Gold Nanoclusters as Electrocatalysts for Energy Conversion

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Abstract: Gold nanoclusters (Au n NCs) exhibit a size-specific electronic structure unlike bulk gold and can therefore be used as catalysts in various reactions. Ligand-protected Au n NCs can be synthesized with atomic precision, and the geometric structures of many Au n NCs have been determined by single-crystal X-ray diffraction analysis. In addition, Au n NCs can be doped with various types of elements. Clarification of the effects of changes to the chemical composition, geometric structure, and associated electronic state on catalytic activity would enable a deep understanding of the active sites and mechanisms in catalytic reactions as well as key factors for high activation. Furthermore, it may be possible to synthesize Au n NCs with properties that surpass those of conventional catalysts using the obtained design guidelines. With these expectations, catalyst research using Au n NCs as a model catalyst has been actively conducted in recent years. This review focuses on the application of Au n NCs as an electrocatalyst and outlines recent research progress.

Keywords: gold; cluster; catalyst; hydrogen evolution reaction; oxygen evolution reaction; oxygen reduction reaction; water splitting; fuel cells; alloy; ligand-protected

1. Introduction

Gold nanoclusters (Au n NCs) have physical/chemical properties that differ from those of bulk Au owing to their size-specific electrical/geometrical structure [1–22]. Therefore, Au n NCs have been actively studied since the 1960s from the viewpoints of both basic science and application. Since Brust et al. discovered a method for synthesizing Au n NCs protected by thiolate (Au n(SR) m) in 1994 [1], researches on Au n NCs in particular have grown [6]. Au n(SR) m NCs exhibit high stability both in solution and in the solid state because Au forms a strong bond with SR. In addition, Au n(SR) m NCs can be synthesized by simply mixing reagents under the ambient atmosphere. Au n(SR) m NCs with these unique characteristics have a low handling threshold even for researchers unfamiliar with the chemical synthesis of metal clusters. Au n(SR) m NCs are thus currently one of the most studied metal NCs [1–18]. For these Au n(SR) m NCs, it became possible to synthesize a series of Au n(SR) m NCs with atomic precision in 2005 [19]. In addition, since 2007, the geometric structures of many Au n(SR) m NCs have been determined through single-crystal X-ray diffraction (SC-XRD) analysis [20]. Since 2009, partial replacement of the Au atoms of Au n(SR) m NCs with other elements such as silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), cadmium (Cd), and mercury (Hg) has also been realized [3–5,23–44].

In parallel to these synthesis and structural analysis studies, studies on the functions of Au n NCs have also been actively conducted. Au n NCs have been observed to possess catalytic activity for several reactions, including carbon monoxide oxidation [45–55], alcohol oxidation [56–65], styrene...
oxidation [66–70], aromatic compound oxidation [71,72], sulfide oxidation [73–75], and carbon dioxide reduction [76–83]. One of the reasons for these active studies on the catalysis of Au NCs is that their electronic and geometric structures are well understood. Thus, if the obtained catalytic properties are compared with the electronic/geometrical structures of Au\(_n\)(SR)\(_m\) NCs, information on active sites, mechanisms, and key factors for high activation in catalytic reactions can be obtained. With these expectations, Au\(_n\)(SR)\(_m\) NCs have received great attention as model catalysts [45–83].

In addition, several studies on Au\(_n\)(SR)\(_m\) NCs as electrocatalysts have also been performed recently. To prevent serious environmental issues including the depletion of fossil fuels and global warming, the establishment of a system in which hydrogen (H\(_2\)) is generated from water and solar energy using a photocatalyst is desired, with the generated H\(_2\) used for the generation of electricity using fuel cells [84,85]. Once such an energy conversion system is established, it will be possible to circulate an energy medium (H\(_2\)) in addition to obtaining electricity only from solar energy and abundant water resources. However, realization of such an ultimate energy conversion system requires further improvement of the reaction efficiency of each half reaction of water splitting and fuel cells, including the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HOR), and oxygen reduction reaction (ORR; Figure 1A).

