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# Controlled Thiolate-Protected Gold and Alloy Clusters

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Additional information is available at the end of the chapter

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## Abstract

Small metal clusters exhibit physical and chemical properties that differ substantially from those of corresponding bulk metals. Furthermore, the properties of clusters vary greatly depending on the number of constituent atoms. Metal clusters with these characteristics currently attract great attention in a wide range of fields as new nanoscale functional materials. In recent years, the techniques to precisely synthesize metal clusters protected with organic ligands and polymers with atomic precision have advanced dramatically. In addition, substantial knowledge of the size-specific physical/chemical properties exhibited by these metal clusters has been accumulated. In this chapter, we describe the precise synthesis methods of the most studied thiolate (SR)-protected gold clusters  $Au_n(SR)_m$  and their heteroatom-substituted clusters (alloy clusters).

**Keywords:** gold clusters, alloy clusters, precise synthesis, fractionation, size focusing, metal exchange

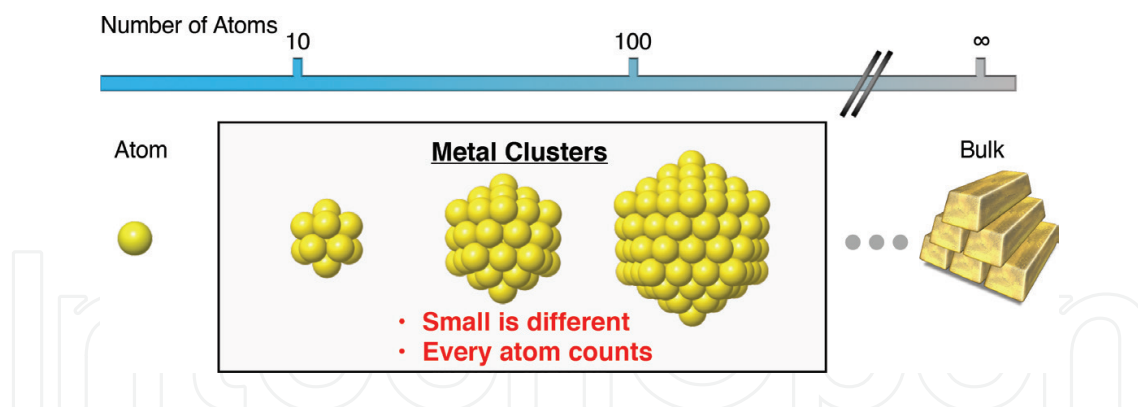
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## 1. Introduction

Substances in our surroundings are composed of assemblies of atoms. For example, a metal is a conglomerate of a nearly infinite number of metal atoms. By contrast, certain substances are made up of a countable number of metal atoms. These substances are called “metal clusters” because their shape resembles grape clusters. Although no clear definition of metal clusters has been established, the term generally refers to an aggregate of two to several hundred metal atoms (**Figure 1**); most such aggregates have a superfine size of 2 nm or less.

The proportion of surface atoms in metal clusters differs substantially from that in bulk metals. Taking a metal cluster with an icosahedral structure as an example, a metal cluster with

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**Figure 1.** Relation of metal clusters discussed in this chapter to a single atom and the bulk metal.

55 atoms (**Figure 1**) has 42 surface atoms, corresponding to 76.3% of the total atom number. In the case of a 13-atom metal cluster (**Figure 1**), 12 atoms are on the surface, corresponding to 92.3% of the total atoms. In bulk metals (**Figure 1**), the proportion of surface atoms is only approximately 0.00001% in a cube of 1 cm<sup>3</sup>. Thus, compared with bulk metals, metal clusters have a much higher proportion of surface atoms available to react with other substances. Moreover, in addition to these geometric features, metal clusters also exhibit particular characteristics related to their electronic structures. Bulk metals have an electronic structure in which the valence and conduction bands are connected. Conversely, discretization of the electronic structure occurs in metal clusters because of the small number of constituent atoms.

Because of these geometric and electronic features, metal clusters exhibit physical and chemical properties that differ from those of the corresponding bulk metals. For example, although bulk gold (Au) is an inactive metal, as its size decreases to the cluster level, Au exhibits high catalytic activity in various oxidation and reduction reactions [1, 2]. Furthermore, the size-specific properties of clusters greatly vary depending on the number of constituent atoms. **Figure 2** shows a photograph of aqueous solutions of thiolate (SR)-protected Au clusters (approximately 1 nm in size) with 10–39 gold atoms [3]. The color of the cluster solutions differs substantially depending on the number of constituent atoms in the clusters. This diversity of colors can be attributed to the aforementioned discrete electronic structure of clusters.

