Nanosized Gadolinium and Uranium – Two Representatives of High-Reactivity Lanthanide and Actinide Metal Nanoparticles

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SUPPLEMENTARY INFORMATION (SI)

Contents

1. Analytical Techniques

General: All analytical data and sample handling was performed under inert conditions (argon or vacuum) in order to avoid contact to oxygen and moisture.

Transmission electron microscopy (TEM): Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted with an aberration-corrected FEI Titan^3 80-300 microscope operated at 300 kV and a FEI Osiris microscope at 200 kV. TEM samples were prepared by evaporating suspensions in toluene on amorphous carbon (Lacey-)film suspended on copper grids. The deposition of the samples on the carbon (Lacey-)film copper grids was performed under Argon atmosphere. The grids were thereafter transferred with a suitable vacuum/inert gas transfer module from a glove-box into the transmission electron microscope without any contact to air. Average particle diameters were calculated by statistical evaluation of at least 100 particles (ImageJ 1.47v software).

Selective area electron diffraction (SAED) patterns of nanoparticles may show only few and rather diffuse reflections on Debye-Scherrer rings at large reciprocal lattice distances. A way to prevent the loss of this valuable diffraction information is the calculation of radially averaged SAED intensities (for short radial scan) which is obtained by a 2π integration of each spatial frequency in the initial SAED pattern. Radial scans can be used to investigate the structure on nanoparticles similar to XRD patterns. Lattice parameters and crystal structure of nanoparticle material were determined from radial scans by using the peak positions obtained by fitting a Voigt function to each individual peak profile after subtraction a linearly interpolated background.

Alternatively, HRTEM images were evaluated by calculating the two-dimensional Fourier transform, denoted as diffractogram, which yields information on the crystal structure (lattice parameters and crystal symmetry) of single nanoparticles. The analysis was performed by comparing the experimental diffractograms and calculated diffraction patterns with Miller indices, where the latter were obtained by using the Jems (Java version of the electron microscopy simulation) software. The zero-order beam (ZB) is indicated by using a white circle.

X-ray powder diffraction (XRD): X-ray powder diffraction (XRD) was performed with a Stoe STADI-P diffractometer operating with Ge-monochromatized Cu-Kα-radiation (λ = 1.54178 Å) and Debye-Scherrer geometry.

2. Practical Handling of Highly Reactive Base Metal Nanoparticles

Due to the high reactivity of the Gd^0 and U^0 nanoparticles strict handling under inert conditions and exclusion of all traces of oxygen and moisture throughout for all sample handling including the purification procedure (e.g. centrifugation) as well as the analytical characterization (e.g. transfer to and in the electron microscope) are required. The transfer of samples to the electron microscope needs to be performed via suitable vacuum and inert gas transfer modules. Most importantly, it turned out as essential that the resting time of the sample grid with the deposited Gd^0 and U^0 nanoparticles in the transfer module is as short as possible (<30 min) in order to avoid oxygen contamination (Figure S1).

