Atom counting of Au clusters using Cs-corrected HAADF-STEM

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It is essential to know the size of metallic clusters, which lays the foundation of understanding their catalytic properties [1]. Currently, high-resolution transmission electron microscopy (HREM) has been commonly employed, in which the cluster diameter can be measured on phase contrast images. However, the data obtained by this method may not be reliable, particularly when the particles are very small (< 2nm) and/or the substrate is thick. In contrast, the intensity in high-angle annular dark-field (HAADF) images taken in a scanning transmission electron microscope (STEM) is dependent of the atomic numbers of the constituent elements. Using either size-selected clusters or single atoms as a calibrator, the size and shape of nanoparticles can be readily obtained and then linked directly to their catalytic performances [2-4]. In this context, size-controlled Au clusters (N = 25 and 39, when N is the number of atoms in a cluster) were used to verify the methodology of mass quantification reported in one of our earlier works [4, 5]. We demonstrate that precise mass information from clusters in this size range can still be extracted. Further, we show that the technique of HAADF-STEM imaging is in an advantage position over HREM in the structural characterisation of nanoclusters.

The size-controlled Au clusters were prepared on either carbon nanotubes (CNTs) or hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, by a chemical route, with details reported previously [6]. HAADF-STEM images were taken in a JEOL 2100F transmission electron microscope, equipped with a CEOS probe aberration corrector, operated at 200 kV. The semi-convergence angle for the incident electron beam was ~14 mrad and the inner and outer collection angles for the JEOL ADF detector were 55 mrad and 148 mrad, respectively. The integrated intensity of each observed cluster was obtained after a background subtraction with reference to the surrounding areas.

Figure 1 shows a typical pair of a bright-field (BF) and a dark-field (DF) images from the $Au_{25}(SR)_{18}$ (SR = $SC_{12}H_{25}$) clusters on CNTs, taken simultaneously under STEM. The lattice fringes arising from phase contrast from some CNTs are clear in the BF image. The presence of Au clusters is apparent in the DF mage, whilst some of them are hardly visible in the BF image without reference to the DF counterparts. Single Au atoms can be also located in the DF case (circled in Figure 1b). Using the single atoms as an internal intensity standard, we show that majority of the size-controlled $Au_{25}(SR)_{18}$/CNT exist as monomers and very few are identified as dimers.

In the case of Au clusters on HAP, the same atom counting method is applied [7]. Figure 2 is the distribution of the integrated intensities for the Au_{25} clusters, in which multiple peaks are identified by fitting the data using Gaussian functions assessed by the Integrated Complete Likelihood (ICL) criterion. The multiple increment of the peak intensity allows us to associate the first peak with the Au_{25} monomers and the rest to their multiples. This is cross-checked using images from Au39/HAP taken under identical conditions.

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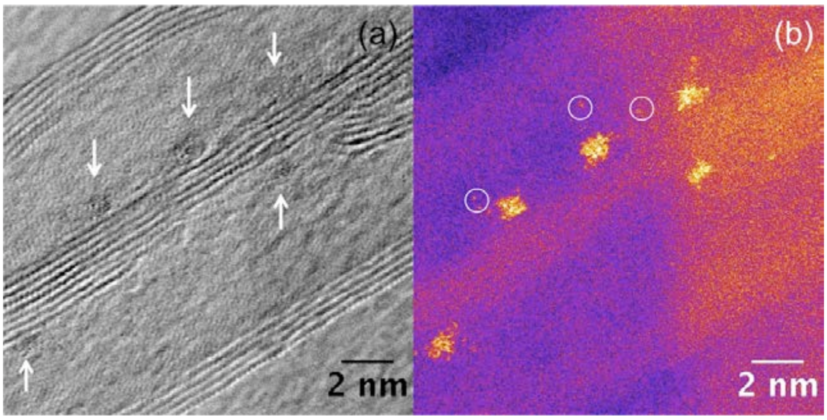

Figure 1. *(a) Bright-field and (b) HAADF images from the Au_{25}/CNT clusters, taken simultaneously in STEM. The locations of the clusters in the bright-field image is arrowed with reference to the dark-field image, where a better contrast is achieved. Single Au atoms are also visible in the dark-field image (circled).*

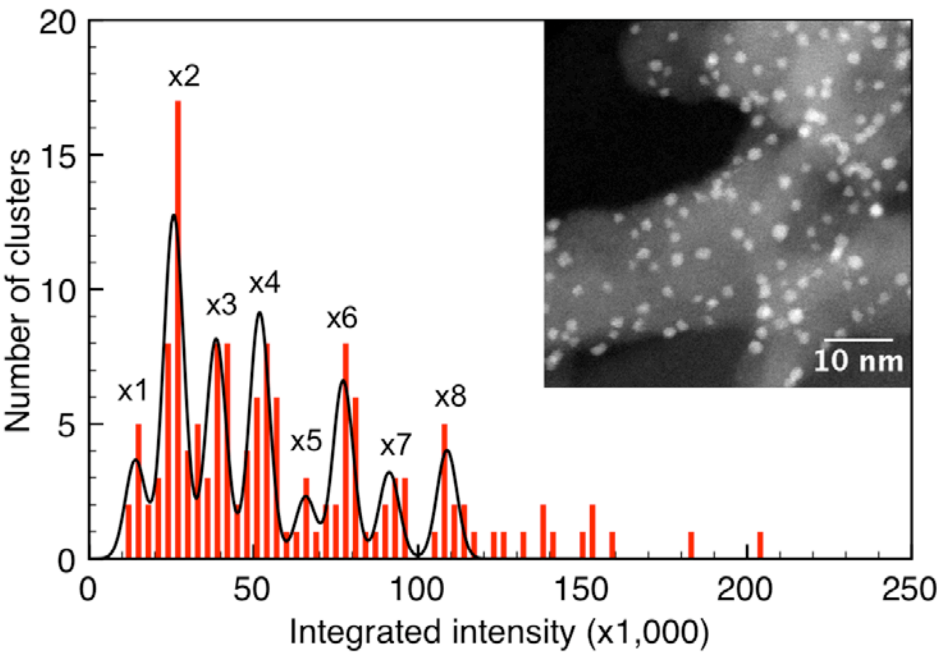

Figure 2. *Histogram of integrated intensity from the Au_{25}/HAP clusters. The data was fitted using the Integrated Complete Likelihood (ICL) criterion for Gaussian functions. The inset is a HAADF-STEM image from this sample.*