Sodium-Metal and Strontium-Metal Nanoparticles

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– Supporting Information –

Content

1. Analytical Techniques

Transmission electron microscopy (TEM). TEM and high-resolution (HR)TEM analyses were performed on an aberration-corrected FEI $Titan^3$ 80-300 microscope at 300 keV electron energy. For sample preparation, diluted suspensions of the as-prepared Na(0) and Sr(0) nanoparticles in toluene were deposited and evaporated on commercial 400 µm mesh Cu-grids (Plano) covered by amorphous holey carbon film with a nominal thickness of 3 nm. The deposition was performed in a glove box (MBraun, Germany) under argon atmosphere to avoid any oxidation. With a suitable vacuum/inert gas transfer module (GATAN, USA), the sample grids were finally transferred into the microscope without any contact to air. (HR)TEM images were evaluated by calculating the two-dimensional Fourier transform (FT), which yields information on the crystal structure (lattice parameters and crystal symmetry) of single nanoparticles. The analysis was performed by comparing the experimental FT and the calculated diffraction patterns with Miller indices, where the latter were obtained by using the Jems (Java version of the electron microscopy simulation) software.[S1] The zero-order beam (ZB) is indicated by using a white circle.

X-ray powder diffraction (PXRD). Diffraction measurements were performed on a Stoe Stadi-MP diffractometer (Stoe, Germany) operating with Ge-monochromatized Cu-Kα-radiation ($\lambda = 1.54178$ Å). For sample preparation, the Na(0) and Sr(0) nanoparticles were diluted with glass spheres (9-13 µm, Sigma-Aldrich, Germany) and filled into glass capillaries (0.3 mm in diameter, Hilgenberg, Germany) with argon.

Rietveld refinement of the alkalide $[Na(2,2,2\text{-cryptand})]^+Na^-$ was performed using the program TOPAS Academic (Version 5). For the refinement, the Crystallographic Information File (cif) data of the reported single-crystal structure[S2] were used as starting model and compared with the experimental powder diffraction data. The Rietveld refinement was carried out with a simple axial model. The used experimental diffractogram was baseline corrected.

Fourier-transformed infrared (FT-IR) spectroscopy. FT-IR spectra were recorded on a Vertex 70 FT-IR spectrometer (Bruker, Germany). To avoid any oxidation of the Na(0) and Sr(0) nanoparticles, a Platinum A 225 ATR device (Bruker, Germany) with a specially protected sample unit was used to perform the analysis under inert conditions (argon).

Elemental analysis (C/H/N/S analysis). EA was performed with dried Na(0) and Sr(0) nanoparticles (10^{-3} bar, 2 h) via thermal combustion at a temperature of about 1100 °C with an Elementar Vario Microcube device (Elementar, Germany).

Centrifugation. The centrifugation of the as-prepared Na(0) and Sr(0) nanoparticles was performed with a Sigma 3-30KS centrifuge (Sigma, Germany). The centrifuge was placed in a glove box (MBraun, Germany) to avoid any contact to air.

2. Starting Materials and Synthesis

The purity of SrI_2 as starting material was verified via X-ray powder diffraction (PXRD) (Figure S1).

The purity of NaCp as a starting material was verified via Raman spectroscopy (Figure S2). The observed vibrational bands agree with literature data.[S3]

The syntheses of the Na(0) nanoparticles and Sr(0) nanoparticles as well as of the alkalide $[Na(2,2,2\text{-cryptand})]^+Na^-$ are described in the main paper (*see main paper: Experimental Section*).

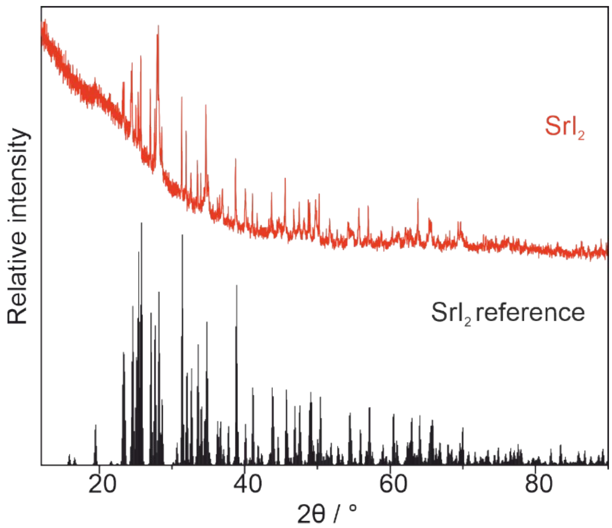

Figure S1. XRD of SrI_2 (bulk-SrI_2: ICDD-No. 01-071-2302 as a reference).

