数理物質科学研究科　博士論文の要約

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博士論文題目　　Synthesis and Optical Properties of Polyhedral Inorganic Nanostructures
（多面体無機ナノ粒子の合成と光学特性）

論文目次

Chapter 1　General Introduction

Shape, size, composition and crystal structure are important factors that determine intrinsic properties of nanocrystals. Particularly, the synthesis of nanocrystals with various morphologies is necessary for demonstrations of their shape- and facet-dependent optical, catalytic, electrical, and surface properties. In this study, polyhedral gold nanocrystals with well-controlled shapes and sizes were synthesized (chapter 2), and a comparative study of the polyhedral gold nanocrystals as surface-enhanced Raman scattering (SERS) were carried out (chapter 3). Furthermore, the shape of nanocrystals can be used to control the crystal structure of nanocrystals via ion exchange reactions. Crystal structure is an important factor to greatly affect electronic and optical properties of semiconductor nanocrystals. Cu_xS and CdS nanocages with well-controlled crystal structure were synthesized by using different shapes of Cu_2O nanocrystals as templates (chapter 4). Metal-semiconductor binary hybrid nanocrystals have offered potential enhanced functions. The crystal structural and size controlled nanocages with encapsulated gold nanocrystals were also synthesized, and the structure-specific optical properties are under investigation (chapter 5).

Chapter 2　Shape-Controlled Synthesis of Polyhedral Gold Nanocrystals

We report the synthesis of gold nanocrystals with a systematic shape evolution from cubic to rhombic dodecahedral structures by a seeding growth approach. Briefly, an Au seed (~3 nm) nanocrystal solution was prepared first. A small volume of this solution was added to an aqueous growth solution (10 mL) containing

cetyltrimethylammonium chloride (CTAC, 1.0 mmol) surfactant, $HAuCl_4$ (2.5 μmol), NaBr (0.1 μmol), and ascorbic acid (3.6 ~ 6.0 μmol). After mixing for ~5 s, a small volume of this solution (Au: 0.25 mM) was added to another growth solution. The solution was left undisturbed for 15 min in a 30^{o}C water bath for nanocrystal growth. Unusual cubic, trisoctahedral, and rhombic dodecahedral structures can be synthesized by using CTAC surfactant as a capping agent and ascorbic acid as a reducing agent for $HAuCl_4$ in the presence of NaBr (see **Figure 1**). The transitional products can also be prepared. The shape evolution can be achieved by adding different amounts of ascorbic acid. By increasing the amount of ascorbic acid, the gold nanocrystals formed can be transformed from cubes to trisoctahedra, and then to rhombic dodecahedra.

Structural characterization confirmed that the cubes are bounded by {100} facets, whereas the rhombic dodecahedra are bounded by {110} facets. We have successfully used a systematic method to synthesize gold nanocrystals with entirely {100} or {110} facets and found the relationships among these shapes. Truncated cubes can also be synthesized by using this growth approach. These nanocrystals should allow the examination of their various properties as a function of particle shapes and surfaces.

By introducing different quantities of the seed solution, we were able to successfully control the size of the cubic and rhombic dodecahedral gold nanocrystals. The more seed solution was added, the smaller the particle size is. As the amount of the seed solution increased from 25 μL to 45 μL and 65 μL, the edge length of the gold cubes and rhombic dodecahedra changed from 75 nm to approximately 55 nm and 40 nm. The gold nanocubes became smaller to a size of approximately 30 nm by adding 100 μL of the seed solution.