Figure 1. (A) Schematic illustration of gold nanoclusters (Au\(_n\) NCs) for an electrocatalytic reaction in water splitting (hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)) and fuel cells (oxygen reduction reaction (ORR)). (B) Current–potential characteristics for (a) HER, (b) OER, and (c) ORR.

To improve the reactivity per unit volume, it is necessary to increase the specific surface area of the active sites and increase the reaction rate at the active sites. For the former, size reduction of the catalyst is one effective method. However, the latter is strongly related to the adsorption energy of reactive molecules on the catalyst surface. The activity of the chemical reaction on the catalyst surface is the highest when the Gibbs energy of adsorption between the catalyst and reactant is moderate according to the Sabatier principle [86]. This is because the reaction does not occur without the adsorption of reactants but is inhibited by the strong adsorption of reactants. Therefore, the relationship between the reaction efficiency and the Gibbs energy for the adsorption of reactants follows a curved line called an activity volcano plot [87]. Fine nanoparticle catalysts suitable for the HER [88–92], OER [93–95], and ORR [96–101] have been developed based on theoretical predictions of activity volcano plots using various metals and alloy nanoparticles (NPs). Au\(_n\) NCs have recently been observed to possess catalytic activity for the HER, OER, and ORR [77,102–116] (Figure 1). Therefore, Au\(_n\) NCs are expected to become a model catalyst even in such an energy conversion system. A better understanding of the correlation between electronic/geometrical structures and the catalytic activity of the HER, OER, and ORR in Au\(_n\) NCs might lead to the discovery of new key factors for achieving high activation. Furthermore, because Au\(_n\) NCs are composed of several tens of atoms or less, the use of fine Au\(_n\) NCs as a catalyst is also effective in reducing the consumption of expensive noble metals. Thus, it may be possible to create HER, OER, and ORR catalysts with properties that surpass those of conventional catalysts using these unique characteristics of Au\(_n\) NCs. With these expectations, several groups are conducting research on the application of Au\(_n\) NCs as
electrocatalysts. This article reviews the basic theory of electrocatalysts and recent research on HER, OER, and ORR catalysts using Auₙ NCs and their alloy NCs.

2. Electrocatalytic Reaction in Water Splitting

H₂ is expected to be an important energy source to support a sustainable energy society. Currently, H₂ is generated as a by-product during steam reforming or coke production. However, if a water-splitting reaction using an electrocatalyst can be applied for hydrogen production, the large-scale facility of the current system would not be required. In addition, it would be possible to produce H₂ only with water and electricity using the surplus power from a power plant. Therefore, water electrolysis is considered one of the cleanest energy production reactions for a sustainable energy society.

The water-splitting reaction consists of two half reactions, the HER and OER. When a voltage is applied to the metal electrode, a reduction reaction proceeds at the cathode and an oxidation reaction proceeds at the anode, resulting in the decomposition of water molecules into H₂ and O₂ at each electrode. However, the reactions do not proceed even if a potential equal to or higher than both the oxidation and reduction potentials in each reaction (HER: 0 V vs. SHE, OER: 1.23 V vs. SHE; SHE = standard hydrogen electrode) is applied to the electrode. This is because the activation energy of each reaction is too high. Therefore, noble metal NPs are used as a catalyst to reduce the activation energy of the reaction.

Table 1. Representative references on HER activity of Auₙ NCs and related alloy NCs.

| Ligand | Support | Experimental condition | Activity | Reference |
|--------|---------|------------------------|----------|-----------|
| SC₆H₁₃ | –       | 1.0 M TFA and 0.1 M Bu₄PF₆ in THF | Au₂₅Pt(SC₆H₁₃)₁₈ > Au₂₅(SC₆H₁₃)₁₈ | [102] |
| SC₆H₁₃ | carbon black | 1 M Britton–Robinson buffer solution in 2 M KCl | Au₂₅Pt(SC₆H₁₃)₁₈ > Au₂₅(SC₆H₁₃)₁₈ | [103] |
| SC₆H₁₃ | carbon black | 1 M Britton–Robinson buffer solution in 2 M KCl | Au₂₅Pt(SC₆H₁₃)₁₈ > Au₂₅(SC₆H₁₃)₁₈ | [103] |
| PPh₃  | –       | 0.5 M phosphate buffer solution (pH 6.7) | Au₂₅Pd(SC₆H₁₃)₁₈ > Au₂₅(SC₆H₁₃)₁₈ | [104] |
| PPh₃  | –       | 0.5 M H₂SO₄ | Au₂₅Pd(SC₆H₁₃)₁₈ > Au₂₅(SC₆H₁₃)₁₈ | [107] |
| Cl⁻    | MoS₂    | 0.5 M H₂SO₄ | Au₁(1.3 nm)(porphyrin SC₆P) > Au₁(1.3 nm)(PET) | [108] |
| PhF₂S  | –       | 0.5 M H₂SO₄ | Au₁(1.3 nm)(porphyrin SC₆P) > Au₁(1.3 nm)(PET) | [108] |