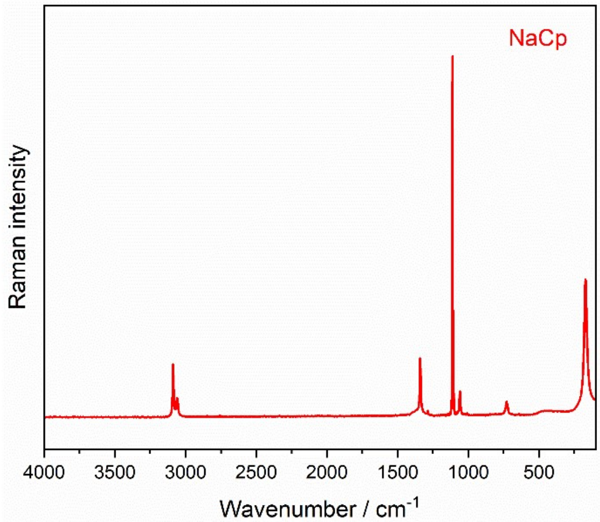

Figure S2. Raman spectrum of NaCp used as a starting material.

3. Characterization of Na(0) and Sr(0) Nanoparticles

The synthesis of the Sr(0) nanoparticles is illustrated in Figure S3. Accordingly, [LiNaph] was dissolved with N,N,N´,N´-tetramethylethylendiamine (TMEDA) in toluene, which results in a deep greenish-black solution. Thereafter, SrI_2 was added as a powder at room temperature. Since the dissolution of SrI_2 is very slow whereas the reduction of dissolved Sr^{2+} by [LiNaph] is very fast, this synthesis strategy results in small-size Sr(0) nanoparticles. In fact, the dissolution of SrI_2 takes 1-2 weeks to be completed. Successful reduction and nucleation of Sr(0) nanoparticles was indicated by formation of greyish suspensions with a slightly bluish colour (Figure S3). The as-prepared Sr(0) nanoparticles were very small (1-2 nm) and difficult to separate via centrifugation. Therefore, certain heating (100 °C, 6 h) of the suspension was applied to slightly increase the particle size (3-5 nm).

The synthesis of the Na(0) nanoparticles is illustrated in the main paper (*see Figure 1*).

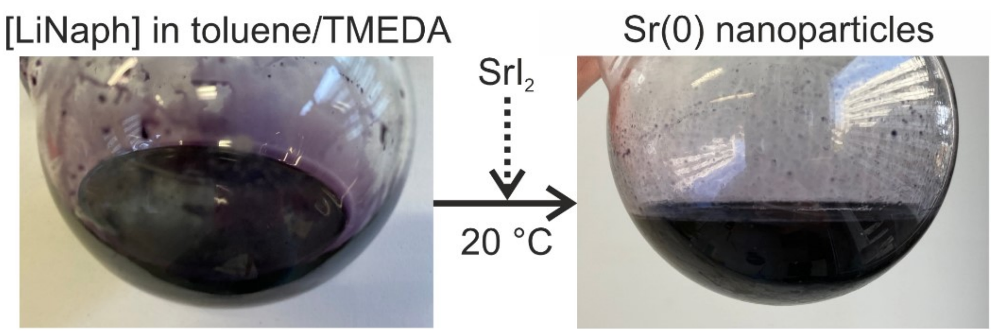

Figure S3. Scheme illustrating the synthesis of Sr(0) nanoparticles.

After centrifugation and purification by centrifugation/redispersion from/in toluene and THF and drying (vacuum, 20 °C), the as-prepared Na(0) and Sr(0) nanoparticles are highly reactive and show instantaneous combustion when in contact to air (Figures S4,S5).

