Atlas of simulated images for Au_{55} nanoclusters using multislice method

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Research of nanoclusters is crucial for to understanding of why and how nanostructures are different from bulk materials in many aspects. Their structures have strong connections to their unusual properties. To probe their structures experimentally, we employed aberration-corrected scanning transmission electron microscopy that could provide us with resolution of sub-Angstrom level on these nanoclusters of only from tens to a hundred Angstroms in diameter. However, the structure of clusters cannot be resolved solely by high-resolution images, because STEM images are 2D projections of electron-atom interaction with 3D structure of clusters. To solve this problem, we conduct image simulation based on a multislice method which interaction between electrons and clusters are treated as electron interaction with each slice of the 3D structure individually in orders. We generate simulated images from various directions of the cluster and portrait simulated image atlas for the cluster. We then match each experimental image with a simulated image in the atlas. In this research, we find the positive matches between experimental images of size-selected Au55 clusters and simulated images calculated from a DFT theoretically predicted Au55 chiral model.

A Nano cluster is defined as an aggregation of atoms containing between 2 to 200,000 atoms. Clusters have attracted a lot of research interests due to their sizes and structures, which are between molecular and microcrystalline and are essential for their properties. Now clusters are considered a new kind of nanomaterial. Size-selected clusters are used to etch nanoscale structures for nanofabrication [1], some small clusters are catalysts for chemical reactions [2,3] while some big clusters can be used to mark protein molecules in biology [4].

$Au_{55}(PPh_3)_{12}Cl_6$ is a very famous cluster due to its unique electronic properties given that it can act as a single electron switch. It has the potential application to be the next generation fast and energy saving electronic switch or transistor [2]. But since it firstly synthesized in 1981, the argument about what structure it has have never been agreed upon. At first Schmid proposed it had a cuboctahedral structure by the molecular weighing that determined the molecular formula and Mossbauer spectra that showed 4 types of Au atoms. Later, the X-ray powder diffraction research showed that the icosahedral structure seemd more likely to be the structure of the $Au_{55}(PPh_3)_{12}Cl_6$ clusters [5-7]. To investigate the atomic structure of $Au_{55}(PPh_3)_{12}Cl_6$, aberration corrected High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) was used.

Electron microscopy is a powerful tool to characterize the structure of material [8] and make one of the inventors, Ernst Ruska, to win a nobel prize in 1986. A Scanning Transmission Electron Microscope uses an electron source to produce the electron beam to scan over the specimen, a detector under the sample is employed to detect the scattering signal to form an image [9]. By the developing of aberration correction technology, the resolution of an aberration corrected STEM can reach sub-Angstrom now. The HAADF imaging uses a detector to select the high angle scattered electron which can be regard as Rutherford scattered electrons. So the intensity of a HAADF image is directly proportional to Z^n. (Z is atomic number of the object material, n is an index which is determined by each STEM) So HAADF image are also called Z-contrast images.

When the high-resolution STEM images were gotten, how to characterize the clusters' structure would be a problem. An idea is to assume a structure, then simulate the STEM images of it, then check if the real-space STEM images matched with them. If yes, this material should be has the same structure of the model. The multislice method is the most popular approach of EM image simulation. The principle of it is to divide the material potential to many slices and projected onto a plane vertical to the observation orientation. Then calculate the first slice's beam diffraction and do the propagation from one slice to another and finally get the wave function of the surface of the material. In our research, a software package called QSTEM that is based on multislice method was used to do the STEM image simulation.

