Aberration corrected and 3D cryo-tomography
HAADF-STEM surface studies of ZnO tetrapods

M R Ward¹,², H Sugiura³, K Yoshida²,⁴, N Tanaka³, P L Gai¹,²,⁵ and E D Boyes¹,²,⁶

¹ Department of Physics, University of York, York, YO10 5DD, UK
² York JEOL Nanocentre, University of York, York, YO10 5DD, UK
³ Ecotopia Science Institute, Nagoya University, Chikusa-ku, Nagoya, 464-8603, Japan
⁴ Japan Fine Ceramics Centre, 2-4-1 Mutsuno, Atsuta-ku, Nagoya, 456-8587, Japan
⁵ Department of Chemistry, University of York, York, YO10 5DD, UK
⁶ Department of Electronics, University of York, York, YO10 5DD, UK

E-mail: mrw502@york.ac.uk

Abstract. We present a morphology study of ZnO tetrapods using aberration corrected TEM, HAADF-STEM and 3D HAADF-STEM cryotomography as an alternative to more conventional TEM and SEM techniques. We use 3D IMOD reconstructions to show that the \{1\bar{1}0\} facets dominate the total surface area of uniform hexagonal prism tetrapods. Using HRTEM we show that the small tetrapods have a zincblende phase core from which the four legs extend. The facets and the edges of these legs were found to be atomically clean and flat with the potential for ZnO tetrapods as model substrates. We deposited ultrafine Pt/Pd nanoparticles onto the tetrapods and investigated the resulting morphologies. We found using HAADF-STEM cryotomography and reconstruction techniques that the nanoparticle coverage gave separate nanoparticles and overall uniform coverage. We believe these techniques and the results from them could be useful for the development of nanoparticle-ZnO tetrapod composite systems with applications in optoelectronics, gas sensing and catalysis.

1. Introduction
ZnO is a semiconductor with a large direct band gap of 3.37 eV [1]. At the nanoscale, it forms many different structures that range from simple rods to complex 3D formations such as flowers. The simplest 3D structure is the tetrapod which consists of four tetrahedrally coordinated arms that grow from a central nucleus [1]. The arms are usually single crystal wurtzite with lattice parameters a = 0.25 nm and c = 0.52 nm. The structure of the nucleus is of some debate because for different tetrapod sizes and morphologies different conclusions about its core structure have been made [2].

Nanoscale ZnO is a candidate material for use in UV optoelectronics, field emission displays, solar cells and gas sensors but the branched nature of ZnO tetrapods enable it to have a more diverse range of applications compared to its non-branched equivalents (e.g. rods). For example, branching enables multiple interfaces to be made and as a result entire devices have been demonstrated with single tetrapods [3].

The applications of ZnO have been further expanded by adding metals to ZnO structures to form metal-metal oxide composite structures. The addition of metallic nanoparticles, usually
larger than 5 nm in diameter leads to a profound change in the band structure and the chemical properties of the structure as a whole [4]. The metal-metal oxide composite systems have also been found to increase the catalytic activity of both metal and the substrate [5].

Although ZnO tetrapods and related composite systems are abundant in the literature, most of the data revolves around conventional SEM and TEM data. Here we present an alternative approach to characterising the morphology of such structures using a combination of aberration corrected HRTEM and HAADF-STEM, and 3D HAADF-STEM cryotomography. Using these techniques we have indicated that small tetrapod structures can have a zincblende nucleus and that the tetrapod legs are formed from atomically clean surfaces. A mixture of 1.5 nm Pt/Pd nanoparticles were sputtered onto the surfaces and with HAADF-STEM cryotomography a detailed analysis of the resulting morphology was performed which showed that the nanoparticle coating was uniform. We believe these techniques and the results could be useful for the development of tetrapod and metal particle composite systems.

2. Experimental Procedure
The ZnO tetrapods were synthesised by rapidly heating pure Zn pellets in air. The pellets were placed into a tungsten wire cup and a large current was fed through to rapidly heat the pellets. The resulting vapour oxidised in air and a substrate was transported through the vapour to make TEM specimens. Controlling the current through the wire allowed some control over the growth rate. A mixture of 1.5 nm Pt/Pd nanoparticles was used to coat the ZnO TEM grids using a JEOL JFC-2300HR depositing machine. The overall coating thickness was 0.2 nm.

HAADF-STEM was preferred for the cryotomography series because it suffers less from diffraction contrast and interference effects that can sometimes appear in TEM images [6]. Furthermore, the focus here was the morphology of the tetrapods before and after the coating process hence the Z dependent intensities of HAADF-STEM allowed for more quantitative analysis of the morphologies. HRTEM however was used primarily for examining the overall structure of the tetrapods.