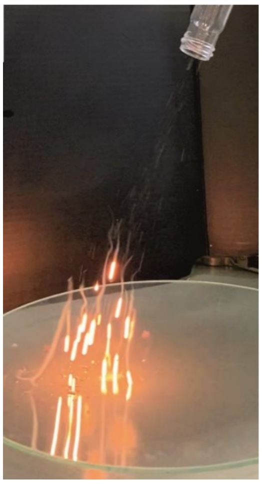

Figure S4. Photo illustrating the reactivity of Na(0) nanoparticles (10 mg) when in contact to air.

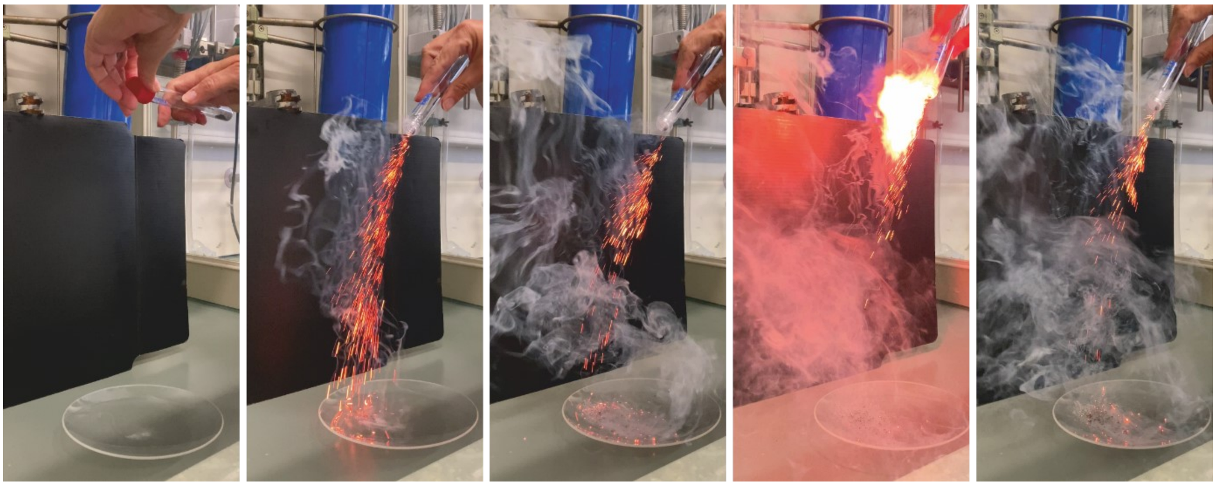

Figure S5. Photos illustrating the reactivity of Sr(0) nanoparticles (15 mg) when in contact to air.

In addition to the TEM and STEM analysis shown in the main paper (*see Figures 2,3*), further images were recorded to verify the particle size, shape and crystallinity of the as-prepared Na(0) nanoparticles (Figure S6) and of the as-prepared Sr(0) nanoparticles (Figure S7).