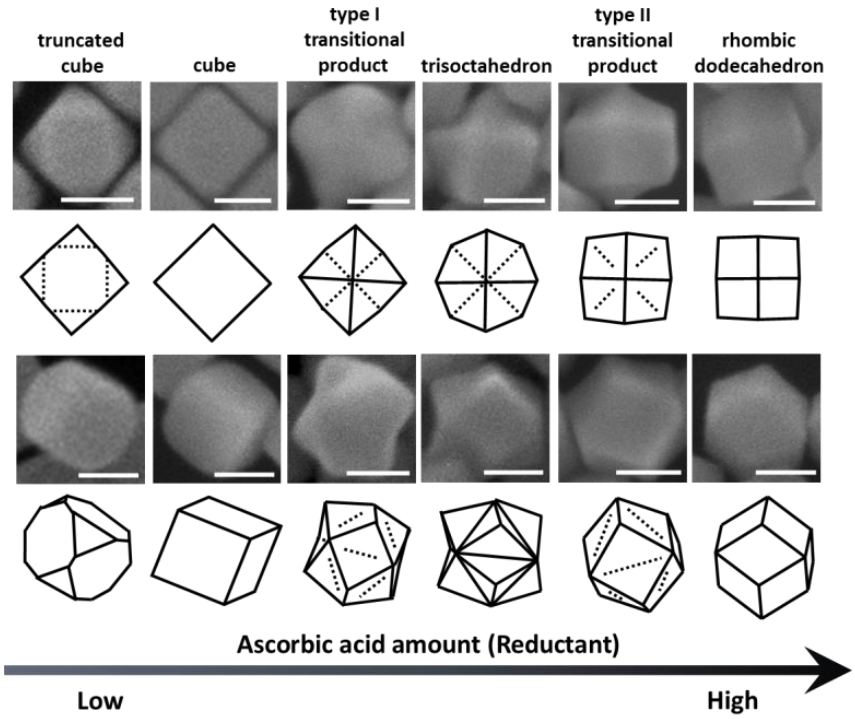

Figure 1. SEM images and the corresponding drawings showing the morphological evolution of the gold nanocrystals synthesized by varying the amount of ascorbic acid added to the reaction solution. Two different particle orientations are shown for each sample. All scale bars represent 50 nm.

Furthermore, the shape evolution from trisoctahedral to octahedral structure was also achieved by decreasing the amount of ascorbic acid (see **Figure 2**).

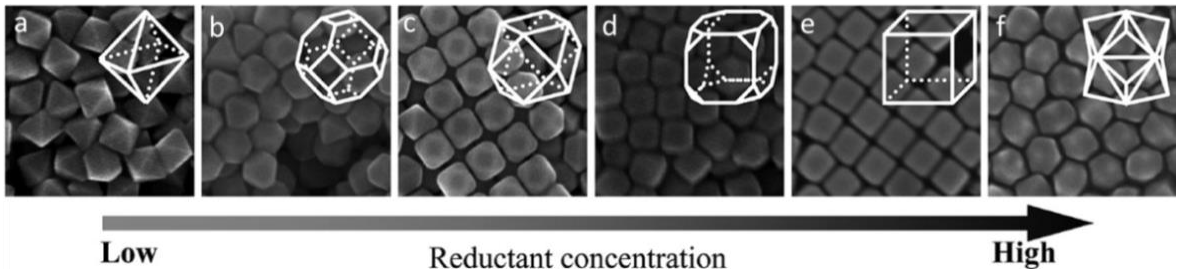

Figure 2. SEM images of well-faceted polyhedral Au nanocrystals. The shape and the concentration of ascorbic acid for each nanocrystal type were (a) octahedron, 0.6 mM; (b) truncated octahedron, 1.2 mM; (c) cuboctahedron, 1.4 mM; (d) truncated cube, 1.8 mM; (e) cube, 2.0 mM; and (f) trisoctahedron, 10 mM.

By adjusting the concentration of ascorbic acid in the growth solution, the feeding rate of gold atom on the crystal surface changes, that is, the relative growth rates along the lattice directions, <111>, <100> and <110> directions, can be tuned to form the various nanostructures.

Chapter 3 A Comparative Study of Polyhedral Gold Nanocrystals as Highly Sensitive SERS Substrates

Gold nanocubes, octahedra, and rhombic dodecahedra with roughly two sets of particle sizes have been successfully synthesized via a seed-mediated growth approach (see **Figure 3**). All six samples were analyzed for comparative surface-enhanced Raman scattering (SERS) activity. All of these Au nanostructures were found to yield strong enhancement at a thiophenol concentration of 10^{-7} M, and are excellent SERS substrates. Rhombic dodecahedra with a rhombus edge length of 32 nm showed significantly better enhancement than the other samples, and can reach a detection limit of 10^{-8} M. The SERS intensity can be expressed as $I_{SERS} = k \times P \times I^2 \times N$, where k is a proportional constant including the information on the detection efficiency of the optical system, P is the polarize ability of the molecules binding to the surface, I is the electric near-field intensity, and N is the average number of molecules binding to the metal surface that give SERS signals. The calculation results showed that rhombic dodecahedra with a rhombus edge length of 32 nm had the largest binding energy of thiophenol on gold faces and electric near-field intensities among these nanocrystals, which accounted for the experimental observation of these nanocrystals as the best and most sensitive SERS substrates. Superior SERS activity of these nanocrystals can be expected toward detection of many other molecules.

