

Characterization of 0-3 nanocomposites by means of HRTEM

L. Kienle¹, A. Lotnyk¹, V. Duppel², F. Beiroth³, B. Hesseler³, K. Gerwien³ and W. Bensch³

1. Faculty of Engineering, Institute for Material Science, Synthesis and Real Structure, Christian Albrechts University of Kiel, Kaiserstr. 2, D-24143 Kiel, Germany

2. Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany

3. Faculty of Mathematics and Natural Sciences, Institute for Inorganic Chemistry, Christian Albrechts University of Kiel, Olshausenst. 40-60, D-24098 Kiel, Germany

lk@tf.uni-kiel.de

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The synthesis of multinary nanomaterials is generally complicated by separation phenomena, e. g. by the formation of mixtures containing binary compounds instead of ternary nanoparticles. Such limitation particularly applies when using soft chemical approaches for the syntheses, since the low diffusion coefficients at low temperatures favor metastable and inhomogeneous products. In this contribution, we report about a well-defined phase separation occurring during attempts to prepare ternary nanoparticles with a composition of CdCr_2Se_4 . Our examinations demonstrate the use of soft chemistry for gaining access to homogeneous 0-3 nanocomposites, e. g. CdSe nanoparticles homogeneously dispersed within a matrix of an amorphous chromium selenide.

The material was prepared as follows: 7.2 mmol Se powder was dissolved in 24 mL of oleylamine (OLA) at 330 °C (N_2 atmosphere). 0.9 mmol of Cd(II)acetylacetonate and 1.8 mmol Cr(III)acetylacetonate were dissolved in 6 mL of OLA at 175 °C under vacuum. This mixture was added to the Se solution and heated to 370 °C under stirring and maintained for 1 h. After cooling a mixture of hexane and ethanol (1:3) was added to the solution, and a black product was isolated.

The bulk analysis by powder X-ray diffraction shows the presence of CdSe nanoparticles with the wurzite type structure, however, no information about the chromium containing constituent could be derived. Via HRTEM, the nanodispersive nature of the samples becomes evident, cf. the bright field image in Fig. 1a, top. The presence of the CdSe nanoparticles with average dimensions below 10 nm was verified by selected area electron diffraction (SAED, [1]) and HRTEM. Anyhow, EDX analyses performed in scanning and nanoprobe mode (spectral imaging) show an average composition close to the intended one of CdCr_2Se_4 and a low variance for distinct point measurements. Even the SAED patterns give no clear information about the chromium containing constituent. Such finding could be rationalized by assuming a composite of CdSe nanoparticles homogeneously distributed inside a matrix of amorphous Cr_2Se_3 with a ratio of $\text{CdSe} : \text{Cr}_2\text{Se}_3 = 1$.

Consequently, after long-term exposure very faint and diffuse intensity on concentric rings with the characteristic d-values calculated for Cr_2Se_3 were observed in SAED patterns. Moreover a third component (Fig. 1b, top) was identified which forms short nanoslabs built from adjacent layered structural motifs. Taking into account EDX analyses and the distance of adjacent layers of ca. 0.58 nm, this component can be assigned to partially crystalline Cr_2Se_3 [2]. The composite character of the material could further be evidenced via the well reproduced elimination of CdSe nanoparticles under the influence of massive electron beam impact. Note that no chemical and structural change occurs in the average setup for HRTEM, but a higher dose of radiation must be selected by adjusting the emission parameters and removing the condenser aperture. The increase of the current density of such transformation

mode vs. the average setting is estimated to be 40-fold. During the transformation, the composite particles do not change their shape; cf. Fig. 1a, despite the complete removal of the CdSe nanoparticles as demonstrated by quantitative EDX. After the transformation, the SAED patterns only display the diffuse intensity assigned to amorphous Cr_2Se_3 . Comparisons of HRTEM micrographs recorded before and after the transformation evidence the removal of CdSe nanoparticles, cf. Fig. 1b, while both Cr_2Se_3 species remain unaffected by the electron irradiation. Thus, the elimination of the CdSe nanoparticles frequently produces holes inside the amorphous matrix material.