As illustrated above, metal clusters exhibit physical and chemical properties that differ substantially from those of bulk metals despite being composed of the same elements. Furthermore, the properties of clusters vary greatly depending on the number of constituent atoms. Because of their very small size, clusters contribute to the miniaturization of materials and conservation of resources. Thus, metal clusters currently attract great attention in a wide range of fields as new nanoscale functional materials.



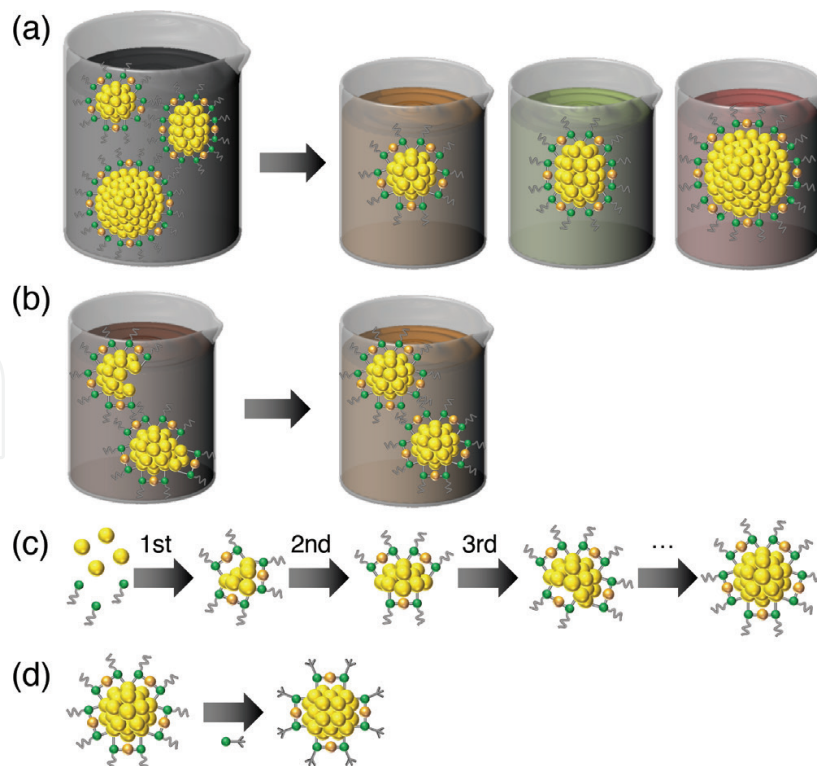
**Figure 2.** Photograph of aqueous solutions of glutathionate-protected Au<sub>n</sub> clusters [3].

In recent years, the atomically precise synthesis of metal clusters protected with organic ligands [4–19] and polymers [20, 21] has advanced dramatically. In addition, substantial knowledge about the size-specific physical/chemical properties exhibited by these metal clusters has been gathered. In this chapter, we describe the precise synthesis methods of the most-studied SR-protected Au clusters,  $\text{Au}_n(\text{SR})_m$ , and their heteroatom-substituted clusters, which are called alloy clusters.

## 2. Gold clusters

As described in Section 1, the properties of metal clusters vary greatly depending on the number of constituent atoms (**Figure 2**). Therefore, it is important to synthesize clusters with atomic precision to produce clusters with controlled functions. Typically,  $\text{Au}_n(\text{SR})_m$  clusters with a defined number of constituent atoms are synthesized by one of the following four methods [22]:

- (i) High-resolution separation of a mixture of clusters of various sizes according to the number of constituent atoms (**Figure 3(a)**).
- (ii) Exposure of a mixture of clusters of various sizes to extreme conditions followed by the collection of only those clusters stable under such conditions (**Figure 3(b)**).



**Figure 3.** Typical methods for the precise synthesis of  $\text{Au}_n(\text{SR})_m$  clusters [22]: (a) fractionation, (b) size focusing, (c) slow reduction, and (d) transformation from one stable size to another.