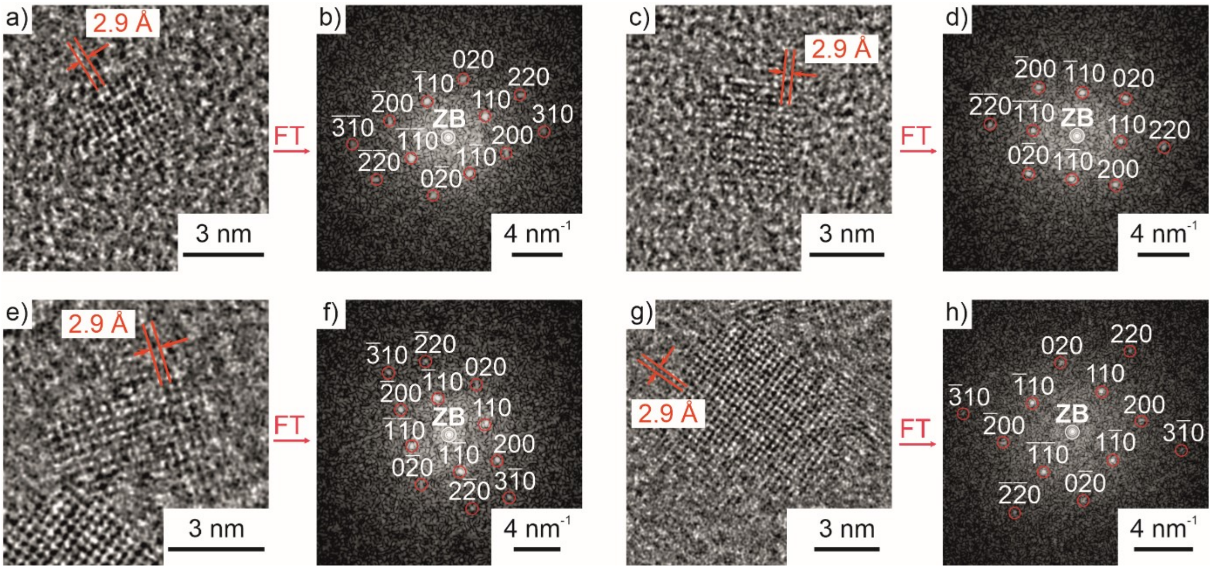

Figure S6. Crystallinity of different Na(0) nanoparticles: HRTEM images (a,c,e,g) and corresponding FT patterns together with calculated patterns (red circles and Miller indices) of bcc-bulk Na (*Im*-3*m*, *a* = 4.2820 Å) within the [001]-zone axis (b,d,f,h) of different Na(0) nanoparticles.

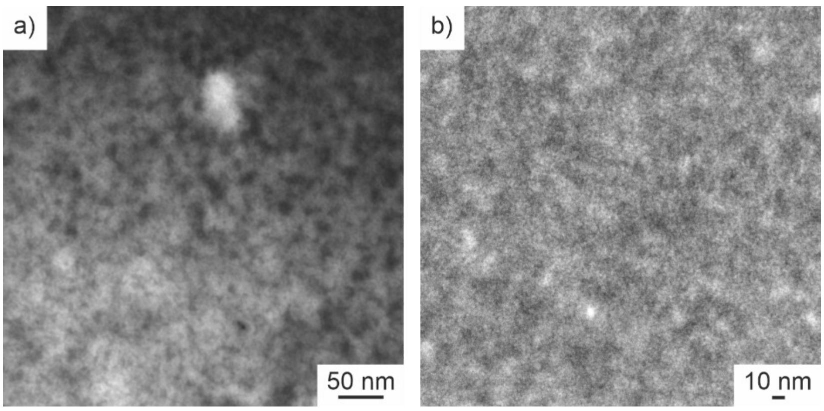

Figure S7. STEM images of Sr(0) nanoparticles.

Thermal analysis of the Na(0) and Sr(0) nanoparticles in air shows the oxidation of Na(0) to NaO_2 and, at even higher temperature, to Na_2O with release of O_2 (*see main paper: Figure 6a*). Na_2O as a strong base thereafter reacts with the corundum crucible, so that no solid material remained after thermal analysis to perform XRD. For the Sr(0) nanoparticles, thermal analysis indicates the formation of $SrCO_3$, which, after thermal decomposition to SrO and CO_2 (*see main paper: Figure 6b*), also reacts with the corundum crucible, so that XRD of the thermal remnant indicates the presence of SrO as well as of $Sr_3Al_2O_6$ (Figure S8).

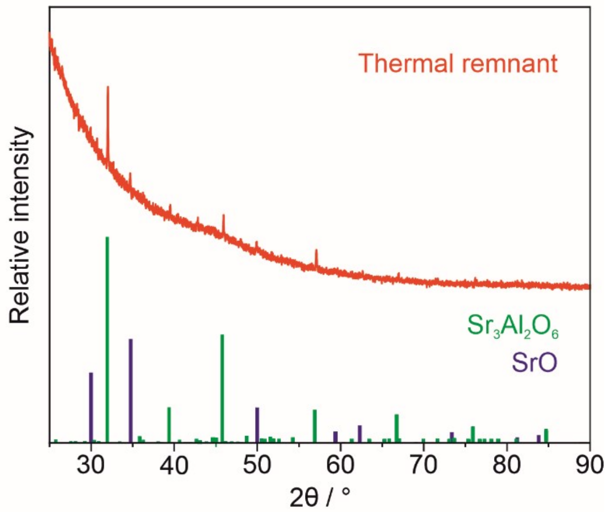

Figure S8. XRD of the thermal remnant of the Sr(0) nanoparticles after TG (references: SrO ICSD-No. 163625, $Sr_3Al_2O_6$ ICSD-No. 71860).

3. References

(S1) P. A. Stadelmann, https://www.jems-swiss.ch/

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