doi:10.1017/S1431927621013532
Microsc. Microanal. 27 (Suppl 2), 2021

Ionizing Radiation Induced Formation of CeO_2 Mesocrystals: γ-Irradiation versus High-Energy Electron Irradiation

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Ceria-related materials have been widely investigated due to their high importance on an extensive range of applications, such as catalysts [1], radiation protection [2] or medicine [3]. There are numerous methods to synthesize CeO_2 nanoparticles and guide assembly processes [4]. Different synthesis methods can cause significant modifications in the resulting structure and morphology of the formed nanoparticles. Therefore, studying mechanisms of the nanoparticles' formation at the atomic scale is crucial in order to control their properties.

A standard approach would be to perform *ex-situ* transmission electron microscopy (TEM) investigations at specific reaction steps to study structural and morphological details and to reconstruct the mechanism of nanoparticles formation. Recently, liquid-phase transmission electron microscopy (LP-TEM) emerged as one of the most exciting methods to study particles formation in solution. It enables *in-situ* observation of particles' nucleation and growth triggered by electron beam. γ- and high-energy electron irradiation of Ce^{3+} water solutions is expected to cause the same CeO_2 nanoparticle formation process. However, significant differences in the experimental setups (the absorbed irradiation dose rates, irradiated volumes, presence of surfaces, etc.) require better understanding and, thus, a comparative study of both processes.

We performed a study of CeO_2 nanoparticle formation from $CeCl_3{\times}7H_2O$ solutions using both γ- and high-energy electron radiation-induced synthesis. The solutions were exposed to different total irradiation doses in a Cs-137 GammaCell. *Ex-situ* transmission electron microscopy combined with electron pair distribution function analysis on the γ-irradiated samples allowed determining several stages of the process. We believe that at first the oxidation of Ce^{3+} ions and formation of condensed amorphous droplets occurs, followed by nucleation of CeO_2 primary particles and further growth of mesocrystals (compare figure 1). *In-situ* liquid-phase investigation of the initial solutions was carried out in both transmission and scanning modes, that enables to vary not only the dose rates but also local electron current densities. The observed processes can be directly correlated to the stages of the nanoparticles formation found through *ex-situ* TEM [5].

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[5] The authors are grateful for the financial support from Max Planck Society.

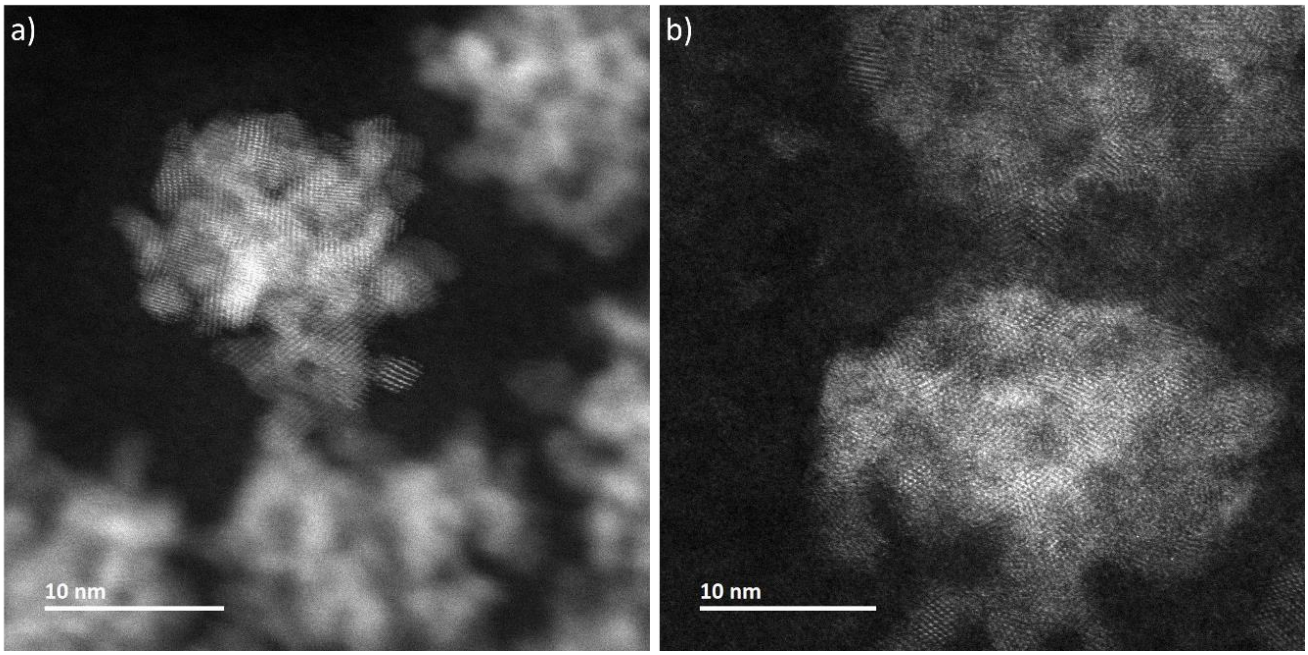

Figure 1. Ceria nanoparticles grown by ionizing radiation. a) Gamma irradiation in a GammaCell. b) High energy electron irradiation in a transmission electron microscope. The morphology is similar with slight variations occurring potentially because of different applied dose rate and accumulated dose. The presented ex-situ high-angle annular dark-field scanning transmission electron microscopy investigation was performed after drying the samples.

https://doi.org/10.1017/S1431927621013532 Published online by Cambridge University Press