

## Identification of Sample Preparation Artifacts in Powder Analysis

Andreas Taubert, Max-Planck-Institute for Polymer Research  
taubert@seas.upenn.edu

The synthesis of inorganic materials of a specific size and shape is a key aspect in modern powder technology. During the past two decades, solution-based precipitation reactions have been explored for controlled particle formation. A wide variety of particle shapes, sizes, and compositions<sup>1</sup> has been demonstrated. However, several questions, especially concerning particle nucleation, remain. Some of these questions are currently addressed by investigating precipitate (*ex situ*) at different reaction stages by means of powder x-ray diffraction (PXRD), scanning (SEM) and transmission electron microscopy (TEM)<sup>2</sup>.

Preparation of these precipitates for microscopy can lead to artifacts. These may, if not recognized, lead to errors in data interpretation and possibly to false conclusions. This contribution aims to point out some of these sample preparation effects. Both the sample under investigation and any artifacts introduced during sample preparation contribute to the images obtained via SEM or TEM. Some examples of how sample preparation can affect sample properties, such as particle morphologies and how these effects can be identified, are discussed here.

Figure 1 a is a PXRD pattern of a zinc oxide (zincite) powder sample precipitated from aqueous solution in presence of a poly(methacrylic acid) homopolymer. The pattern only shows zincite reflections.

Powder morphologies were investigated with a JEOL 6400F

SEM. The powders were deposited on conducting carbon tape and sputter-coated with a thin gold layer. The corresponding images show that the sample contains particles of very different shapes and sizes. All particles are of about the same brightness (Figure 1b). Thus, one might conclude that the sample consists of chemically pure zincite of a wide variety of particle shapes.

However, when the same sample was examined in a LEO 1530 SEM for which no sputter-coating is necessary, the powder morphology looks different. The small spherical particles appear much darker than the large particles (Figure 1c). What could possibly be the origin of that?

To answer this question, transmission electron microscopy (TEM) experiments were performed on a series of similar samples. Results from one sample are shown in Figure 2. Bright field im-

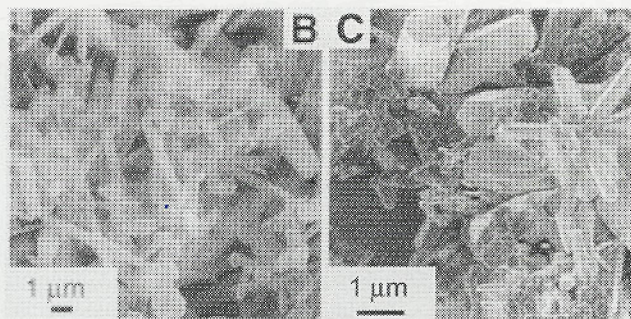
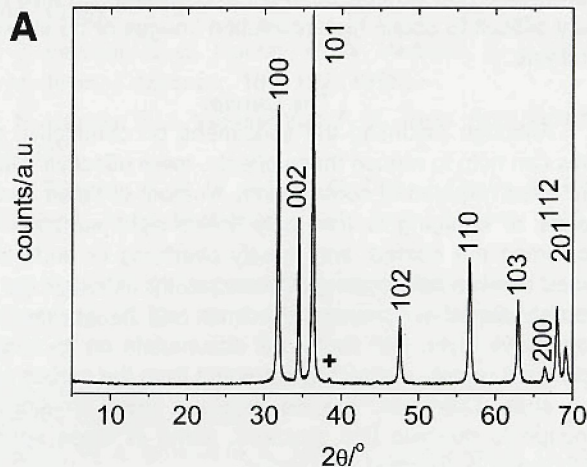


Figure 1: a) PXRD pattern from a zinc oxide (zincite) powder sample precipitated from aqueous solution in the presence of a poly(methacrylic acid) homopolymer. + indicates a peak associated with the aluminum sample holder. b) SEM image of the sample obtained with a JEOL6400F SEM. c) SEM image of the sample obtained with a LEO1530 SEM.