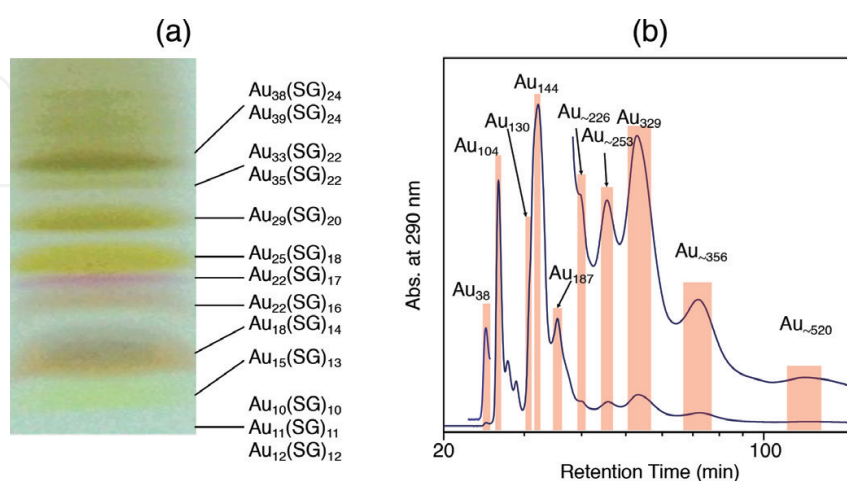
- (iii) Controlling the growth rate of the clusters to obtain a uniform chemical composition (**Figure 3(c)**).
- (iv) Replacing the ligands of the cluster with ligands having different bulkiness to render clusters with a different chemical composition stable (**Figure 3(d)**).

Hereafter, each of these methods is explained in detail.

## 2.1. Fractionation

$\text{Au}_n(\text{SR})_m$  clusters are generally prepared by adding a reducing agent to a solution containing a thiol and Au ions [23]. The aggregation of the resultant Au atoms leads to the formation of  $\text{Au}_n(\text{SR})_m$  clusters, and the products obtained by this method normally have a distribution in their number of constituent atoms [3, 4, 24–29]. The high-resolution separation of such a mixture according to the number of atoms is one of the most efficient methods of obtaining  $\text{Au}_n(\text{SR})_m$  clusters with well-defined numbers of constituent atoms (**Figure 3(a)**).

Polyacrylamide gel electrophoresis is a highly effective technique for separating hydrophilic SR-protected  $\text{Au}_n(\text{SR})_m$  clusters [3, 25, 26, 30, 31]. Using this method, clusters, such as  $\text{Au}_{10}(\text{SG})_{10}$ ,  $\text{Au}_{15}(\text{SG})_{13}$ ,  $\text{Au}_{18}(\text{SG})_{14}$ ,  $\text{Au}_{22}(\text{SG})_{16}$ ,  $\text{Au}_{22}(\text{SG})_{17}$ ,  $\text{Au}_{25}(\text{SG})_{18}$ ,  $\text{Au}_{29}(\text{SG})_{20}$ ,  $\text{Au}_{33}(\text{SG})_{22}$ , and  $\text{Au}_{39}(\text{SG})_{24}$  (SG = glutathionate), have been isolated with high purity (**Figure 4(a)**) [3]. Fractional precipitation [32] and fractional extraction [33–35] have been primarily employed to separate hydrophobic RS-protected  $\text{Au}_n(\text{SR})_m$  clusters. In addition to these frequently used conventional methods, reverse-phase high-performance liquid chromatography has also recently proved very effective for the high-resolution separation of both types of  $\text{Au}_n(\text{SR})_m$  clusters [27–29, 36–38].  $\text{Au}_n(\text{SC}_{12}\text{H}_{25})_m$  clusters with a wide range of sizes, from  $\text{Au}_{38}(\text{SC}_{12}\text{H}_{25})_{24}$  to  $\text{Au}_{-520}(\text{SC}_{12}\text{H}_{25})_{-130}$ , have been systematically isolated by this method (**Figure 4(b)**) [28]. Thus, several methodologies have been established to date for the fractionation of  $\text{Au}_n(\text{SR})_m$  clusters, and precise systematic isolation can be now achieved for  $\text{Au}_n(\text{SR})_m$  clusters protected with either hydrophilic or hydrophobic SR using these techniques.



**Figure 4.** Examples of the precise synthesis of  $\text{Au}_n(\text{SR})_m$  clusters by fractionation: (a) separation of  $\text{Au}_n(\text{SG})_m$  clusters by polyacrylamide gel electrophoresis and (b) separation of  $\text{Au}_n(\text{SC}_{12}\text{H}_{25})_m$  clusters by reverse-phase high-performance liquid chromatography. Figures were adapted from Refs. [3, 28], respectively.



