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Image-Based Nanocrystallography by Means of Tilt Protocol / Lattice Fringe-Fingerprinting: Proof of Principle on TiO_2 Nanoparticles

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Crystalline nanoparticles promise materials with new and enhanced properties for novel products and applications. Imaged-based nanocrystallography (IBN) is a very general approach to describing the crystallography (i.e. ideal and real structure as well as shape) of crystalline nanoparticles. Experimental proof-of-principle demonstrations of IBN by means of transmission electron goniometry (TEG) were published recently [1,2]. Employing the so called "cubic minimalistic" tilt protocol, Fig. 1,WC_{1-x} nanocrystals were analyzed in a Philips EM430 ST [1].
As a new branch of IBN, *Lattice Fringe-Fingerprinting* (LFF) was recently developed [3,4]. The fringe-visibility map theory [3] enables calculations of the probabilities to image lattice fringes (reciprocal lattice vectors) or crossed lattice fringes (zone axes or direct lattice vectors) for randomly oriented nanocrystals. These probabilities depend on the directly interpretable (point or Scherzer) resolution of the transmission electron microscope (TEM), lattice spacings, crystallographic multiplicities, electron wavelength, crystal thickness, and an empirical visibility factor that accounts for the signal to noise ratio. On the basis of the fringe-visibility map theory [3], nanocrystal "fingerprints maps as resolved in a particular TEM" that are uniquely characteristic for any material can be calculated [4]. These maps can then be compared with experimental plots of resolved lattice spacings versus intersection angle with other resolved lattice spacings. An unknown crystal phase (of a pre-identified chemical stoichiometry) may then be identified out of a range of candidate structures. Possibly in the future, search and match routines and a specifically generated fringe-fingerprint database may speed up the identification processes.
An application of IBN by means of TEG to titania (TiO_2) nanoparticles was presented elsewhere [5]. In this paper, we apply IBN by means of LFF on the same titania nanoparticles. We present a brief introduction on how LFF works, and apply it to the TiO_2 polymorphs rutile, anatase and brookite. It was shown earlier that the viability of IBN increases super-linearly with the directly interpretable image resolution of a TEM [6]. Our model calculations are, therefore, made for the point-resolutions 0.24 nm (corresponding to a FEI tecnai F20 ST at 200 kV, Fig. 2) and 0.12 nm (corresponding to a spherical aberration corrected FEI tecnai F20 ST at 200 kV [7]).

[1] W. Qin and P. Fraundorf, Ultramicroscopy **94** (2003) 245.
[2] P. Moeck et al., Mat. Res. Soc. Symp. Proc. **829** (2005) B9.4.1.
[3] P. Fraundorf et al., arXiv:cond-mat/0212281v2 (2005).
[4] P. Fraundorf et al., Microscopy and Microanalysis, Vol. **10**, Suppl. **2** (2004) 1262
[5] P. Moeck et al., *ibid.* Suppl. **3**, p. 50; a similar poster is freely accessible at URL http://www.physics.pdx.edu/~bseipel/poster_breakthrough_conference.pdf.
[6] P. Moeck et al., Mat. Res. Soc. Symp. Proc. **839** (2005) P4.3.1 and **818** (2004) M11.3.1.
[7] http://www.physik.tu-dresden.de/isp/member/wl/TBG/Equipment/equipment.htm.
[8] This work was supported by a grant from Research Corporation and benefited indirectly from support by the US Department of Energy, the Missouri Research Board, as well as Monsanto and MEMC electronic materials companies. Financial support form Portland State University is also acknowledged.