| a Diphenylphosphine. b Chlorine. c WE: Working electrode; GCE. d WE: Containing Nafion. e WE: Carbon tape. |

2.1. Hydrogen Evolution Reaction
In the HER, metal surface atoms of the catalyst form bonding orbitals with protons (H⁺) through the Volmer–Heyrovsky or Volmer–Tafel mechanism, producing molecular hydrogen [117].

Under acidic conditions, the following reactions occur:

Volmer reaction: \( M + H^+ + e^- \rightarrow M-H \)  
(1)

Heyrovsky reaction: \( M-H + H^+ + e^- \rightarrow M-H_2 \)  
(2)

Tafel reaction: \( 2M-H \rightarrow 2M + H_2 \)  
(3)

However, under alkaline conditions, the following reactions occur:

Volmer reaction: \( 2M + 2H_2O + 2e^- \rightarrow 2M-H + 2OH^- \)  
(4)

Heyrovsky reaction: \( M-H + H_2O + e^- \rightarrow M-H_2 + OH^- \)  
(5)

Tafel reaction: \( 2M-H \rightarrow 2M + H_2 \)  
(6)

Bulk Au possesses almost no HER activity, whereas \( \text{Au}_n(\text{SR})_m \) NCs possess HER activity. In addition, their activity can be further improved by doping \( \text{Au}_n(\text{SR})_m \) NCs with appropriate heterogeneous elements. These effects were reported by Lee and Jiang et al. in 2017 [102]. They evaluated the HER activity using linear sweep voltammetry (LSV) in tetrahydrofuran (THF) solution with 1.0 M trifluoroacetic acid (TFA) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) in the absence (black) and presence of \( \text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18} \) or \( \text{Au}_{24}\text{Pt}(\text{SC}_6\text{H}_{13})_{18} \) (\( \text{SC}_6\text{H}_{13} = \) 1-hexanethiolate) on a glassy carbon electrode (GCE). The onset potential of the HER (Figure 1B (a)) occurred at \(-1.25 \text{ V}\) for the GCE blank (Figure 2A, black line), whereas it occurred at \(-1.1 \text{ V}\) for the GCE with \( \text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18} \) (Figure 2A, red line). In addition, for the GCE with \( \text{Au}_{24}\text{Pt}(\text{SC}_6\text{H}_{13})_{18} \), the onset potential of the HER was further reduced to \(-0.89 \text{ V}\) (Figure 2A, blue line). These findings indicated that \( \text{Au}_n(\text{SR})_m \) NCs has catalytic activity for the HER and that the HER activity can be further improved by substituting one Au atom of the \( \text{Au}_n(\text{SR})_m \) NCs with a Pt atom (Table 1). They estimated the HER energies of \( \text{Au}_{25}(\text{SC}_3\text{H}_3)_{18} \) and \( \text{Au}_{24}\text{Pt}(\text{SC}_3\text{H}_3)_{18} \) (\( \text{SC}_3\text{H}_3 = \) methanethiolate) using density functional theory (DFT) calculations to elucidate the reasons for this behavior (Figure 2C). In these DFT calculations, H⁺ solvated by two THF molecules was used as H⁺. The resulting energy change in the Volmer step was 0.539 eV for [\( \text{Au}_{25}(\text{SC}_3\text{H}_3)_{18} \)]⁻, indicating that this reaction is endothermic. However, the energy change in the Volmer step was \(-0.059 \text{ eV}\) for [\( \text{Au}_{24}\text{Pt}(\text{SC}_3\text{H}_3)_{18} \)]²⁻, indicating that there is almost no energy change (Figure 2C, step 1). The higher HER activity of \( \text{Au}_{24}\text{Pt}(\text{SC}_3\text{H}_3)_{18} \) was explained by these differences in the energy barriers in the reaction. In addition, \( \text{Au}_{24}\text{Pt}(\text{SC}_3\text{H}_3)_{18} \) possessed higher HER activity even compared with Pt NPs, which are highly active materials for the HER (Figure 2B).
Lee and Jiang et al. observed that a high HER activity and a high catalyst turnover frequency (TOF) can be achieved by doping Au$_{25}$(SC$_6$H$_{13}$)$_{18}$ with not only Pt but also Pd (Au$_{24}$Pt(SC$_6$H$_{13}$)$_{18}$ > Au$_{24}$Pd(SC$_6$H$_{13}$)$_{18}$) [103]. They reported that TOF values of Au$_{25}$(SC$_6$H$_{13}$)$_{18}$, Au$_{24}$Pd(SC$_6$H$_{13}$)$_{18}$, and Au$_{24}$Pt(SC$_6$H$_{13}$)$_{18}$ were 8.2, 13.0, and 33.3 mol H$_2$ (mol catalyst)$^{-1}$ s$^{-1}$ at $-0.60$ V vs. the reversible hydrogen electrode (RHE), respectively. In addition, it was revealed that the doping of Au$_{38}$(SR)$_{24}$ with different elements results in a similar activity enhancement effect with Au$_{25}$(SC$_6$H$_{13}$)$_{18}$ (Au$_{24}$Pt(SC$_6$H$_{13}$)$_{24}$ > Au$_{24}$Pd(SC$_6$H$_{13}$)$_{24}$ > Au$_{24}$Cu(SC$_6$H$_{13}$)$_{24}$) [103]. These results are in good agreement with the DFT calculation results. In addition to these studies, Jiang et al. also investigated the doping effects of various elements (Pt, Pd, Ag, Cu, Hg, and Cd) in Au$_{25}$(SC$_6$H$_{13}$)$_{18}$ using DFT calculations [105]. The results predicted that Au$_{24}$Pt(SC$_6$H$_{13}$)$_{18}$, Au$_{24}$Pd(SC$_6$H$_{13}$)$_{18}$, and Au$_{24}$Cu(SC$_6$H$_{13}$)$_{18}$, in which the heteroatom (Pt, Pd, or Cu) is located at the center of the metal core, have a higher HER activity than Au$_{25}$(SC$_6$H$_{13}$)$_{18}$. Zhu et al. reported that another fine alloy NC, Au$_{36}$Pt(SC$_6$H$_{13}$)$_{24}$ (PPPh$_3$ = triphenylphosphine, PhF$_2$S = 3,4-difluorobenzenethiolate), also exhibits HER activity (Table 1) [106]. These studies revealed that Au$_{m}$(SR)$_{m}$ and their alloy NCs have HER activity and it can be improved by controlling the electronic structure of Au$_{m}$ NCs through heteroatom doping.