## 2.2. Size focusing

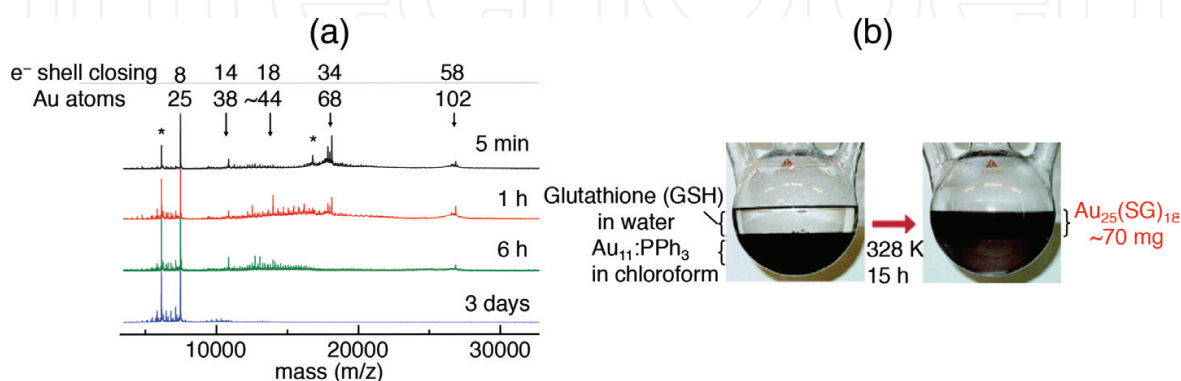
The fractionation methods noted above are suitable for the systematic isolation of a series of  $\text{Au}_n(\text{SR})_m$  clusters. However, these methods are not suitable for mass production. To synthesize  $\text{Au}_n(\text{SR})_m$  clusters with a specific chemical composition on a large scale (~100 mg), it is necessary to conduct selective synthesis, and size focusing is an effective means of doing so (**Figure 3(b)**). Several  $\text{Au}_n(\text{SR})_m$  clusters show higher resistance to deterioration in solution [3] or thiol etching [39–42] than other clusters of the same type. The less stable clusters can be converted into stable clusters when exposed to extreme conditions [39–42]. As an example, when  $\text{Au}_n(\text{SR})_m$  clusters ( $\text{SR} = \text{SC}_2\text{H}_4\text{Ph}$ ;  $25 \leq n < 102$ ,  $\text{SR} = \text{SG}$ ;  $25 \leq n < 38$ ) are exposed to extreme conditions, unstable  $\text{Au}_n(\text{SR})_m$  clusters are transformed into stable  $\text{Au}_{25}(\text{SR})_{18}$  cluster. Stable clusters can be precisely synthesized on a large scale with this size-focusing method (**Figure 5(a)** and **(b)**).

## 2.3. Slow reduction

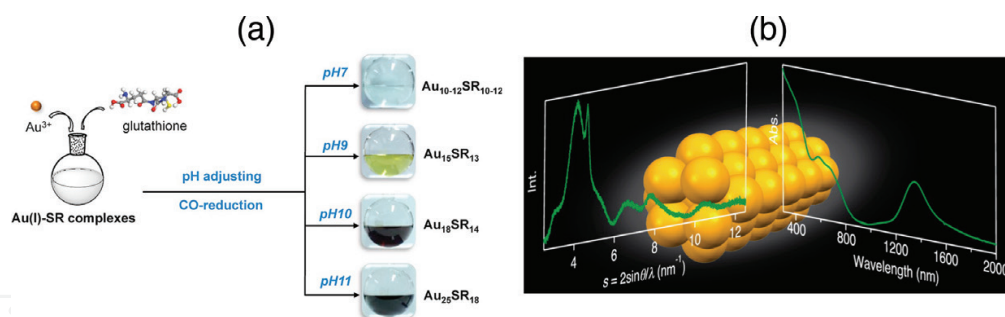
Typically,  $\text{NaBH}_4$  is employed as the reducing agent to generate Au atoms. However, CO can also be used as the reducing agent. Au atoms are generated more slowly using CO than using  $\text{NaBH}_4$  and so the  $\text{Au}_n(\text{SR})_m$  clusters are formed at a slower rate [43]. This slower synthesis rate tends to produce more uniform clusters (**Figure 3(c)**). The precise and size-selective synthesis of  $\text{Au}_n(\text{SR})_m$  clusters up to  $\text{Au}_{25}(\text{SG})_{18}$  has been realized by this method (**Figure 6(a)**). Even when using  $\text{NaBH}_4$  as the reducing agent, slow reduction can be achieved by controlling the pH of the solution.  $\text{Au}_{76}(\text{4-MEBA})_{44}$  (4-MEBA = 4-(2-mercaptoethyl) benzoic acid) has been synthesized in this manner (**Figure 6(b)**) [44]. However, this method is only applicable to small hydrophilic  $\text{Au}_n(\text{SR})_m$  clusters. It is expected that size-selective synthetic methods based on this principle will be established for  $\text{Au}_n(\text{SR})_m$  clusters protected by hydrophobic SR as well as for large hydrophilic  $\text{Au}_n(\text{SR})_m$  clusters.