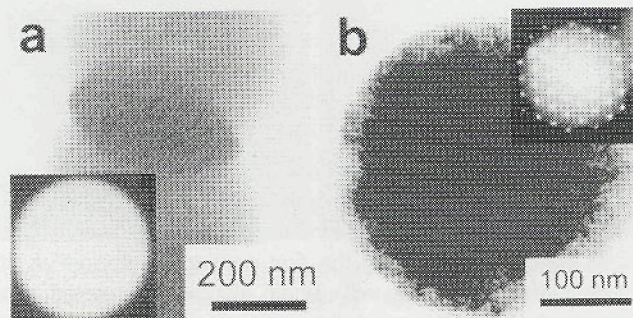


Figure 2: a) Bright field image and SAD pattern (inset) of two spheres. b) Bright field image and SAD pattern (inset) of a hexagonal particle.

## YOUR OFFICIAL Nikon PROFESSIONAL DIGITAL SLR D1 DEALER!

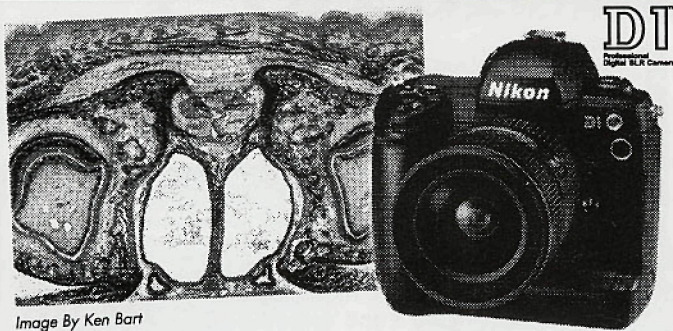


Image By Ken Bart

2.74-megapixel • Superhigh-speed, high-quality  
4.5 frames per second • 3D Digital Matrix Image Control  
High-speed AF system including Dynamic AF operation  
3D Multi-Sensor Balanced Fill-Flash for D1  
Compatible with virtually any F-mount Nikkor lens

\$4,999 Nikon D1 Digital SLR Camera Set: D1 Camera Body, EN-4 Battery Pack  
MH-16 Quick Charger, Video Cable, Nikon View DX Browser, Nikon Video Cable for D1  
D1 Neck Strap, Instruction Manual, Nikon Limited One Year Warranty Document. \*LENS SOLD SEPARATELY

**Nikon.**  
We take the world's  
greatest pictures®  
Yours.

**NATIONAL**  
Graphic Supply



**1.800.223.7130 ext. 3109**

226 North Allen Street, Albany, New York 12206 • Fax 800-832-2205  
www.ngscorp.com • E-mail: scisales@ngscorp.com

ages confirm that two different particle shapes are present in the sample. In agreement with SEM images, spherical and roughly hexagonal particles were found. Selected area diffraction (SAD) on individual particles (either spherical or hexagonal) provides information on the internal structure. SAD on the spheres (inset in Figure 2a) resulted in a broad halo consistent with an amorphous structure, whereas SAD on the hexagonal particles (inset in Figure 2b) demonstrated a single crystalline structure.

This more careful investigation of the two types of particles demonstrates that the initial conclusion of a single phase, polydisperse and non-uniformly shaped zincite powder was wrong. The initial interpretation was based on data that did not include evidence of the second amorphous phase. The contribution of the amorphous component to the PXRD patterns could not be distinguished from background. The sputter-coated gold layer necessary for conventional SEM masked the difference in signal between the spheres and the hexagonal particles, which was observed in the uncoated sample examined in the LEO SEM. Both the PXRD and conventional SEM data supported the initial incorrect interpretation.

A second example of sample preparation-induced artifacts is found in Figure 3. Here zinc oxide was precipitated in the presence of a water-soluble diblock copolymer. SEM images (Figure 3a) show a continuous matrix containing single particles. Additional structural information is provided by TEM on the same sample.

