

Characterisation of Nanoparticle Structure by High Resolution Electron Microscopy.

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Abstract. Whilst the use of microscopic techniques to determine the size distributions of nanoparticle samples is now well established, their characterisation challenges extend well beyond this. Here it is shown how high resolution electron microscopy can help meet these challenges. One of the key parameters is the determination of particle shape and structure in three dimensions. Here two approaches to determining nanoparticle structure are described and demonstrated. In the first scanning transmission electron microscopy combined with high angle annular dark field imaging (HAADF-STEM) is used to image homogenous nanoparticles, where the contrast is directly related to the thickness of the material in the electron beam. It is shown that this can be related to the three dimensional shape of the nano-object. High resolution TEM imaging, combined with fast Fourier transform (FFT) analysis, can determine the crystalline structure and orientation of nanoparticles as well as the presence of any defects. This combined approach allows the physical structure of a significant number of nano-objects to be characterised, relatively quickly.

1. Introduction

Nanoparticles are generally defined as those particles which have at least one dimension in the 1 - 100 nm range. Such materials have been produced and used for many hundreds of years. Medieval red stained glass windows are dependent on colloidal gold nanoparticles and the distinctive dark hair colour dye used by the ancient Egyptians had nanoparticles of lead sulfide as its core ingredient. Interest in engineered nanoparticles as the basis for new and improved products has increased strongly since their emergence in the 1970s [1]. They effectively act as a bridge between the bulk properties of materials and the behaviour of individual atoms and molecules and as such often display unique properties. For example, the optical properties of gold nanorods are highly dependent on their aspect ratio (with colours ranging from red to dark purple) and could be incorporated into thin films for new optical devices. [2]. Recently concerns have been raised regarding the short and long term health and environmental impact of such materials [3].

Parameters which define the properties of nanoparticle production batches include the size distribution, shape, crystal structure (different outermost crystal planes will behave differently) and chemical composition and homogeneity. To ensure the continued innovation and safety of nanoparticles and their related products nanoparticle production batches must be fully and accurately characterised.



Here it will be demonstrated how all of these parameters can be determined in an effective way using conventional and scanning transmission electron microscopy, with a sample of titanium dioxide nanoparticles produced in the gas phase.

2. Experimental

A novel method of producing nanoparticles in the gas phase has recently been developed as described in reference [4]. Briefly titanium dioxide nanoparticles were prepared by sputtering a titanium hollow cathode in a reactive atmosphere containing oxygen. These particles were deposited directly onto a silicon wafer coated with gold (200 nm) with an adhesion layer of titanium (2.5 nm). Once deposited onto the substrate the particles were transferred onto gold TEM grids coated with a thin film of amorphous carbon by gently wiping the substrate and grid together.

All transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) measurements were taken using a FEI Tecnai G² TF20 UT microscope equipped with a field emission gun operating at a voltage of 200 kV with an emission current of 38 μ A. Scanning transmission electron microscopy images were taken with a high angle annular dark field (STEM-HAADF) detector with a camera length of 220 mm. All the measurements were taken in a single experimental session within a 2 hour period.

3. Results and Discussion

The nature of nanoparticles means that determining the size distribution is critical for understanding their overall properties. Due to the high resolution capabilities of transmission electron microscopy, it is now routinely used to determine the size distribution of nanoparticle samples. However the contrast in conventional bright field is strongly affected by the crystalline orientation of the sample. This can lead to incorrect results when analysing polycrystalline particles. This is not the case for HAADF-STEM, where contrast is primarily affected by the average atomic number and thickness of the sample. A HAADF-STEM image of the produced particles is shown in Figure 1(a). The particles are widely dispersed across the TEM foil with the individual particles clearly visible. Rather than the traditional view of nanoparticles as being spherical, here the particles appear highly faceted with either four or six visible faces. The latter also appear to be anisotropic. Using automatic image analysis using the ImageJ software package the size distribution can be determined [5]. A common method of doing this is to record the minimum and maximum Feret dimensions (Figures 1(b and c)), which is the maximum and minimum calliper distances respectively for each particle [6]. The minimum Feret distribution shows a high monodisperse distribution with an average particle diameter of 25 nm. The larger particle sizes measured (above 60 nm) are primarily due to agglomerated particles being detected as a single particle. The maximum Feret distribution is more widely dispersed, reflecting the anisotropy of some of the particles. Another advantage of the HAADF-STEM approach for homogeneous materials is the fact the image intensity is directly related to the thickness, for very small or thin specimens. This provides a route for determining the thickness distribution for the particles without the need for expensive and time consuming tomography measurements [7]. The HAADF image intensity for each particle is plotted against the minimum Feret dimension and shown in Figure 1(d). It can be seen that there is a strong linear relationship between the two, indicating that the particles grow uniformly and that they have a uniform chemical composition.