## 2.4. Transformation from one stable size to another

The chemical composition of stable clusters varies depending on the bulk of the SR functional group [45]. Therefore, when the ligand of a stable cluster is replaced with a bulkier

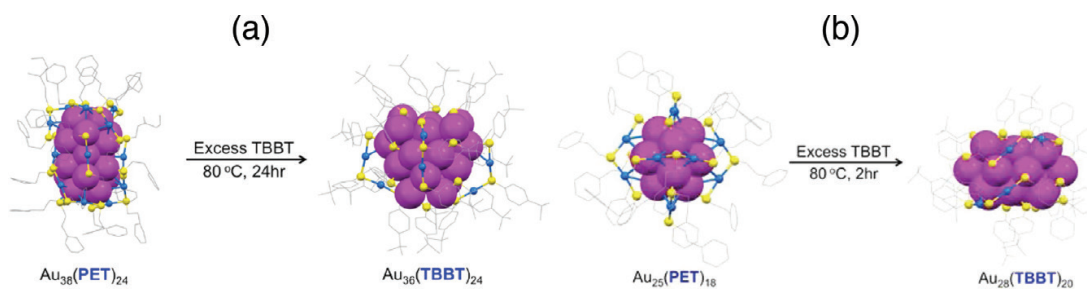


**Figure 5.** Examples of the precise synthesis of  $\text{Au}_n(\text{SR})_m$  clusters by size focusing: (a) synthesis of hydrophobic  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  and (b) synthesis of hydrophilic  $\text{Au}_{25}(\text{SG})_{18}$ . Figures were adapted from Refs. [40–42], respectively.



**Figure 6.** Examples of the precise synthesis of  $Au_n(SR)_m$  clusters by slow reduction: (a)  $Au_n(SG)_m$  clusters synthesized by CO reduction and (b)  $Au_{76}(4-(2\text{-mercaptoethyl})\text{benzoic acid})_{44}$  synthesized by controlling the pH of the solution. Figures were adapted from Refs. [43, 44], respectively.

SR, distortion of the metal core is induced, resulting in the formation of clusters with a different composition (**Figure 3(d)**) [46]. An example is the reaction of phenylethanethiolate ( $SC_2H_4Ph$ )-protected  $Au_{38}(SC_2H_4Ph)_{24}$  with 4-*tert*-butylbenzenthiole ( $HSPH^tBu$ ) in solution, which generates  $Au_{36}(SPh^tBu)_{24}$  as the primary product (yield of ~90%) (**Figure 7(a)**). This technique enables the synthesis of stable clusters with different chemical compositions from  $Au_n(SC_2H_4Ph)_m$  or  $Au_n(SC_xH_{2x+1})_m$  ( $SC_xH_{2x+1}$  = alkanethiolate) clusters. Clusters such as  $Au_{28}(SPh^tBu)_{20}$  (**Figure 7(b)**),  $Au_{36}(SPh^tBu)_{24}$  and  $Au_{133}(SPh^tBu)_{52}$  have been synthesized by this method [46].



**Figure 7.** Examples of the precise synthesis of  $Au_n(SR)_m$  clusters by transformation from one stable size to another: (a) from  $Au_{38}(SC_2H_4Ph)_{24}$  to  $Au_{36}(SPh^tBu)_{24}$  and (b) from  $Au_{25}(SC_2H_4Ph)_{18}$  to  $Au_{28}(SPh^tBu)_{20}$ . Figures were adapted from Ref. [46].

### 3. Alloy clusters

The physical and chemical properties of metal clusters also strongly depend on the chemical composition as well as on the size of the metal core. For example, the catalytic activity of polymer-stabilized  $Pd_{147}$  clusters is remarkably improved when the Pd at the surface is partially substituted by Au [47]. In addition, alloy nanoclusters composed of Pd and Ru exhibit markedly different catalytic activities compared with those of their monometallic nanocluster counterparts. The catalytic activity obtained by mixing these two metals is higher than that of monometallic nanoclusters of Rh, which is located between these two elements in the periodic table [48]. As illustrated by these examples, synergistic effects caused by mixing different

elements generate physical and chemical properties that differ from those of monometallic clusters. Thus, the composition control of metal clusters is very interesting from the viewpoint of modification of the physical and chemical properties of clusters, and results in new applications for clusters.