The TEM sample was prepared as follows: the powder was suspended in two mL of ethanol and ultrasonicated for five minutes. A drop of the suspension was then allowed to slowly dry on a carbon coated copper grid. TEM images (Figure 3b) show that

the matrix material is lamellar with a lamellar spacing of ca. 3.4 nm. However, in contrast to the SEM images, the matrix material was found as much smaller particles than observed in the SEM images of the as-dried sample.

This discrepancy in particle size arose from the ultrasonication step used for TEM sample preparation. Apparently, the initially large particles are reduced in size by ultrasonication and subsequently deposited as flakes on the TEM grid. The ultrasonication step can thus be considered a convenient method to obtain structural information about the matrix, since the resulting single flakes are thin enough to be electron transparent. However, it is clear that the samples prepared for TEM are not representative of the as-dried samples. In this case, SEM of the as-dried powder prevented the incorrect conclusion that the sample is made up lamellar flakes and hexagonal particles with no correlation to one another. In fact, the material is a complex structure of particles embedded in a matrix that in turn has a lamellar structure.

Figure 4 demonstrates a sample preparation artifact often neglected in SEM powder analysis, mechanical treatment. The two images show the same sample. The only difference is the sample preparation procedure. Figure 4a is an SEM image of a precipitate that was first deposited on conductive carbon tape and then lightly pressed into the tape with a spatula in order to ensure that the material remains in place. The SEM image of Figure 4b shows the effect of spatula pressure on the sample. This sample was prepared in an identical way as that in Figure 4a, but without pressing the powder into the tape with a spatula. The difference is striking: whereas the first image shows thin platelets of various shapes and

*Continued on following page*



*4pi Analysis provides EDS and digital imaging systems, components, and software for both the Mac® OS and Windows® 98 or NT. Whether you need a complete system or want to upgrade outdated electronics, 4pi's products meet the high standards you demand.*



## Features

- light element x-ray detection
- detector resolution of 133eV or better
- peak to background ratio of 20,000:1
- qualitative and quantitative analysis
- slow and fast x-ray mapping
- x-ray and SEM line scans
- x-ray image mapping
- micron markers on acquired images
- fast easy-to-use software

**4pi Analysis, Inc.**  
3500 Westgate Dr. #403  
Durham, NC 27707  
(919) 489-1757  
sales@4pi.com  
www.4pi.com

## Identification of Sample Preparation Artifacts in Powder Analysis

Continued from preceding page

sizes, the second image shows that the sample actually consisted of very thin hexagonal platelets of fairly uniform diameter. It is obvious from these images that even simple actions such as scratching the powder from the walls of the reaction vessel or light pressure exerted on the powders may profoundly influence the particle morphology observed.

This short article attempts to demonstrate that the results of powder analysis often contain not only information on the sample, but also on sample preparation. Interpretations based on such analyses can be misled if the possibility of sample preparation artifacts is not taken into account. Perhaps the best approach to minimize the sample preparation artifacts is to employ a variety of techniques and to vary the sample preparation methods, even if they have been proved to be very convenient in the past. ■

**Acknowledgement.** The author would like to thank Dr. G. Lieser, G. Glasser, Prof. D. C. Martin and Dr. C. K. bel for very useful discussions on various aspects of microscopy and diffraction. Dr. C. C. Honeker is also thanked for reviewing the manuscript.

[1] For a recent review see e.g.: Adair, J.H.; Suvaci, E. *Curr. Op. Coll. Interf. Sci.*, 2000, 5 (1-2), 160. see also: Matijevic, E. *Chem. Mater.* 1993, 5, 412. Matijevic, E. *Langmuir*, 1986, 2, 12. Matijevic, E., *Acc. Chem. Res.*, 1981, 14, 22.

[2] see e.g: C lfen, H.; Limin, Q. *Chem. Eur. J.*, 2000, 7 (1), 106. Rieger, J.; Thieme, J.; Schmidt, C. *Langmuir*, 2000, 16, 8300.