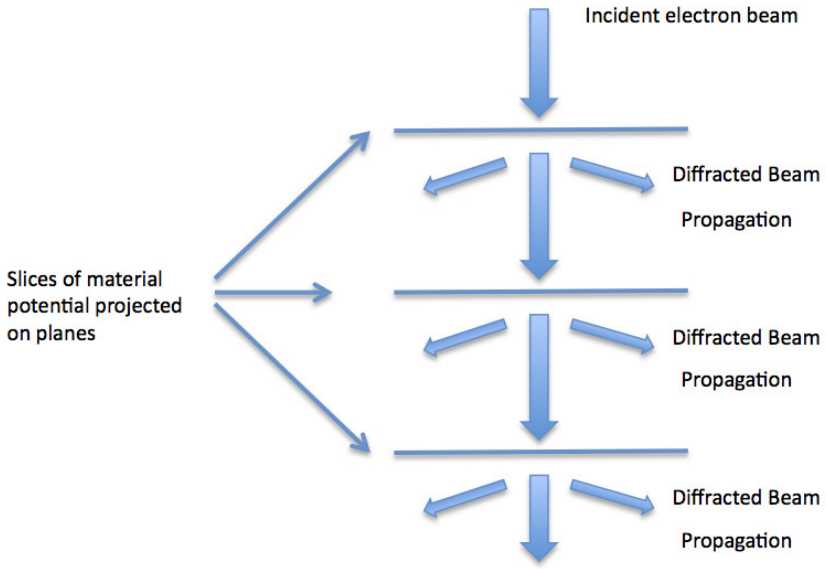

Figure 1: Schematic of multislice method

Although we can simulate the STEM image of nanoclusters, the image can only give us 2D information. To avoid this drawback, we present a simulation atlas which is a set of simulation images from every possible observation orientations. So no matter from which orientation the cluster was imaged, we can find a relevant simulation image to compare with. This approach extremely increases the efficient of cluster structure characterization. In our research, there are 4 structure models (chiral, cuboctahedral, icosahedral and decahedral) used to simulate the STEM images. There are hundreds simulation images, so to simplify the comparison work we divide all the simulation images into 7 groups base on their image pattern features. When do the comparison work, at first, classify the experimental image with their pattern feature, then compare it with its corresponding simulation group, finally find the closest simulation. This will avoid wasting time comparing obviously different images.

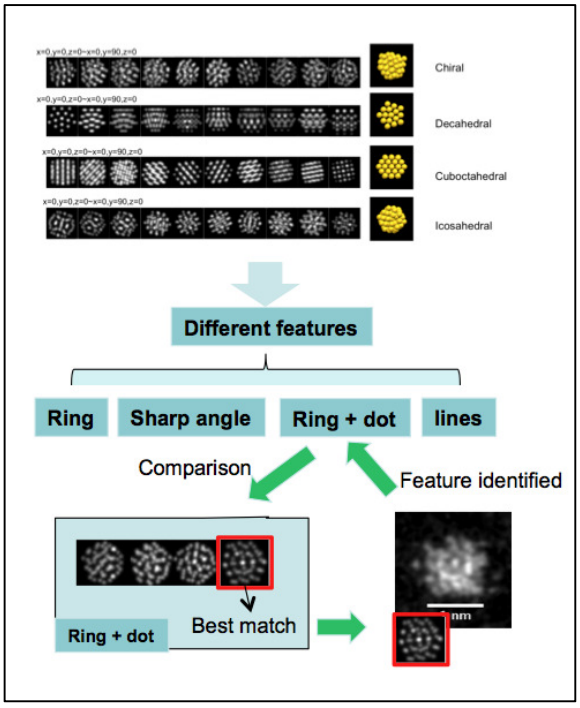

Figure 2 the schematics of the simulation atlas and comparison process

Before characterizing the cluster structure, the cluster weighing is necessary to verify the cluster we investigate is the $Au_{55}(PPh_3)_{12}Cl_6$ cluster. Using the Z-contrast feature of HAADF image, size-selected Au_{309} clusters were used as mass balance to weigh the $Au_{55}(PPh_3)_{12}Cl_6$ cluster. The result showed that the $Au_{55}(PPh_3)_{12}Cl_6$ clusters have 53.38 ± 3.16 Au atoms in average. So they can be considered as $Au_{55}(PPh_3)_{12}Cl_6$ clusters. We also measure the clusters' radius and their aspect ratio. The figure below shows the distribution of their radius and aspect ratios, they have an average radius of 1.405nm which convinced with many previous studies on the $Au_{55}(PPh_3)_{12}Cl_6$ clusters that they have a diameter of 1.4 nm [1-3]. Their aspect ratios are not focus on one peak but last from 1.05 to 1.6. Which shows the clusters do not have a symmetry structure.