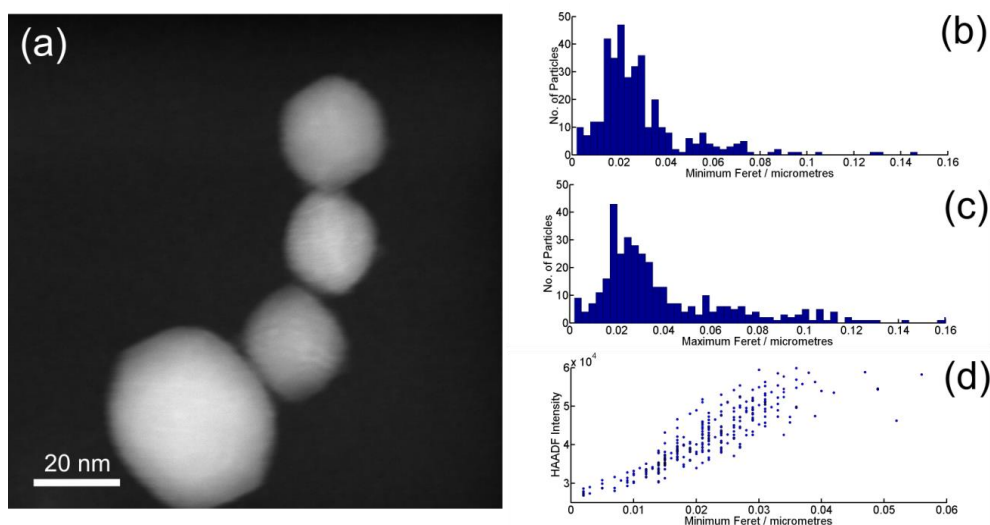


Figure 1: (a) HAADF-STEM image of obtained nanoparticles. (b) and (c) minimum and maximum Feret diameter distributions respectively and (d) the variation HAADF image intensity with Feret dimension.

High resolution electron microscopy images of the particles were used to determine the crystalline structure. Typical high resolution images of particles with different orientations are shown in Figures 2(a) and (c). The crystalline lattice is clearly resolvable. Processing of the high resolution images with 2D fast Fourier analysis produces a pattern which can be indexed to various crystalline structures Figures 2(b) and (d). A close fit was obtained to the rutile titanium dioxide structure, indicating the primary composition of the particles. This was confirmed with X-ray diffraction (data not shown). If a significant number of the particles contain a number of crystalline defects then this will also be revealed. This is shown in Figure 2(e) where a particle with the same orientation as that shown in Figure 2(a) is shown, containing a large number of either twin or stacking faults.

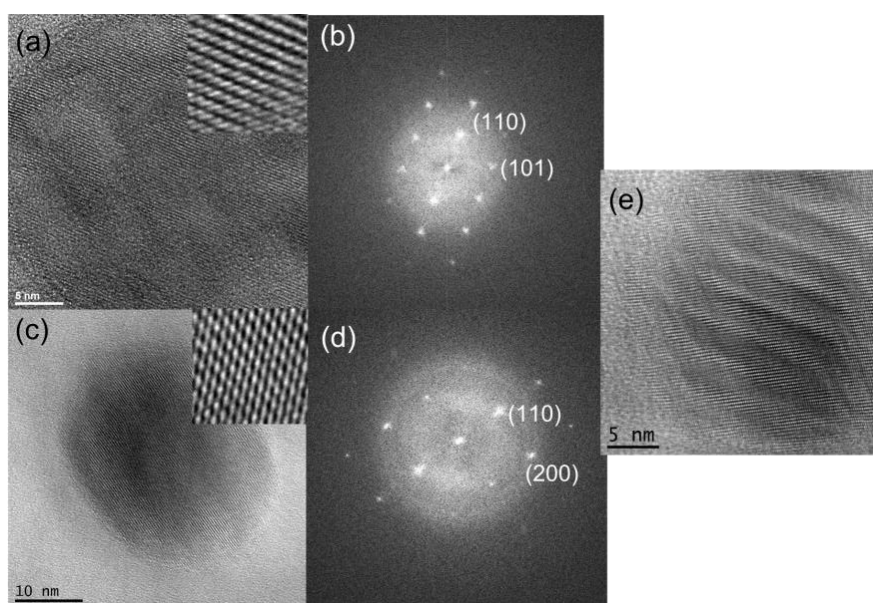


Figure 2: Bright field TEM analysis of individual particles. (a) and (c) high resolution TEM images and (b) and (d) their respective FFT patterns which could be fitted to a rutile TiO₂ structure as indicated and (e) a high resolution image showing crystalline defects within the particle.

As expected from the previous measurements, chemical analysis of the particles by EDS revealed the presence of titanium and oxygen (Figure 3(a)). Chemical line profiles across several particles (Figure 3(b)) confirms that both (and only) of these elements are associated with the particles. This allows the composition of individual particles to be determined and, as expected, remains consistent.

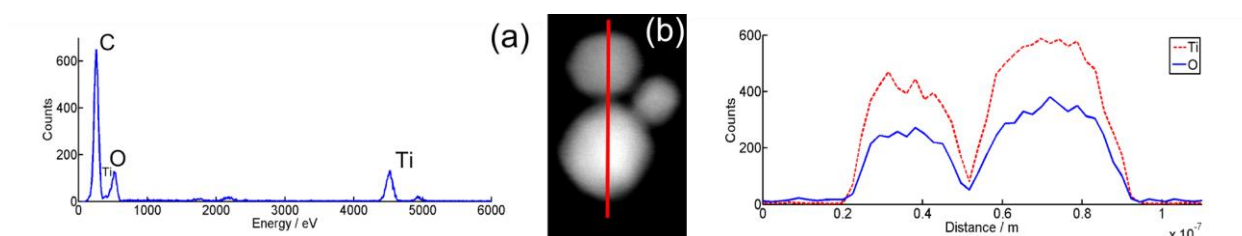


Figure 3: EDS analysis of the nanoparticles. (a) Spectra showing the presence of oxygen and Titanium along with carbon from the substrate and contamination. (b) HAADF image of several nanoparticles and the associated EDS line scan.

4. Conclusions

A nanoparticle sample produced by a novel process has been analysed using (scanning) transmission electron microscopy. In a single experimental session enough data was obtained to determine their dimensional distributions (length, width and thickness). In addition, two particular shapes of particles were described. The crystalline structure was determined and confirmed by chemical analysis which also confirmed the homogeneity of the particles.

5. Acknowledgements

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