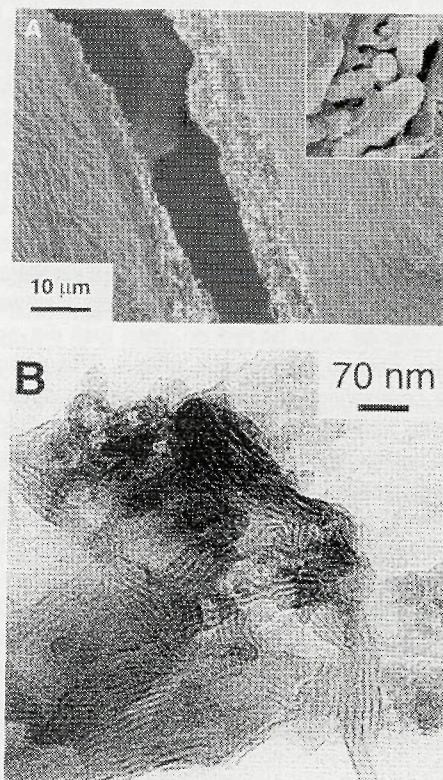
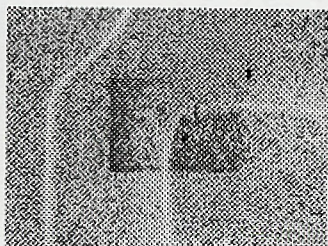


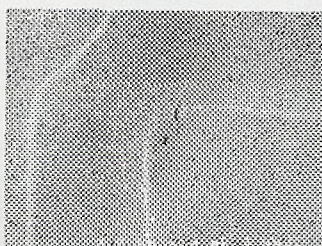
Figure 3: a) SEM image before and b) TEM image after ultrasonication of a precipitate.

**Remove the Veil from SEM Samples!**

**EVACTRON™**  
**In-situ Plasma Cleaning stops contamination inside your SEM!**



**Unwanted Artifact**  
A short SEM scan started a contamination deposit.



**After Evactron Cleaning**  
2 minutes of cleaning *in-situ* removed the deposit and prevented new artifacts.

**XEI SCIENTIFIC**

**SEM-CLEAN™ Systems for SEMs**  
3124 Wessex Way, Redwood City, CA 94061  
(650) 369-0133, FAX (650) 363-1659  
Email: RVaneXEI@concentric.net  
[www.semclean.com](http://www.semclean.com)

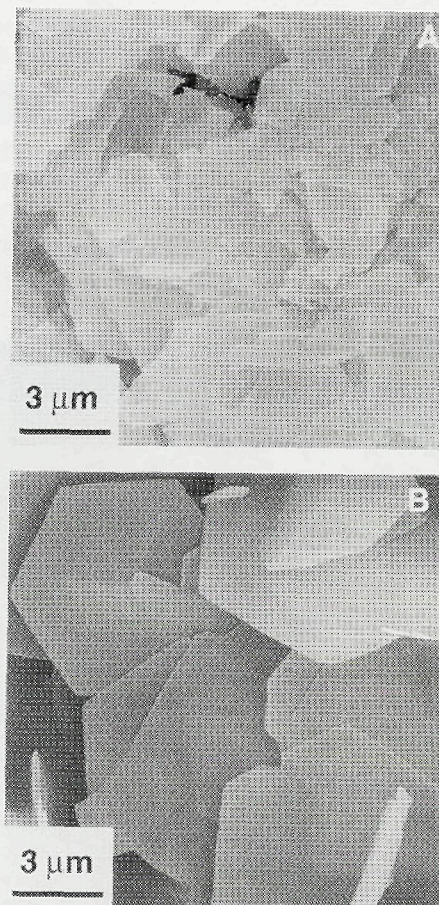


Figure 4: SEM images of the effect of mechanical treatment of a powder sample.