The HER activity varies depending not only on the chemical composition of the metal core but also on the properties of the ligand. In 2018, Teranishi and Sakamoto et al. used Au$_{m}$ NCs coordinated with SR-containing porphyrin (porphyrin SC-P). They investigated the effects of the ligand structure on the HER activity of Au$_{m}$(SR)$_{m}$ NCs [107]. In these clusters, the porphyrin ring coordinates horizontally to the gold core. Then, the distance between the porphyrin ring and the Au surface was controlled by changing the length of the alkyl chain between the porphyrin ring and the acetylthio group (Figures 3A,C) [118,119]. The alkyl chain is a methylene chain for porphyrin SC1P and an ethylene chain for porphyrin SC2P. The distance between the porphyrin ring and the acetylthio group (PET). Transmission electron microscope (TEM) images of the synthesized Au$_{m}$(SR)$_{m}$ NCs (SR = porphyrin SC1P, porphyrin SC2P, or PET) with a core size of approximately 1.3 nm are presented in Figure 3B,D,F, respectively. Among these products, matrix-assisted laser desorption/ionization mass spectrometry indicated that Au$_{m}$(porphyrin SC1P)$_{m}$ NCs consisted of 77 Au atoms and 8 porphyrin SC1P molecules and Au$_{m}$(porphyrin SC2P)$_{m}$ NCs consisted of 75 Au atoms and 11 porphyrin SC2P molecules. The effects of the ligand structure and Au core size on the HER activity of Au$_{m}$(SR)$_{m}$ NCs were investigated using the obtained nine types of Au$_{m}$(SR)$_{m}$ NCs. As a result, in Au$_{m}$(SR)$_{m}$ NCs with a core size of approximately 1.3 nm, Au$_{m}$(porphyrin SC1P)$_{m}$ and Au$_{m}$(porphyrin SC2P)$_{m}$ NCs exhibited higher current densities of the HER than Au$_{m}$(PET)$_{m}$ NCs (Table 1). For instance, Au$_{75}$(porphyrin SC1P)$_{75}$ NCs resulted in a 4.6 times higher current density of the HER than Au$_{75}$(PET)$_{75}$ NCs at $-0.4$ V vs. RHE. In addition, using Au$_{m}$(porphyrin SC1P)$_{m}$ NCs, the HER occurred at a smaller overvoltage than using Au$_{m}$(porphyrin SC2P)$_{m}$ NCs. These results indicate that the HER activity of Au$_{m}$ NCs depends on the type of ligand and the distance between the ligand and the metal core in Au$_{m}$ NCs [107]. In this work, the Au$_{m}$(SR)$_{m}$ NCs with a core size of approximately 2.2 nm showed higher catalytic activity than those with a core size of approximately 1.3 nm (Figure 3G,H). This size dependence of the catalytic activity is a little strange considering the surface area of the metal core because a reduction of a core size of Au$_{m}$(SR)$_{m}$ NCs typically leads to the increase in the surface area of Au metal core, which are active sites in HER. The authors have not discussed the details on this point in this paper probably due to the difficulty in precisely estimating the surface area of each Au$_{m}$(SR)$_{m}$ NCs.
The property of the ligand also strongly affects the interaction between \text{Au}_{n}(\text{SR})_{m} \text{NCs} and the electrode as well as the affinity between \text{Au}_{n}(\text{SR})_{m} \text{NCs} and water molecules. Lee and Jiang et al. synthesized \text{Au}_{n}(\text{SR})_{m} \text{NCs} with \text{SC}_{6}\text{H}_{13}, 3-mercapto propionic acid (MPA), or 3-mercapto-1-propanesulfonic acid (MPS; Figure 4B) as a ligand (\text{Au}_{25}(\text{SC}_{6}\text{H}_{13})_{18}, \text{Au}_{25}(\text{MPA})_{18}, \text{and} \text{Au}_{25}(\text{MPS})_{18}) and used them to investigate the effect of ligand properties on the HER activity \cite{109}. In the experiment, \text{Au}_{25}(\text{SC}_{6}\text{H}_{13})_{18}, \text{Au}_{25}(\text{MPA})_{18}, \text{or} \text{Au}_{25}(\text{MPS})_{18} was dissolved at a concentration of 1 mM in 0.1 M KCl aqueous solution, and LSV measurements were performed using a GCE (50 mV s$^{-1}$). Although the blank current was 0.01 mA at $-0.7$ V vs. RHE (Figure 4C, black line), the HER current of the sample including \text{Au}_{25}(\text{MPA})_{18} increased up to 0.13 mA at $-0.7$ V vs. RHE (Figure 4C, red line). When \text{Au}_{25}(\text{MPS})_{18} was used, a higher HER current of 1.0 mA was observed at $-0.7$ V vs. RHE (Figure 4C, blue line). MPS and MPA have a hydrophilic functional group (sulfonic acid or carboxylic acid group, respectively) unlike \text{SC}_{6}\text{H}_{13}. These hydrophilic functional groups have the property of releasing H$^{+}$ in an aqueous solution. In addition, the sulfonic acid group of MPS (pKa < 1) is expected to have higher H$^{+}$ releasing ability than the carboxylic acid group of MPA (pKa = 3.7). For these reasons, it was interpreted that the difference in the HER activity described above is largely related
to the difference in the H⁺ releasing ability of these ligands (Table 1). It was speculated that the energy barrier associated with the intermolecular and intramolecular H⁺ transfer steps is lowered by H⁺ relay in Auₙ NCs with high HER activity (Figure 4A). In this paper, they also reported that the use of Au₂₅Pt(MPS)₁₈, in which Au₂₅(MPS)₁₈ is replaced with Pt, results in even higher HER activity than Au₂₅(MPS)₁₈ (Figure 4D and Table 1). They described that the TOF value of Au₂₅Pt(MPS)₁₈ was 127 mol H₂ (mol catalyst)⁻¹ s⁻¹, which was 4 times higher than that of Au₂₅(MPS)₁₈ at –0.7 V vs. RHE.