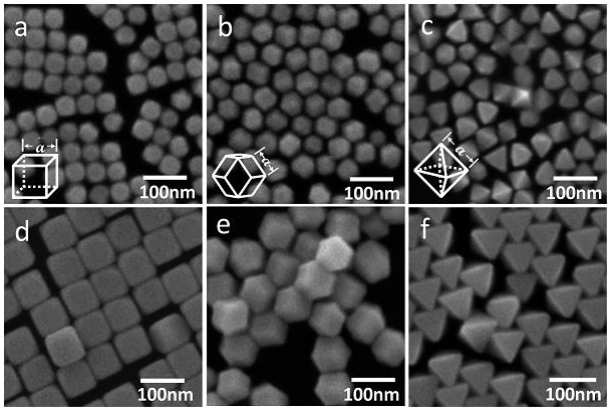

Figure 3. SEM images of (a, d) cubic, (b, e) rhombic dodecahedral, and (c, f) octahedral gold nanocrystals with edge lengths of (a) 44, (b) 32, (c) 53, (d) 72, (e) 43, and (f) 75 nm. Geometric models and edge lengths of these nanocrystals are also provided.

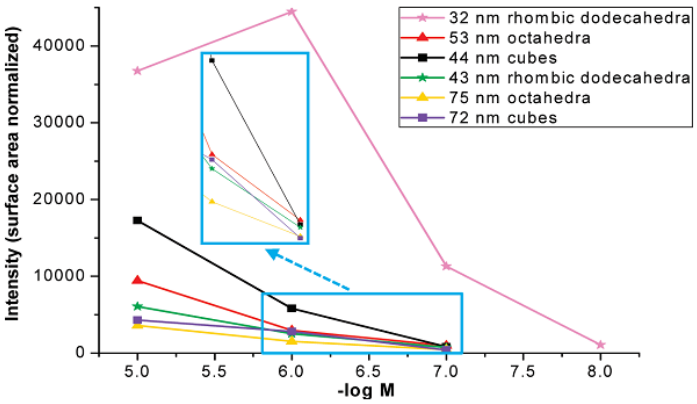

Figure 4. A plot of the total particle surface-area-normalized SERS intensities of the band at 998 cm^{-1} versus thiophenol concentrations in the Au nanocrystal solutions. Data points at a 1.0 x 10^{-6} M thiophenol concentration have been expanded to make their relative intensities visible.

Chapter 4 Shape Dependent Crystal Structural Control of Semiconductor Nanocages

We report a discovery that the crystal structures of Cu_xS nanocages can be controlled by using different shapes but the same crystal phase of Cu_2O as templates. We first synthesized cubic and rhombic dodecahedral Cu_2O nanocrystals. Na_2S solution was used to sulfidate Cu_2O nanocrystals, forming $Cu_2O@Cu_xS$ core-shell nanocrystals, followed by etching the interior Cu_2O cores with HCl solution. By conducting further cation exchange of Cu_xS cages with Cd^{2+}, cubic CdS cages with mainly zinc blende structure and rhombic dodecahedral CdS cages with wurtzite structure were obtained.

Chapter 5 Crystal Structural and Size Control of CdS Shells with Encapsulated Gold Nanocrystals

Binary hybrid nanocrystals have offered potential enhanced functions, such as energy/charge transfer between metal and semiconductor, which has been used as photocatalyst. The CdS shells with encapsulated gold nanocrystals were synthesized by the Cu_2O-templated method, which was similar to the method for shape dependent crystal structural control of Cu_xS and CdS nanocages. By using rhombic dodecahedral gold nanocrystals as the cores, both cubic and rhombic dodecahedral CdS shells could be achieved. When using cubic gold nanocrystals as the cores, only cubic CdS shells were formed. The size of the CdS shells could be controlled by adjusting the amount of Cu precursor while synthesizing Cu_2O templates. The CdS cubic cage's size deceased from ~160 nm to ~100 nm, whereas the CdS rhombic dodecahedral cages directly contacted gold cores instead of forming cages. In order to elucidate the interaction between the CdS shell and the gold core, transient absorption measurements of these special Au@CdS yolk-shell nanostructures were investigated.

Chapter 6 Conclusions

In this study, polyhedral gold nanocrystals with well-controlled shapes and sizes were synthesized and they were found to serve as highly sensitive SERS substrates. In addition to the shape control of polyhedral gold nanocrystals, the shape of nanocrstals could be applied to control the crystal structure of semiconductor ionic nanocrystals via ion exchange reactions. Different shapes of Cu_2O nanocrystals were used as a template to control the crystal structure of Cu_xS and CdS nanocages. The crystal structure-controlled CdS nanocages with encapsulated gold nanocrystals, Au@CdS yolk-shell nanocrystals, were also synthesized by using specific shape of gold nanocrystals. Optical properties of these special structural nanocrystals with well-controlled shapes and crystal structures are under investigation. Because of their high quality and unusual structures, these nanocrystals are believed to allow us to examine their various properties as a function of particle shapes, surfaces and crystal structures.

【Publication list】

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