It is well known that SR forms strong bonds with Au (Section 2). Furthermore, stable  $Au_n(SR)_m$  clusters can be produced, and a large number of methods have been established for their isolation (Section 2). Therefore, in the synthesis of alloy clusters protected by SR ligands, Au is often employed as one of the main metal elements, and the cluster size is controlled using a method similar to that used for  $Au_n(SR)_m$  clusters. The important point in these syntheses is how to successfully mix other metallic elements with Au. In this section, we describe three typical procedures used to address this issue (Figure 8).

### 3.1. Co-reduction of multiple kinds of metal ions

The most common method for mixing other metallic elements with Au is the simultaneous reduction of the other metal ions with Au ions using a reducing agent (Figure 8(a)). This approach is called the co-reduction method. For example, to synthesize SR-protected alloy clusters, Au and other metal ions are mixed in solution, followed by the addition of thiol. A strong reducing agent ( $NaBH_4$ ) is then added, resulting in the simultaneous reduction of all of the metal ions present. Examples of alloy clusters synthesized using this method include  $Au_{25-x}Ag_x(SR)_{18}$  ( $R = C_{12}H_{25}$  or  $C_2H_4Ph$ ;  $x = 1-11$ ; Figure 9(a)),  $Au_{25-x}Cu_x(SR)_{18}$  ( $R = C_8H_{17}$  or  $C_2H_4Ph$ ;  $x = 1-5$ ; Figure 9(b)),  $Au_{24}Pt(SC_2H_4Ph)_{18}$  (Figure 9(c)),  $Au_{24}Pd(SC_2H_4Ph)_{18}$  ( $R = C_{12}H_{25}$  or  $C_2H_4Ph$ ; Figure 9(d)),  $Au_{38-x}Ag_x(SC_2H_4Ph)_{24}$  ( $x = 1-12$ ),  $Au_{36}Pd_2(SC_2H_4Ph)_{24}$ ,  $Au_{144-x}Ag_x(SC_2H_4Ph)_{60}$  ( $x \sim 30, 34, 52, 53$ ),  $Au_{143/144/145-x}Cu_x(SC_2H_4Ph)_{59/60/61}$  ( $x = 1-23$ ),  $Au_{144}Cu(SC_6H_{13})_{60}$  and  $Au_{144-x}Pd_x(SC_2H_4Ph)_{60}$  ( $x = 1-7$ ) [49–59]. Using the co-reduction method, it is also possible to synthesize  $Au_{12}Ag_{32}(SR)_{30}$  ( $R = PhF, PhF_2$ , or  $PhCF_3$ ) or  $Au_{12+x}Cu_{32}(SPhCF_2)_{30+x}$  ( $x = 0, 2, 4, 6$ ) alloy clusters, in which Ag or Cu is the base metal element [19, 60]. However, in this method, two or more types of metal atoms need to be generated simultaneously by reduction to successfully form alloy clusters.

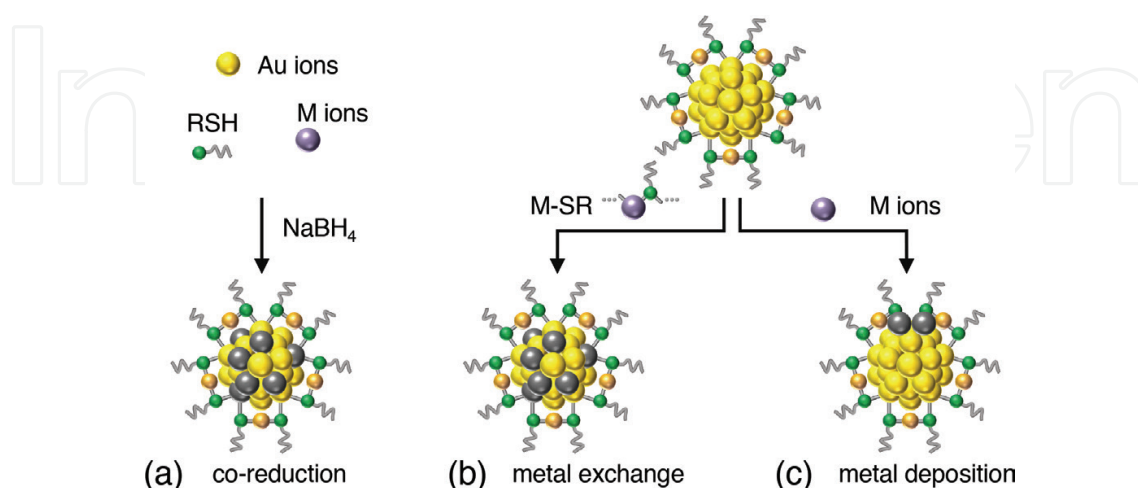
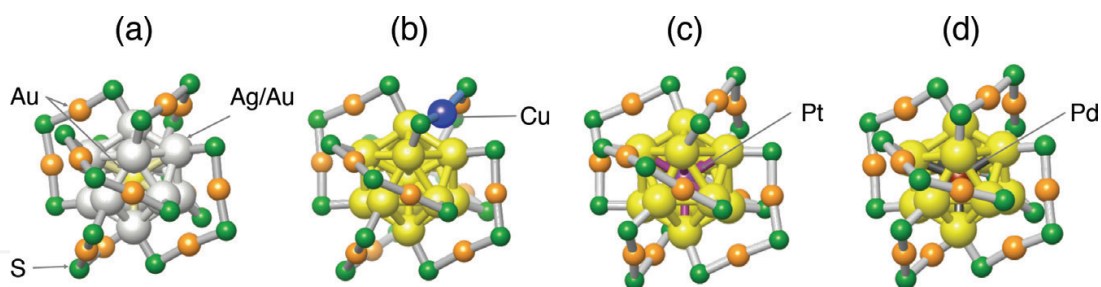