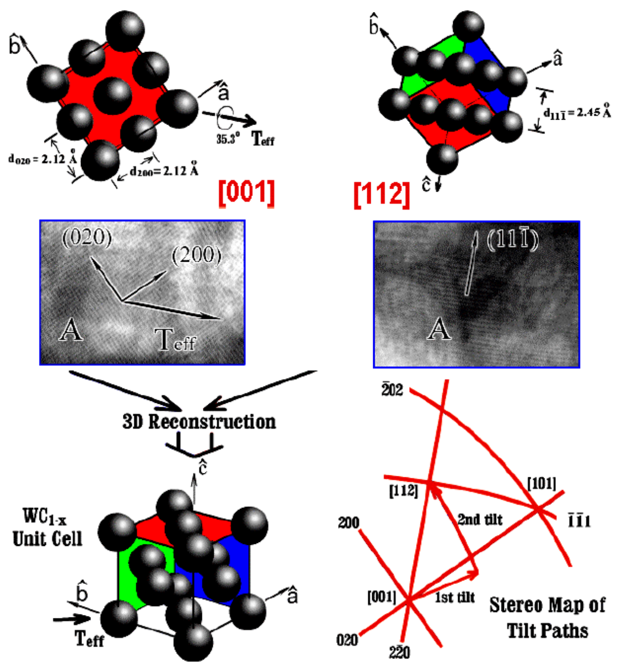

Figure 1: Schematic illustration of imaged-based nanocrystallography by means of transmission electron goniometry (more precisely: goniometry of reciprocal lattice vectors; from W. Qin, *Direct Space (Nano)crystallography via High Resolution Transmission Electron Microscopy*, PhD-Thesis, University of Missouri-Rolla 2000). The basic idea is that three non-coplanar reciprocal lattice vectors measured along two zone axes are sufficient for inferring a subset of the 3D-reciprocal lattice so that the lattice parameters of any nanocrystal can be calculated. The tilt paths for a WC_{1-x} crystal to reach a second zone axis by employing a double-tilt goniometer are shown on a stereo map. The improved directly interpretable image resolution that objective lens aberration correction enables will allow for many more as well as more complex tilt paths and protocols.

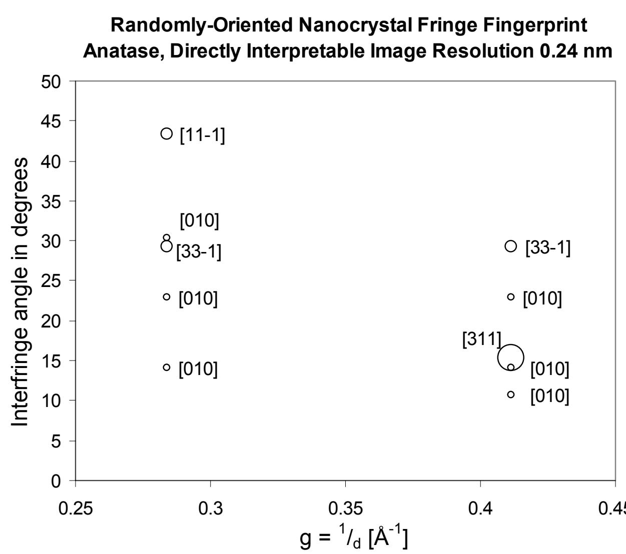

Figure 2: Calculated fringe fingerprint map of randomly-oriented anatase (TiO_2) nanocrystals for a directly interpretable image resolution of 0.24 nm. The radius of the circles is proportional to the probability of seeing a certain zone axis [uvw] in a collection of anatase nanoparticles. Although only the lattice spacings {101} = 3.52 Å and {103} = 2.42 Å can be resolved with an FEI tecnai F20 ST (that is designed to be primarily an analytical TEM, possesses a super-twin objective lens with C_s = 1.2 mm and a directly interpretable image resolution of 2.4 Å at 200 kV), this plot of angles between crossing lattice fringes versus lattice fringe spacings is quite characteristic of the anatase phase.

When a C_s corrector is added to an FEI tecnai F20 ST, the directly interpretable image resolution approaches the information limit (1.2 Å, [7]) and the respective fringe fingerprint map contains an enormously larger amount of detail. This is because the visibility of lattice fringes and zone axes increases super-linearly with improvements in image resolution [6], making such experimental plots uniquely characteristic for any particular nanocrystal phase. Note that an FEI tecnai F20 ST with both C_s corrector and gun monochromator broke recently the so called “one Ångström high-resolution imaging barrier” (http://www.azonano.com/details.asp?ArticleID=733). FEI Company was also selected by the TEAM project (http://ncem.lbl.gov/team3.htm) as R&D partner for developing the capabilities for imaging at a point resolution of 0.5 Å at 300 kV (http://www.voyle.net/Nano Biz 200/NanoBiz-0142.htm).