An electronic interaction also occurs between the Auₙ(SR)ₘ NCs and a catalytic support. This phenomenon was revealed by Jin et al. by measuring the HER activity of MoS₂ nanosheets (catalytic support) carrying Au₂₅(PET)₁₈/Au₂₅(PET)₁₈/MoS₂ [108]. In this experiment, Au₂₅(PET)₁₈/MoS₂ was prepared by mixing the MoS₂ nanosheets synthesized by the hydrothermal method and Au₂₅(PET)₁₈ in dichloromethane for 1 h and drying the obtained products under nitrogen atmosphere. High-angle annular dark-field scanning TEM (HAADF-STEM) images confirmed that Au₂₅(PET)₁₈ was uniformly supported on MoS₂ (Figure 5A). Au₂₅(PET)₁₈/MoS₂ was then loaded on a GCE, and the HER polarization curve of Au₂₅(PET)₁₈/MoS₂ was obtained by scanning the potential in a 0.5 M H₂SO₄ aqueous solution using the rotating disk electrode (RDE) method (Figure 5B,D). MoS₂ without Au₂₅(PET)₁₈ exhibited a HER overvoltage of 0.33 V at a current density of 10 mA cm⁻², whereas Au₂₅(PET)₁₈/MoS₂ exhibited a smaller HER overvoltage of approximately –0.28 V at the same current density. In addition, Au₂₅(PET)₁₈/MoS₂ (59.3 mA cm⁻²) exhibited a 1.79 times higher current density than that of MoS₂ (33.2 mA cm⁻²) at an applied voltage of –0.4 V vs. RHE. Thus, the HER activity of the MoS₂ nanosheets was greatly improved by carrying Au₂₅(PET)₁₈ (Table 1). This improvement of the HER activity was interpreted to be greatly related to the electronic interaction between Au₂₅(PET)₁₈ and MoS₂. In fact, X-ray photoelectron spectroscopy (XPS) analysis confirmed that the binding energy of MoS₂ in the Mo 3d orbit was negatively shifted by 0.4 eV after Au₂₅(PET)₁₈ was loaded (Figure 5C). It was assumed that the charge transfer from Au₂₅(PET)₁₈ to MoS₂ occurred in Au₂₅(PET)₁₈/MoS₂, causing a high HER activity of Au₂₅(PET)₁₈/MoS₂. In this study, the HER activity of MoS₂ nanosheets carrying Au₂₅(SePh)₁₈ (SePh = phenylselenolate) (Au₂₅(SePh)₁₈/MoS₂) was also investigated. Au₂₅(SePh)₁₈/MoS₂ was shown to also exhibit higher HER activity than MoS₂ nanosheets (Table 1). However, the improvement of the activity was smaller than that when carrying Au₂₅(PET)₁₈ (Figure 5D). This difference was attributed to the difference in the electron interaction and electron relay between Au cores of Auₙ NCs and the MoS₂ nanosheet depending on the ligands. In this way, the HER activity of the Auₙ NCs-loaded catalyst was shown to depend on the electronic interaction between the Auₙ NCs and the catalytic support.

