Atomic and isomeric high-resolution separation of thiolate-protected alloy clusters by reversed-phase high-performance liquid chromatography

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By doping heteroatoms to thiolate-protected gold clusters, we can add more functionality to the cluster depending on the number of doped heteroatoms and the difference in doping positions. However, in the synthesis of alloy clusters, the mixture of clusters with a different number of heteroatoms is produced. Therefore, a precise separation of each cluster is required to understand their properties. In this study, we attempted to separate gold-silver alloy clusters precisely, furthermore investigated isomer change by reversed-phase high-performance liquid chromatography (RP-HPLC). Au_{38-n}Ag_{n}(SC_4H_9)_{24} was used as a sample. This cluster was synthesized by two methods, (1) by adding [Ag(SC_4H_9)] complex to Au_{38}(SC_4H_9)_{24} (metal exchange) and gold and silver ions were reduced in the presence of butanethiol in solution (co-reduction). The mixture of alloy clusters was separated by RP-HPLC using gradient program for controlling mobile phase, and core-shell type column. The peaks obtained from the chromatogram were evaluated by electrospray ionization (ESI) mass spectrometry connected to RP-HPLC directly.

Figure 1 (a) shows the chromatogram of Au_{38-n}Ag_{n}(SC_4H_9)_{24} obtained by the metal exchange. Some clear peaks were observed in chromatogram. Each peak was attributed to the cluster having a precise number of silver atoms (Figure. 1(b)). These results indicate that the mixture of Au_{38-n}Ag_{n}(SC_4H_9)_{24} was precisely separated according to the number of silver atom. Furthermore, the shape of chromatogram of Au_{38-n}Ag_{n}(SC_4H_9)_{24} prepared by the metal exchange changed by leaving this cluster in toluene for 6 days (Figure. 1(c)). Interestingly, the shape was similar to that of Au_{38-n}Ag_{n}(SC_4H_9)_{24} prepared by the co-reduction (Figure. 1 (d)). These results suggest that Au_{38-n}Ag_{n}(SC_4H_9)_{24} prepared by the metal exchange contains metastable clusters, these are transformed to the stable clusters by leaving in toluene. In conclusion, we have succeeded in the high-resolution separation of alloy clusters according to each chemical composition, and observation of isomer transformation.

Recent Publications


Biography

Sayaka Hashimoto received her BSc in Applied Chemistry at Tokyo University of Science, Japan, in 2018. Her main research interest and work includes "Establishment of high resolution-separation technique of reversed-phase high-performance liquid chromatography (RP-HPLC)." She has recently succeeded in separating gold-silver alloy cluster by improving the resolution of RP-HPLC.

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