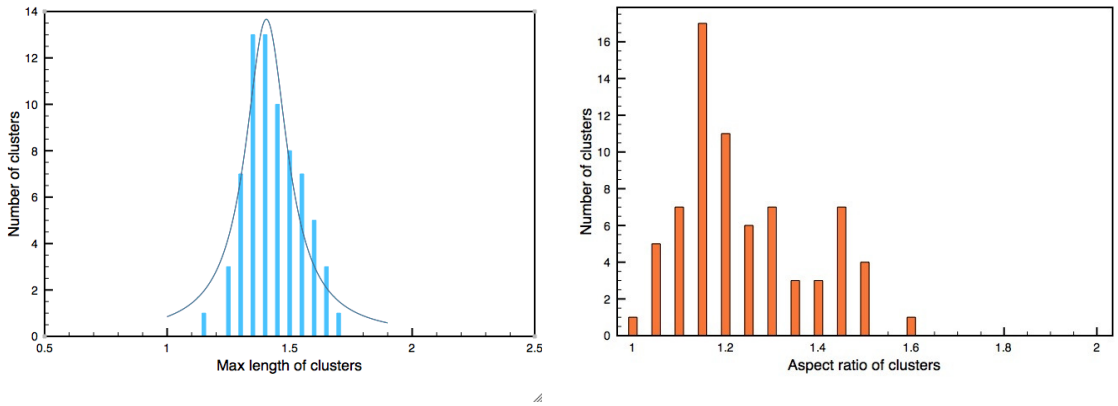

Figure 3 (a) The distribution of the radius of $Au_{55}(PPh_3)_{12}Cl_6$. (b) The distribution of the aspect ratio of $Au_{55}(PPh_3)_{12}Cl_6$.

After the comparison of all 72 clusters that have 55±2.5 Au atoms, there were 38 clusters showed a best match to the chiral structure model simulation. Very few cluster matched the cuboctahedral and

no decahedral and icosahedral have been found. Nearly half of the clusters showed an amorphous structure. This result, combined with the aspect ratio study can suggest that the chiral structure is the majority structure for $Au_{55}(PPh_3)_{12}Cl_6$. Below are some example of structure model and comparison results.

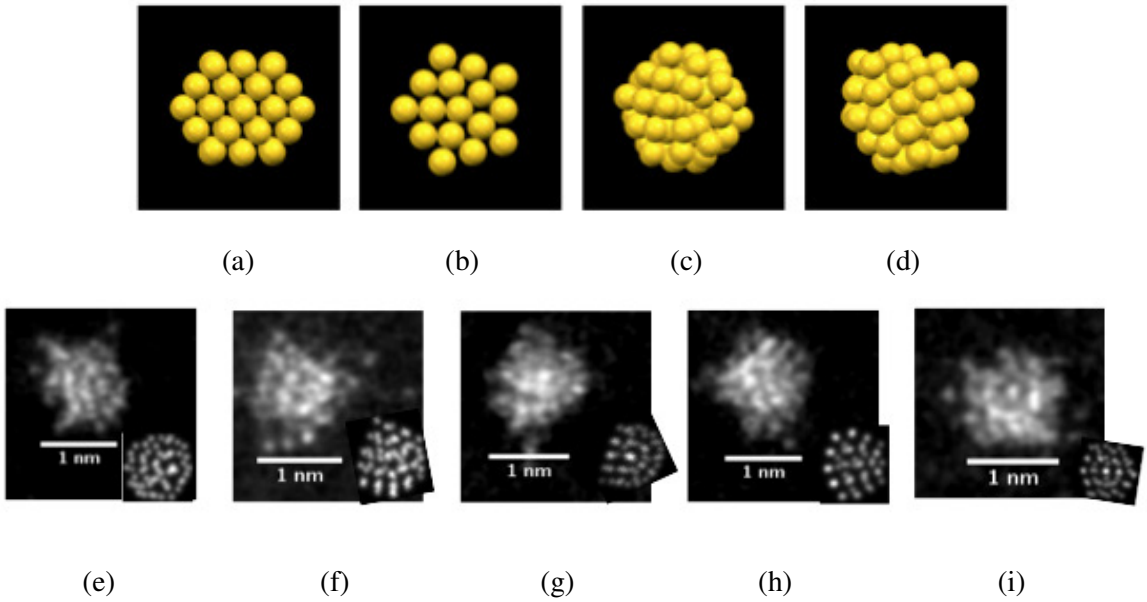

Figure 4 (a)-(d) model of cuboctahedral, decahedral, icosahedral and chiral. (e)-(i) comparison result

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