Figure 4. (A) Schematic illustration of proton relay mechanism of Au₂₄Pt(SR)₁₈ nanocluster for formation of H₂ and (B) ligand structures: SC₆H₁₃, MPA, and MPS. Color codes: blue = Pt; golden = core Au; red = shell Au; and green = S. (C) HER polarization curves in 0.1 M KCl aqueous solution containing 180 mM acetic acid for MPA-Au₂₅ (red) or MPS-Au₂₅ (blue). (D) Turnover frequencies (TOFs) obtained at various potentials in water (3.0 M KCl) containing 180 mM HOAc for MPA-Au₂₅ (red), MPS-Au₂₅ (blue), or MPS-Au₂₄Pt (green). Panels (A–D) are reproduced with permission from reference [109]. Copyright Royal Society of Chemistry, 2018.
2.2. Oxygen Evolution Reaction

The OER is a multi-step four-electron reaction in which the reaction proceeds along different reaction paths depending on the binding energy between the metal and the OER intermediate (O, OH, and OOH).

Under acidic conditions, the following reactions occur:

\[
\begin{align*}
M + H_2O & \rightarrow M-OH + H^+ + e^- \quad (7) \\
M-OH & \rightarrow M-O + H^+ + e^- \quad (8) \\
2(M-O) & \rightarrow 2M + O_2 \quad (9) \\
M-O + H_2O & \rightarrow M-OOH + H^+ + e^- \quad (10) \\
M-OOH & \rightarrow M + O_2 + H^+ + e^- \quad (11)
\end{align*}
\]

However, under alkaline conditions, the following reactions occur:

\[
\begin{align*}
M + OH^- & \rightarrow M-OH^- + e^- \quad (12) \\
M-OH^- + OH^- & \rightarrow M-O + H_2O + e^- \quad (13) \\
2(M-O) & \rightarrow 2M + O_2 \quad (14) \\
M-O + OH^- & \rightarrow M-OOH + e^- \quad (15)
\end{align*}
\]
As described above, because the reaction route of OER depends on the intermediates (O, OH, and OOH) on the surface of catalyst, the OER activity of the catalyst also depends on these intermediates. Catalysts that have neither too high nor too low binding energy with oxygen species are suitable for the OER. Previous studies have demonstrated that iridium oxide and ruthenium oxide have such desirable properties. Therefore, miniaturization of these metal oxides and prediction of their physical properties by theoretical calculation have been actively performed [120–123]. However, because these precious metals are expensive and have the problem of depletion, a search for low-cost catalysts is also being conducted. Related studies have shown that cobalt (Co)-based materials (oxides, hydroxides, selenides, and phosphides) can be used as good OER catalysts. Furthermore, it has been reported that when Au NPs are composited with such Co materials, the OER performance is greatly enhanced as a result of the improved electron conductivity and preferential formation of OOH intermediates on the surface of the catalyst [124–126].

Table 2. Representative reference on OER activity of Auₙ(SR)ₘ NCs.

| Ligand | Support | Experimental condition | Activity | Reference |
|--------|---------|------------------------|----------|-----------|
| PET    | CoSe₂   | 0.1 M KOH aq a,b       | Auₙ(PET)₁₈/CoSe₂ > CoSe₂ | [110]     |

Table 2. Representative reference on OER activity of Auₙ(SR)ₘ NCs.