Cryotomography was achieved using an FEI Tecnai Polara fitted with a large objective polepeice gap to give a high tilt range of ± 70° using a liquid nitrogen cooled specimen holder. The low temperature ensured that the specimen would be more resilient to beam damage during the extended data acquisition time. The specimens were tilted between the two tilt extremes in 1° increments; so 140 frames were recorded in total. Using frames from the tilt series, the 3D reconstructions were generated with IMOD using the general back-projection method. An in-house program was used to evaluate the intensities of the Pt/Pd coated tetrapods to distinguish Pt/Pd intensities from the ZnO and vacuum intensities.

Aberration corrected TEM and HAADF-STEM was carried out using a double aberration corrected JEOL 2200FS with better than 0.1 nm resolution. Correcting the aberrations in the STEM probe ensured that the probe was as sharp as possible to ensure maximum intensity which is necessary for examining small structures such as ultrafine nanoparticles.

3. Results and Discussion
Figure 1 shows three different views using the HAADF-STEM. The low magnification image (a) shows a typical tetrapod leg which has hexagonal prism morphology although other structures can also be seen. We believe this to be a consequence of variations in the growth rate. The aberration corrected image (b) shows a section of a tetrapod leg orientated in the [101] zone axis. The uniform contrast at the edge implies that the edge formed by the (110) atomic planes are atomically clean and the (110) facets are flat. The image in (c) is a frame from an IMOD reconstruction of a HAADF-STEM cryotomography series (not shown here). This technique allows straightforward analysis of the morphologies of the tetrapods. The tetrapod shown in (c) has legs that differ from one another but all generally show a hexagonal prism
Figure 1. HAADF-STEM images of ZnO tetrapods with (a) showing a low-mag image of a tetrapod leg, (b) an aberration corrected HAADF-STEM image and (c) showing a frame from a 3D IMOD reconstruction built using a HAADF-STEM tilt series

with hierarchical step. Figure 2(a) shows an HRTEM image of a thin tetrapod suspended over a hole. The angle between the two legs is approximately $112^\circ$. As indicated, each leg grows out in the [0 0 1] direction from the core. It can be seen that near the core there is a high density of defects which appear to be stacking faults and via these stacking faults, the wurtzite arms grow from the core [7]. For small tetrapods there have been suggestions of a zincblende core. The appearance of the atomic columns in the core in (b) looks much like cubic [1 1 0]. To confirm this, the FFT of 2(a) is shown in 2(b) which identifies the zincblende spatial frequencies assuming zincblende ZnO has lattice parameter $a = 0.462$ nm [8]. The FFT can be seen as an overlap of three diffraction patterns, two WZ[1 1 0] and a ZB[1 1 0]. The three crystal directions are identified in (a) and (b). Unlike the HAADF-STEM images in figure 1, the HRTEM images do not quantitatively suggest that the facets are flat. The HRTEM images show what appear to be atomic steps on the facet edges but we believe these may be a result of electron beam damage as their appearance varied between different images of the same area. Separated nanoparticles offer higher surface areas and such a coverage would represent a more realistic catalyst. Figure 3 shows a HAADF-STEM image of the Pt/Pd coated tetrapods and two alternate 3D views from an IMOD reconstruction. The difference in $Z$ between the Pt and Pd is enough to clearly identify the two. The contrast from such particles on an HRTEM image such as figure 2 (b) would make it difficult to distinguish Pt and Pd from ZnO and would suffer from interference effects (e.g. Moire fringes). Overall, the nanoparticles did not seem to prefer a particular $\{1 \overline{1} 0\}$ facet with the coated surfaces showing individual nanoparticles and no evidence of coalescence. We believe such a system could be useful for model catalyst studies.

4. Conclusions
We have demonstrated quantitatively that the facets of hexagonal prism ZnO tetrapod legs are flat using aberration corrected HAADF-STEM and elucidated with 3D HAADF-STEM cryotomography that the $\{1 \overline{1} 0\}$ facets dominate the tetrapod surface area. To investigate the morphology of nanoparticle-ZnO composite systems we sputtered 1.5 nm particles onto the tetrapods. The resulting 3D HAADF-STEM cryotomography demonstrated that the coverage on the coated sides is uniform with minimal coalescence under normal observations. HRTEM showed directly that smaller tetrapods have a ZnO zincblende phase core with the wurtzite legs growing in the WZ[0 0 1] from the ZB{1 1 1} faces via dislocations. We believe the technique and the results could be useful for similar systems in catalysis and technological applications.
Figure 2. HRTEM image of a small tetrapod (a) with the two leg and core crystal directions labelled and its corresponding FFT (b).

Figure 3. Pt/Pd nanoparticle coated ZnO tetrapods with (a) showing a HAADF-STEM image of a coated tetrapod leg and (b) and (c) showing top and bottom views from within a 3D IMOD reconstruction from a HAADF-STEM tilt series. The brighter areas are the Pt/Pd nanoparticles.

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