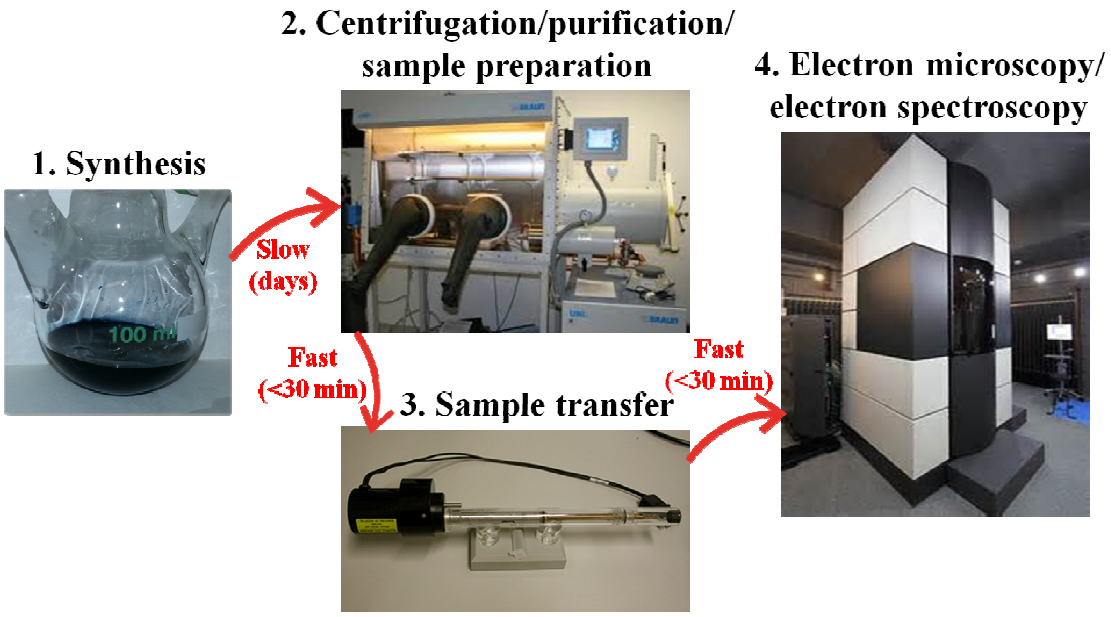

Figure S1. Transfer of reactive Gd^0 or U^0 nanoparticles from Schlenk vessels (subsequent to the synthesis) into the electron microscope (to perform the analytical characterization) under inert conditions.

3. Thermal Behavior

In order to verify the chemical composition and purity, the as-prepared Gd^0 and U^0 nanoparticles were crystallized by sintering at elevated temperature (vacuum, 900 °C). Subsequent to this treatment, more or less bulk-like metals were naturally obtained.

X-ray powder diffraction (XRD) of octylamine-stabilized Gd^0 nanoparticles that were centrifuged and sintered as powder samples (900 °C) in vacuum indicates the presence of pure GdN (Figure S2). This finding and reaction can be ascribed to the thermal decomposition of

surface-adhered octylamine being the only available nitrogen source. The absence of impurities such as Gd_2O_3, $GdCl_3$ or LiCl confirms the purity of the as-prepared Gd^0 nanoparticles. The even more reactive U^0 nanoparticles, subjected to similar sintering conditions (vacuum, 900 °C), show a reaction with the crucible materials (i.e., corundum or boron nitride). XRD confirms UC as a product, whose formation can again be described to the decomposition of octylamine, as well as of non-identified side phases.

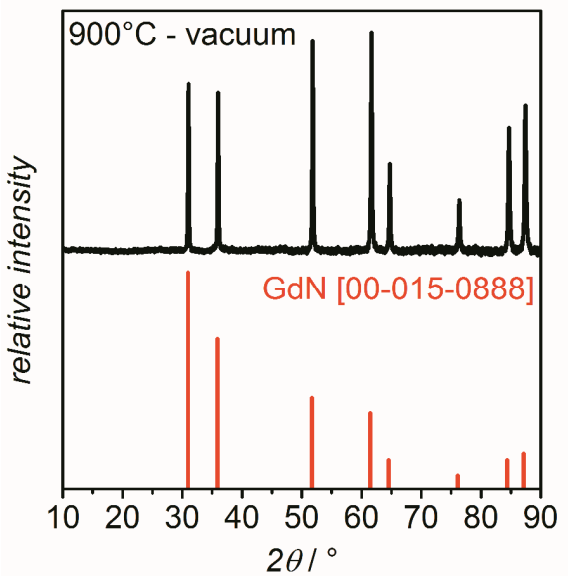

Figure S2. X-ray powder diffractogram of octylamine-functionalized Gd^0 nanoparticles subsequent to sintering (vacuum, 900 °C) showing the reaction to GdN due to thermal decomposition of octylamine.