

Liquid-phase Synthesis of Highly Oxophilic Zerovalent Niobium and Tantalum Nanoparticles

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Analytical Equipment

Transmission electron microscopy (TEM). TEM and high-resolution transmission electron microscopy (HR)TEM were conducted with a FEI Osiris microscope operating at 200 kV. TEM samples of the Nb(0) and Ta(0) nanoparticles were prepared by evaporating pyridine or toluene suspensions on amorphous carbon (Lacey-)films suspended on copper grids. This deposition was performed under dry argon atmosphere in a glove box. Immediately after sample preparation, the samples were slowly heated to 130 °C under vacuum to remove surface adhered volatiles (e.g. solvent). Thereafter, the grids were 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 nanoparticles (ImageJ 1.48v).

X-ray powder diffraction (XRD). XRD was performed on a STOE STADI-MP diffractometer operating with Ge-monochromatized Cu-K_α-radiation ($\lambda = 1.54178 \text{ \AA}$). Nb(0) and Ta(0) powder samples were diluted with dried glass spheres (9-13 μm , Sigma-Aldrich) to reduce the X-ray absorption of the nanoparticles and filled into glass capillaries under argon. Since the scattering power of the metal nanoparticles (diameter $\leq 10 \text{ nm}$) is low, certain non-specific background was observed for all samples. This non-specific scattering was fitted by background correction (Win-XPOW, 1.2v).

Fourier-transformed infrared (FT-IR) spectroscopy. FT-IR spectra were recorded on a Vertex 70 FT-IR spectrometer from Bruker Optics. Accordingly, the transmittance of pellets consisting of 300 mg of dried KBr and 0.5 mg of the dried Nb(0) and Ta(0) nanoparticles was measured.

Elemental analysis (EA). C/H/N elemental analysis was performed with an Elementar Vario Microcube device (Elementar, Hanau, Germany) at a temperature of about 1.100 °C.

Centrifugation. All centrifugation of metal nanoparticles was performed with a high-speed refrigerated centrifuge Sigma 3-30KS. To guarantee inert conditions (argon), the centrifuge was placed in a glove box. Tubes with a volume of 30 mL were used and allow a maximum speed of 30.000 rpm relating to about 65.000 \times g.

Reactivity of as-prepared Metals

The reactivity of the as-prepared metal nanoparticles is exemplarily illustrated by Ta(0) nanoparticle powder samples (Figure S1). Whereas the Ta(0) nanoparticles are chemically stable in Argon atmosphere, they are immediately oxidized by oxygen if the sample is in contact to air for some minutes. The oxidation to Ta₂O₅ is indicated by the colour change from deep black to light ochre.

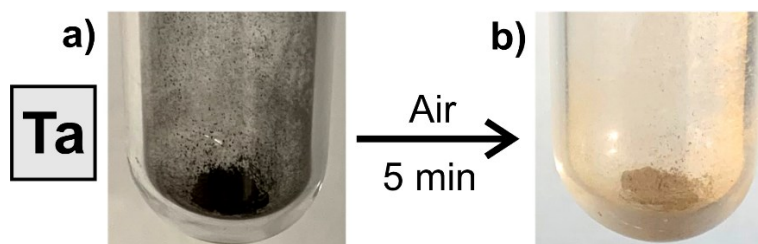


Figure S1. Oxidation of the as-prepared Ta(0) nanoparticles in air: a) under argon, b) after contact to air for 5 min.

X-ray powder diffraction (XRD) analysis of both the as-prepared Nb(0) and Ta(0) nanoparticles did not show any Bragg peaks, which can be ascribed to the small particle size and the low scattering power (*see main paper*). In the case of Nb(0), highly ordered lattice fringes of nanoparticles on HRTEM images as well as the observed lattice fringe distance indicate the crystallinity of the as-prepared Nb(0) nanoparticles (*see main paper: Figure 2d*). For Ta(0), no lattice fringes are observed on TEM images (*see main paper: Figure 3d*), which is not a surprise when taking the high melting point of tantalum into account ($T_{melt}(\text{Ta}(0)) = 3.017 \text{ }^\circ\text{C}$). After sintering at 1100 °C, the Ta(0) nanoparticles are crystalline (*see main paper: Figure 4b*). Here, it needs to be noticed that the nanoparticles need to be sintered in Ar/H₂ atmosphere (95:5) to avoid a reaction of the metal at elevated temperatures with pyridine adhered on the particle surface. Thus, sintering at 1100 °C in Ar/H₂ atmosphere resulted in crystalline tantalum (Figure S2a, *see main paper: Figure 4b*), whereas sintering at 1100 °C in pure Ar atmosphere resulted in the formation of tantalum carbide Ta₄C_{3.04} (Figure S2a,b). The carbide was only observed after sintering and can be attributed to the fragmentation of surface-adhered pyridine at elevated temperature.