Figure 8. Representative synthesis methods of thiolate-protected alloy clusters: (a) co-reduction of multiple kinds of metal ions, (b) metal exchange with metal complexes, and (c) deposition of metal atoms onto metal clusters.



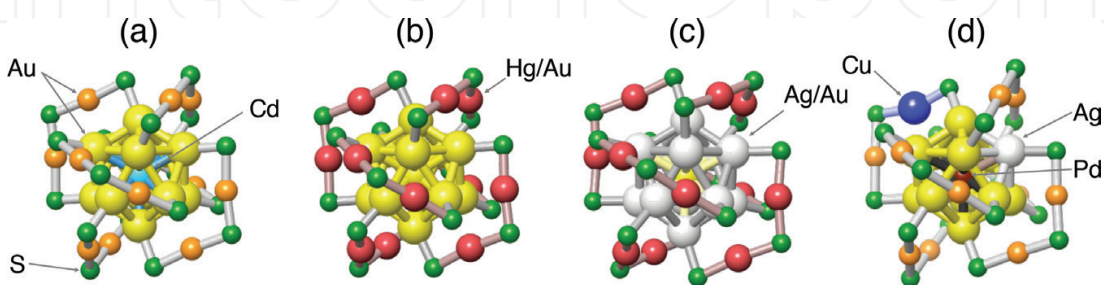


**Figure 9.** Thiolate-protected alloy clusters synthesized by the co-reduction method: (a)  $\text{Au}_{25-x}\text{Ag}_x(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , (b)  $\text{Au}_{25-x}\text{Cu}_x(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , (c)  $\text{Au}_{24}\text{Pt}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , and (d)  $\text{Au}_{24}\text{Pd}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ . Ag/Au indicates Ag or Au. R groups are omitted for clarity. Figures were adapted from Refs. [50, 51, 54].

Therefore, it is difficult to form an alloy cluster using this method when there is a large difference in redox potential between the precursor metal ions. As a result, alloy clusters synthesized by this method are presently limited to those containing Au, Ag, Cu, Pt, and Pd.

