

– SUPPORTING INFORMATION –

Ti⁰ Nanoparticles *via* Lithium-Naphthalenide-driven Reduction

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1. Analytical tools

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

Transmission electron microscopy (TEM): Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted with an aberration-corrected FEI Titan³ 80-300 microscope operating 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 in a glove-box. The grids were thereafter transferred with a suitable vacuum/inert gas transfer module 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).

X-ray powder diffraction (XRD): X-ray powder diffraction (XRD) was performed with a Stoe STADI-P diffractometer operating with Ge-monochromatized Cu-K α -radiation ($\lambda = 1.54178 \text{ \AA}$) and Debye-Scherrer geometry.

Dynamic light scattering (DLS): Dynamic light scattering (DLS) was performed with a Malvern Instruments Nanosizer ZS, equipped with a He-Ne laser (detection via non-invasive back-scattering at an angle of 173°; 256 detector channels). Suspensions were investigated at room temperature in glass cuvettes under argon.

X-ray absorption near edge structure (XANES): X-ray absorption near edge structure (XANES) spectroscopy at Ti-K absorption edge were recorded at the XAS beamline of ANKA synchrotron radiation facility in Karlsruhe, Germany (2.5 GeV ring, 100-150 mA). A double-crystal monochromator equipped with Si(111) crystals was used to scan the energy in a step scanning mode. The spectra were recorded in fluorescence mode using a 5-element Ge-detector. The nanoparticles and bulk-Ti reference were loaded into quartz capillaries (1 mm diameter, 10 μm wall thickness, Hilgenberg) without exposure to air and sealed under Argon. The beam size was kept as $10 \times 1 \text{ mm}^2$. The XANES spectra were energy calibrated using the edge position of a Ti⁰ reference and normalized with the Athena software of the IFEFFIT package.¹

Fourier-transform infrared spectroscopy (FT-IR) was performed on a Bruker Alpha FT-IR spectrometer (Bruker, Germany) in the group of Professor Dr. Frank Breher, Institute of Inorganic Chemistry, KIT. The spectrometer is located inside of a glove box. Here, the as-prepared Ti⁰ powders were characterized under argon atmosphere via attenuated total reflection. These conditions are optimal to investigate the deep blackish powder samples.

Optical spectroscopy (UV-Vis): Diffuse reflectance spectra (UV-VIS) of Ti⁰ powder samples were recorded in a wavelength interval of 250-800 nm with a Varian Cary 100 spectrometer, equipped with an integrating sphere against BaSO₄ as a reference. Oleylamine in toluene was used as a reference.

2. Experimental Details

General aspects: All experiments were carried out under argon inert-gas atmosphere using standard Schlenk or glove-box techniques. This explicitly includes all centrifugation and washing procedures as well as the deposition of the nanoparticles on the sample carrier for TEM analysis. The sample carriers with the nanoparticles were then transferred with a suitable vacuum/inert gas transfer module into the transmission electron microscope without any contact to air.

Materials: Tetrahydrofuran (Seulberger, 99%), and toluene (Seulberger, 99%) were refluxed and freshly distilled over sodium or potassium with benzophenone as indicator of traces water and/or oxygen (Sigma-Aldrich, 99%). Oleylamine (Acros, 80-90%) was stored over activated molecular sieve (3 Å) for at least 30 days and degassed by freeze-pump-thaw cycles. Naphthalene (Sigma-Aldrich, 99%), lithium (Sigma-Aldrich, 99%) and titanium(IV)chloride tetrahydrofuran complex (Sigma-Aldrich, 97%) were used as received and handled in argon inert-gas atmosphere.

[LiNaph]: 55.2 mg lithium (8.0 mmol) and an excess of 1200 mg naphthalene (9.4 mmol) were dissolved in 10 ml THF over 12 h.

Ti⁰ nanoparticles: 667.8 mg TiCl₄·2 THF (2.0 mmol) were dissolved in 15 ml THF. [LiNaph] was injected rapidly at room temperature. The reaction mixture was steered for 2 h and stored for further 24 h without stirring. The nanoparticles were separated by centrifugation and washed by redispersion and centrifugation in/from THF (2x) and toluene (2x). Suspensions were obtained by redispersion in

10 ml toluene and 0.5 ml oleylamine. To gain powder samples the nanoparticles were dried under reduced pressure. The powders are extremely pyrophoric as illustrated by a short video (Video S1). This video shows the reaction of the as-prepared Ti^0 nanoparticles with air resulting in instantaneous ignition. Here, about 10 mg of a Ti^0 powder sample were poured out of an argon-filled glass vessel onto a steel tray (*CAUTION: Ti^0 nanoparticles need to be handled with great care in order to avoid uncontrolled ignition and/or combustion! Strictly use inert conditions.*) Optional transformation to TiC nanoparticles was performed by heating the Ti^0 nanoparticles to 800 °C under argon inert-gas atmosphere.

3. Surface conditioning of Ti^0 nanoparticles

Subsequent to synthesis and purification, the as-prepared Ti^0 nanoparticles were deposited on the ATR unit of an infrared spectrometer that was located in a glove box under argon. Via attenuated total reflection, the deep black powder samples can be optimally investigated in view of the surface conditioning of the Ti^0 nanoparticles (Figure S1). As a result, very high IR reflectivity is observed over the complete spectral range of 4000 to 500 cm^{-1} . Even C–H vibrations (3000-2800 cm^{-1}) and C–O vibrations (1200-1000 cm^{-1}) only occur with negligible intensity. This confirms the absence of any significant amount of THF or naphthalene remaining on the particle surface.

