Particle size distribution of supported gold single atoms and sub-nano clusters analyzed by global high-resolution HAADF-STEM observation with morphological image-processing operation

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Au sub-nano clusters have been investigated their high catalytic activities for aerobic oxidation, CO oxidation, etc.[1-3] Catalytic performance has correlation with particle size variations on the atomic level not only for Au but for other various metals.[4] HAADF-STEM employing Cs-corrected TEM is very useful for characterization of supported metals. However, the atomic resolution observation displays very narrow areas. To avoid intentional analysis, global observation and particle-size analytical methods are demanded. Therefore, we propose a morphological image process.[5]

Morphological image-processing operation was performed by dilation and/or erosion processing of an original image (X) by a structure element (Y). The X and Y are in Euclidean N-space defined as E^N. The dilation of X by Y is defined as below:

$$X \oplus Y = \{z \in E^N \mid z = x + y, x \in X, y \in Y, z \in Z\} = \cup_{y \in Y} (X + y)$$

where Z is the resulting image. The erosion of X by Y is defined as follows:

$$X \ominus Y = \{y + z \in X, y \in Y, z \in Z\} = \cup_{y \in Y} (X - y)$$

The morphological opening operation is erosion followed by dilation, which keeps objects bigger than a defined Y, but can blend out objects smaller than the Y. The morphological closing operation is dilation followed by erosion, which can fill in the hollows smaller than a defined Y between objects.

Figure 1(a) shows Z-contrast image of Au supported on Al_2O_3. Figure 1(b) created by the opening operation is a background-image of Figure 1(a). The image subtracted Figure 1(b) from Figure 1(a) was then binarized, removed the remained noises by an opening operation, connected divided spots that were originally one cluster by a closing operation, and corrected the size difference between electron probe and the atomic diameter by dilation. The resulting image is Figure 1(c). For comparison of background processing, the Gaussian blurring filter was applied to Figure 1(a). The image subtracted filtered Figure 1(a) from Figure 1(a) was applied same image processing as above. As shown in the resulting Figure 2, some clusters were divided into smaller clusters. In addition, the number of single atom was less than Figure 1(c). They are considered due to the blurring effect of Gaussian filter.

Figure 3 is the size distribution histogram which was obtained from fifty non-overlapping images by the morphological operations. Isolated individual Au atoms were present in the greatest number, and the cluster number decreased with an increase in the size. The number of Au atoms comprising each cluster was calculated under assumption of all clusters were semispherical. Figure 4 shows the histogram for the number of atoms. Au clusters ranging 0.6–0.9 nm showed the highest number, which is consistent with the size of Au_{13} cluster. The EXAFS analysis which provides average structural information also suggested the formation of Au_{13} cluster. Therefore, this analytical method gives quantitative particle size distribution.

References
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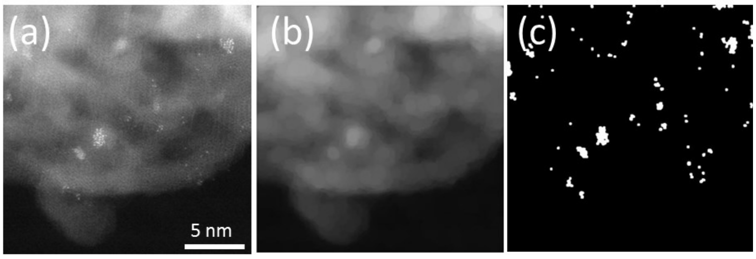
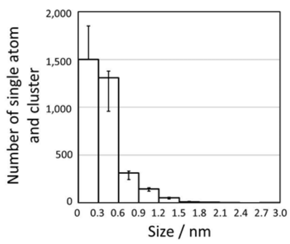


FIG. 1. (a) an original image, (b) background-image of (a), (c) the resulting image.



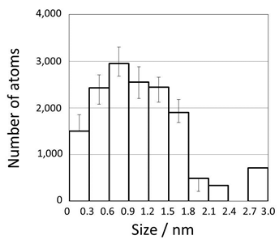


FIG. 2. the resulting image of FIG.1(a) processed by Gaussian filter.
FIG. 3. Particle size distribution for the number of clusters and individual atoms.
FIG. 4. Histgram for the number of atoms. (starting from the left)