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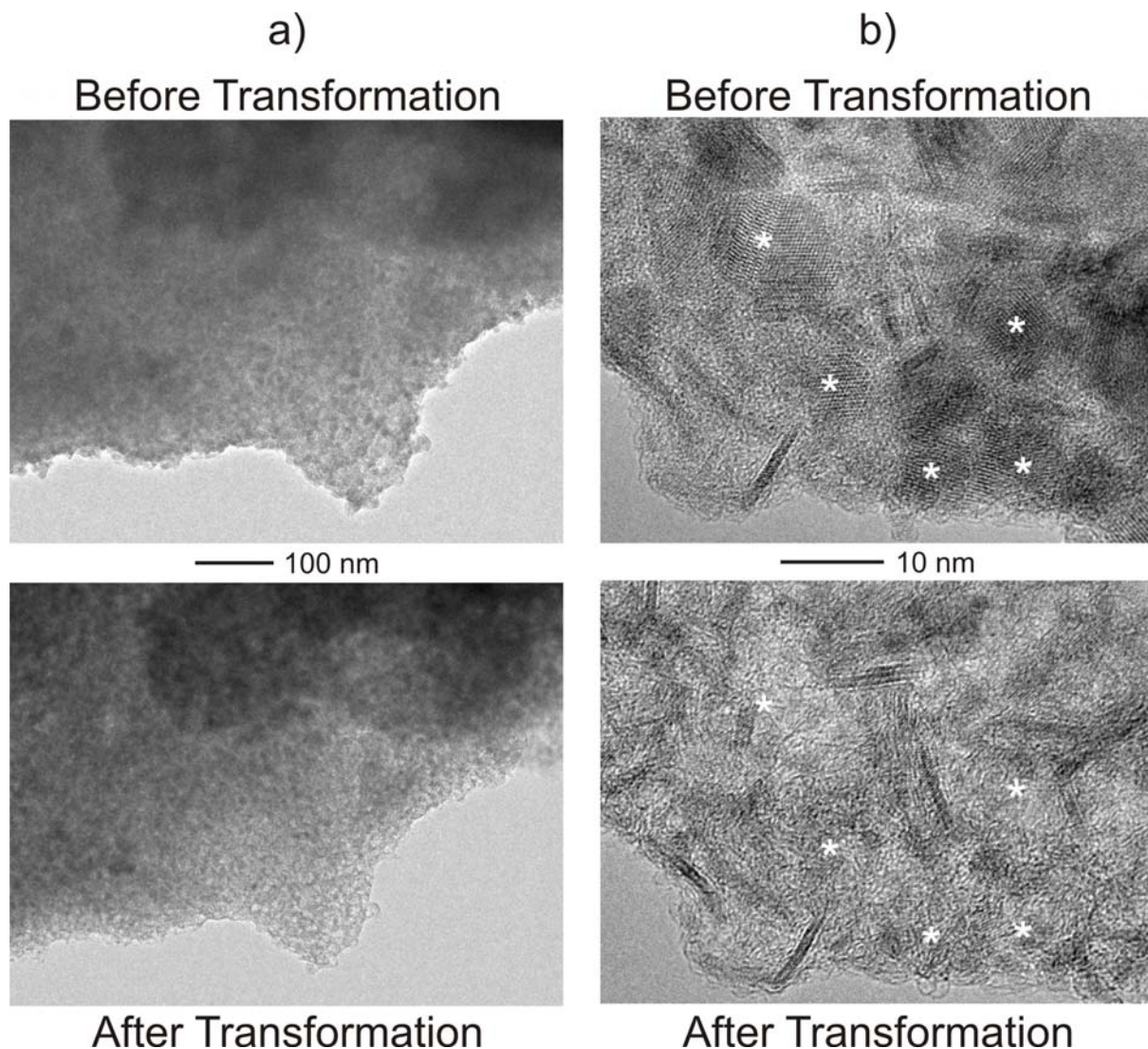


Figure 1. a) Bright-field images recorded on a compact particle of the 0-3 nanocomposite, before (top) and after in-situ transformation (bottom). b) HRTEM micrographs recorded before (top) and after in-situ transformation (bottom), the asterisks mark the positions of the CdSe nanoparticles present before the in-situ transformation.