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