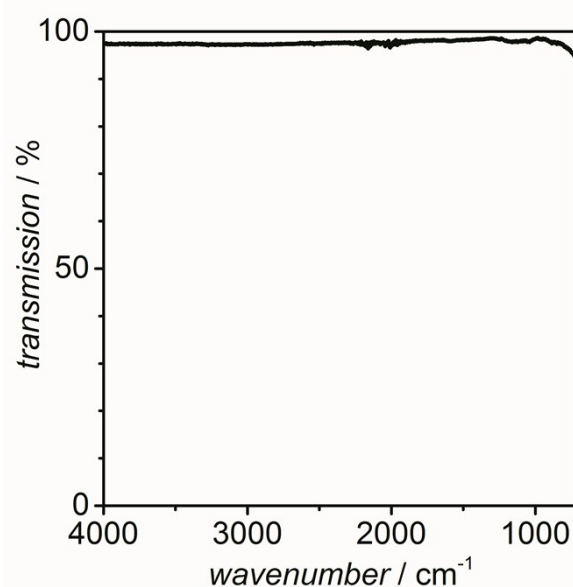


Figure S1. FT-IR spectrum of the as-prepared Ti^0 nanoparticles.

4. Electron microscopy of Ti⁰ nanoparticles

In addition to HAADF-STEM and HRTEM images (*main text: Figure 2a, Figure 2d*), size and size distribution of the as-prepared Ti⁰ nanoparticles were also analyzed by transmission electron microscopy (TEM) (Figure S2). Some nanoparticles are marked by red circles. The nanoparticles are clearly visible based on their highly ordered lattice fringes. The contrast is weak due to the fact that the electron-beam absorption of the Ti⁰ nanoparticles – 1.5±0.4 nm in diameter – is weak.

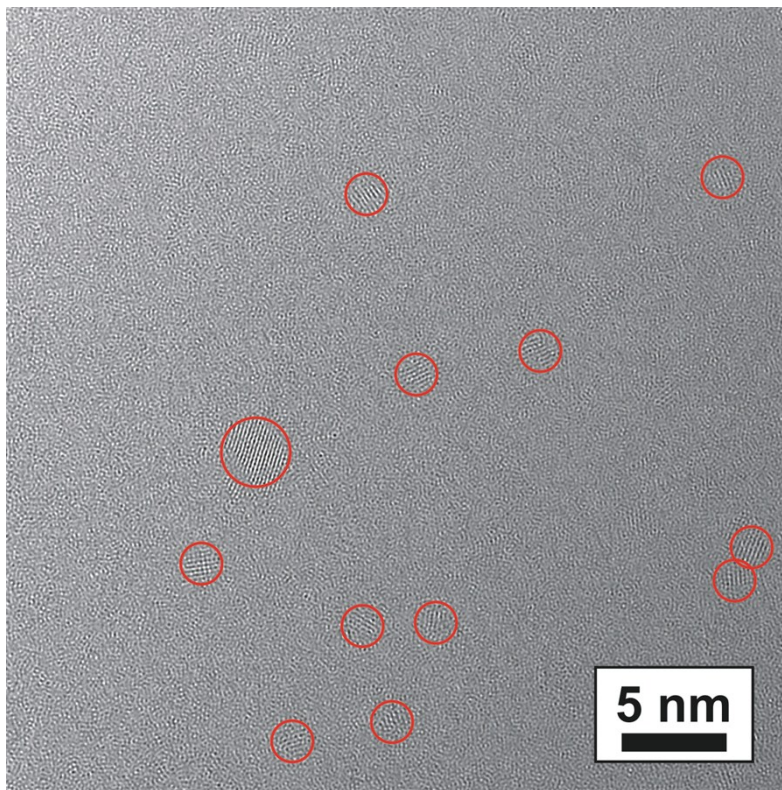


Figure S2. TEM image of the as-prepared Ti⁰ nanoparticles (some nanoparticles are indicated by red circles).

5. Size distribution TiC

The as-prepared Ti⁰ nanoparticles were annealed at 800 °C for 7 h to obtain TiC nanoparticles. TEM images of the heated TiC nanoparticles only show a small increase of the particle size and reveal a mean diameter of 2.8 ± 0.7 nm (Figure S3).

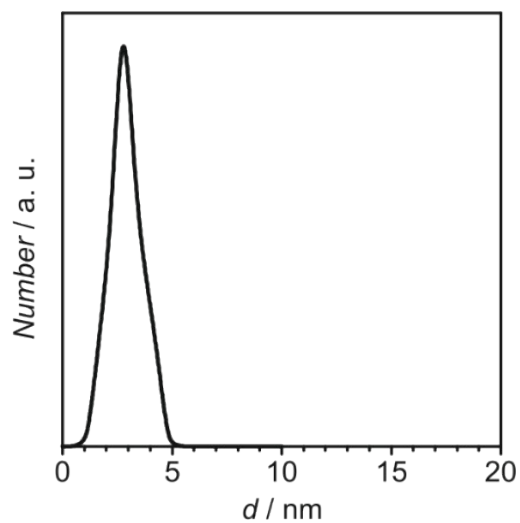


Figure S3. Size distribution of TiC nanoparticles after annealing at 800 °C in argon according to statistical evaluation of at least 100 nanoparticles on TEM images.

References

- 1 B. Ravel, M. Newville, *J. Synchrotron. Rad.*, 2005, **12**, 537.