### 3.2. Metal exchange with metal complexes

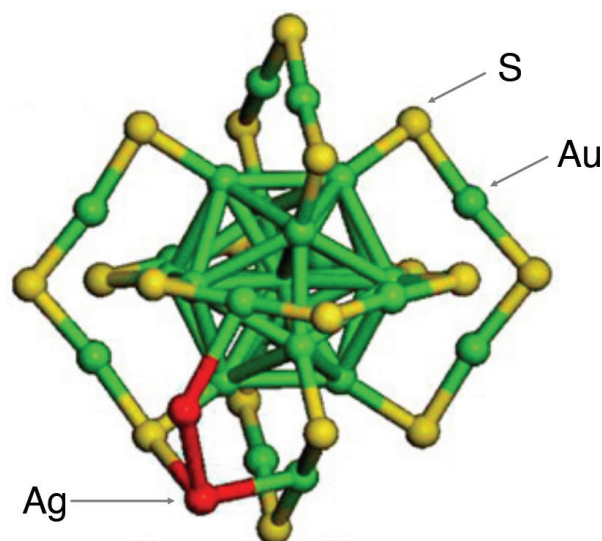
Metal clusters can exchange metal atoms with metal complexes (**Figure 8(b)**). This reaction enables heteroelements to be introduced into metal clusters to synthesize alloy clusters [61]. Although there are some exceptions [62], the number of constituent atoms of the metal core generally does not change during this exchange [63–71]. Therefore, this reaction enables some of the atoms in a cluster to be replaced with other elements while maintaining the original number of constituent atoms and geometry. In addition, this reaction allows heteroelements to be mixed more easily than the co-reduction method. The metal exchange reaction enables the synthesis of alloy clusters composed of metal elements with very different redox potentials, and a larger number of heteroatoms can be replaced than that achieved by the co-reduction method. Using this type of exchange reaction, alloy clusters such as  $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$  ( $x = 1-8$ ),  $\text{Au}_{25-x}\text{Cu}_x(\text{SR})_{18}$  ( $x = 1-9$ ),  $\text{Au}_{24}\text{Cd}(\text{SR})_{18}$  (**Figure 10(a)**),  $\text{Au}_{24}\text{Hg}(\text{SR})_{18}$  (**Figure 10(b)**),  $\text{Au}_{24-x}\text{Ag}_x\text{Cd}(\text{SR})_{18}$  ( $x = 2-6$ ),  $\text{Au}_{24-x}\text{Ag}_x\text{Hg}(\text{SR})_{18}$  ( $x = 1-8$ ; **Figure 10(c)**),  $\text{Au}_{24-x-y}\text{Ag}_x\text{Cu}_y\text{Pd}(\text{SR})_{18}$  ( $x = 1-3$ ,  $y = 1, 2$ ; **Figure 10(d)**),  $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$  ( $x = 1, 2$ ),  $\text{Ag}_{24-x}\text{Au}_x\text{Pt}(\text{SR})_{18}$  ( $x = 1, 2, 4-9$ ), and  $\text{Au}_{38-x}\text{Ag}_x(\text{SR})_{24}$  ( $x = 1-11$ ) have been synthesized to date [63–71].



**Figure 10.** Thiolate-protected alloy clusters synthesized by the metal exchange method: (a)  $\text{Au}_{24}\text{Cd}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , (b)  $\text{Au}_{24}\text{Hg}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , (c)  $\text{Au}_{24-x}\text{Ag}_x\text{Hg}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , and (d)  $\text{Au}_{22}\text{AgCuPd}(\text{SC}_{12}\text{H}_{25})_{18}$ . Hg/Au indicates Hg or Au. R groups are omitted for clarity. Figures were adapted from Refs. [64, 66, 68, 71].

### 3.3. Deposition of metal atoms onto metal clusters

When  $\text{Au}_n(\text{SR})_m$  clusters with fine metal cores (<2 nm) react with Ag ions, the Ag ions are reduced by Au, and Ag is deposited on the cluster surface (**Figure 8(c)**). This type of reaction has been used to synthesize  $\text{Au}_{25}\text{Ag}_2(\text{SC}_2\text{H}_4\text{Ph})_{18}$  by depositing two Ag atoms on the surface of an  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  (**Figure 11**) [72, 73]. A particular feature of this synthesis is that the substrate clusters maintain their chemical composition while the other metal atoms are deposited on the cluster surface. However, the metal clusters and metal ions used for this reaction were the same as those used in the aforementioned metal exchange method (Section 3.2). In the future, it is expected that the reason why the reaction changes from metal exchange to metal deposition under slightly different experimental conditions will be elucidated.



**Figure 11.**  $\text{Au}_{25}\text{Ag}_2(\text{SC}_2\text{H}_4\text{Ph})_{18}$  synthesized by the metal deposition method. R groups are omitted for clarity. This figure was adapted from Ref. [72].

## 4. Conclusions and prospects

In this chapter, we focused on  $\text{Au}_n(\text{SR})_m$  and related alloy clusters as examples of metal nanoclusters and described the latest techniques and knowledge regarding their precise synthesis. The study of  $\text{Au}_n(\text{SR})_m$  clusters has progressed with spectacular speed in recent years. Consequently, the associated synthetic techniques have also advanced dramatically, and a greater understanding of their characteristics has been obtained [74–76]. These clusters are now expected to be applied in various fields such as sensing, imaging, cancer radiation therapy, catalysis, photocatalysis, solar cells, fuel cells, photosensitizers, and single-electron devices. If these  $\text{Au}_n(\text{SR})_m$  clusters can be regularly assembled [77], further new functions could be induced and their fields of application might be further expanded. In the future, it is expected that intensive investigations will be conducted regarding the formation of various nanoarchitectures using  $\text{Au}_n(\text{SR})_m$  clusters as structural units in addition to research on the  $\text{Au}_n(\text{SR})_m$  clusters themselves.

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