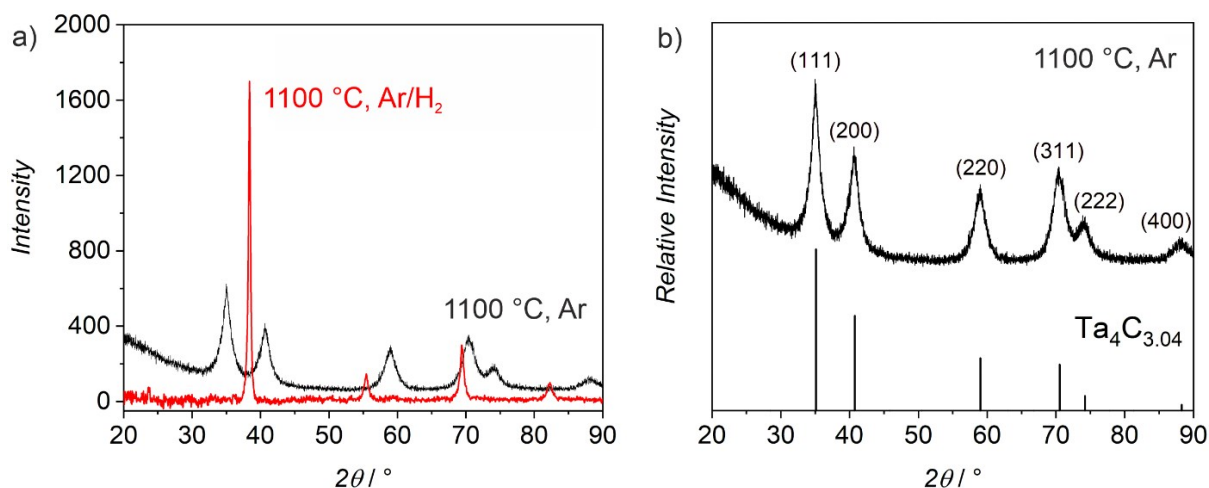


Figure S2. X-ray powder diffraction analysis of Ta(0) after sintering at 1100 °C in Ar/H₂ as well as in Ar only (a) and comparison with Ta₄C_{3.04} as a reference (b) (Ta₄C_{3.04}: ICDD-No. 01-089-2121).

XANES Spectroscopy

X-ray absorption near edge structure (XANES): X-ray absorption near edge structure (XANES) spectroscopy at Ta-*L*₃ absorption edge were recorded at the Cat-Act beamline at the synchrotron radiation facility in Karlsruhe, Germany (2.5 GeV ring, 100-150 mA).^{S1} 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 1-element Si-detector. The nanoparticles and the reference samples 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 0.5×0.5 mm². The XANES spectra were energy calibrated using the edge position of a Ta metal foil and normalized with the Athena software of the IFEFFIT package.^{S2}

A comparison of XANES spectra indicates the similarity of the derived absorption of the as-prepared Ta(0) nanoparticles and of tantalum clusters supported on SiO₂ reported by Gates *et al.*^{S3} Accordingly, shape and energy position of the *L*₃-edge absorption spectra are identical (Figure S3), which confirms the presence of Ta(0) nanoparticles. The presence of Ta(0) was also validated by the colour of the samples (*main text: Figure 1*), their reactivity (Figure S1), as well as by X-ray powder diffraction (*main text: Figure 4*).

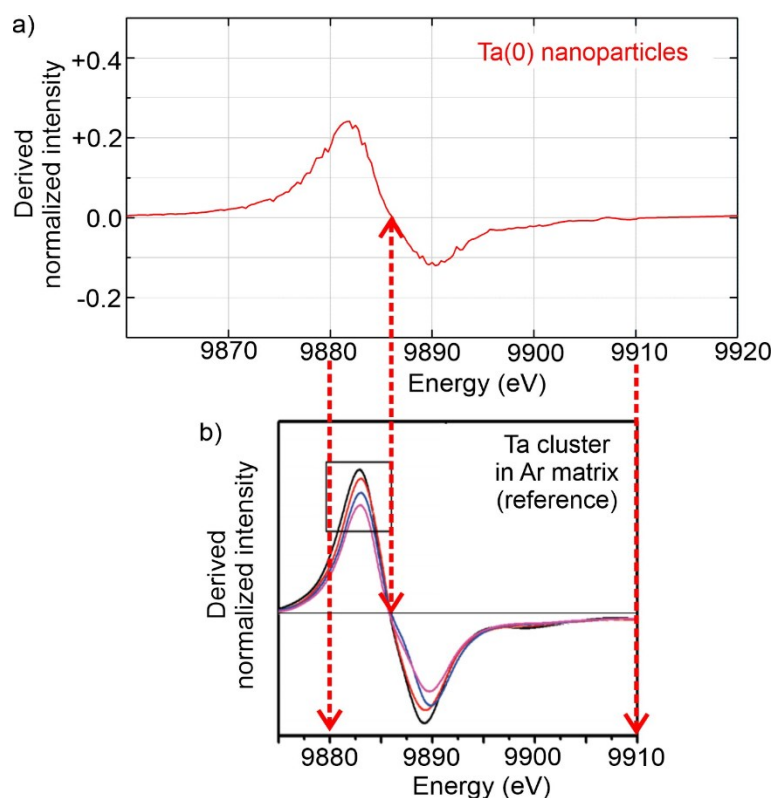


Figure S3. Comparison of the 1st derivative of XANES spectra of the as-prepared Ta(0) nanoparticles (a) with SiO₂-supported Tantalum clusters (b, according to Figure 6 in reference S3).

References

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