Jin et al. have shown that these mixing effects also occur when Auₙ NCs are used instead of Au NPs [110]. In this study, the Auₙ(PET)₁₈-loaded CoSe₂ nanosheet (Auₙ(PET)₁₈/CoSe₂) was prepared by stirring Auₙ(PET)₁₈ and CoSe₂ nanosheets in dichloromethane for 1 h. HAADF-STEM analysis confirmed that Auₙ(PET)₁₈ was uniformly supported on the CoSe₂ nanosheets (Figure 6A,B). Auₙ(PET)₁₈/CoSe₂ was loaded on the GCE, and their OER polarization curves were obtained by scanning the applied potential (5 mV s⁻¹) in 0.1 M KOH aqueous solution. The CoSe₂ nanosheets without Auₙ(PET)₁₈ exhibited an OER overvoltage of 0.52 V at a current density of 10 mA cm⁻² (Figure 1B (b)), whereas Auₙ(PET)₁₈/CoSe₂ exhibited a smaller OER overvoltage of 0.43 V at the same current density (Figure 6C). XPS (Figure 6E) and Raman spectroscopy (Figure 6F) analyses revealed that the electronic interaction occurred between the Auₙ(PET)₁₈ and CoSe₂ nanosheet even in such a composite catalyst. Furthermore, DFT calculation revealed that the formation of the intermediate via OH⁻ is more advantageous by 0.21 eV mol⁻¹ at the interface of Co–Au than at the surface of Co. It was thus interpreted that Auₙ(PET)₁₈/CoSe₂ exhibited higher OER activity than the CoSe₂ nanosheets because Auₙ(PET)₁₈/CoSe₂ stabilized the generation of an OOH intermediate compared with only the CoSe₂ nanosheet (Table 2). This study also revealed that the OER activity increases with the core size of Auₙ(SR)ₘ NCs (Figure 6D).
3. Electrocatalytic Reactions in Fuel Cells

To establish a circulating energy system that does not use fossil fuels and only produces water and a small amount of carbon dioxide as waste, it is essential to further improve the functions of fuel cells. Fuel cells can be roughly classified into those using hydrogen and those using alcohol as a fuel. In fuel cells using hydrogen as a fuel, the HOR and ORR are involved in the system. The HOR is a one-electron reaction, and generally an HER-active catalyst is also useful for the HOR. However, the ORR is a four-electron reaction, and the reaction process is complicated. In addition, the OER is a reaction under oxidizing conditions, whereas the ORR is a reaction under reducing conditions. The surface state of the catalyst and the accompanying binding to the reactants also differ greatly between the OER and ORR. Therefore, catalysts that are active for OER are not necessarily useful for the ORR. Because the ORR is rate-limiting step in a fuel cell, controlling the ORR is important for further
development of fuel cells. The ORR pathways under acidic and alkaline conditions are as follows [94].

Under acidic conditions:

\[
\begin{align*}
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \\
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
H_2O_2 + 2H^+ + 2e^- & \rightarrow 2H_2O
\end{align*}
\] (17) (18) (19)

Under alkaline conditions:

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \\
O_2 + H_2O + 2e^- & \rightarrow OOH^- + OH^- \\
OOH^- + H_2O + 2e^- & \rightarrow 3OH^- 
\end{align*}
\] (20) (21) (22)

Equations (17) and (20) are four-electron reactions, and Equations (18), (19), (21), and (22) are two-electron reactions. For both sets of reactions, the reactions start with the breaking of the O–O bond. The theoretical redox potential is 1.23 V vs. SHE in the direct four-electron path and 0.68 V vs. SHE in the indirect two-electron path. Therefore, a higher energy conversion efficiency can be achieved using the direct four-electron path, and this reaction path is thus more desirable for fuel cells [81]. Although Pt is a useful catalyst for such a reaction pathway, it is expected to be replaced with another metal element because of the high cost of Pt and the resource depletion issue. In addition, synthesis methods of Pt NCs in ambient atmosphere with atomic precision are limited, and therefore, it is difficult to study the ORR mechanism using Pt NCs as model catalysts. However, for Au NCs, there are many examples of synthesis with atomic precision, and these catalysts are stable in ambient atmosphere. In addition, theoretical calculations [127,128] and experimental results [65,129] have predicted that O2 molecules can be highly activated on the surface of Au NCs. For these reasons, several studies have also been performed on the application of Au NCs as ORR catalysts.

**Table 3.** Representative references on ORR activity of Au NCs.

| Ligand | Support | Experimental condition | Activity | Reference |
|--------|---------|------------------------|----------|-----------|
| PET    | SC6H13  | –                      | 0.1 M KOH aq | [101] |
| Cl     | PPh3    | –                      | Au11(PPh3)Cl3 > Au25(PET)18 > Au55(PPh3)12Cl6 > Au140(SC6H13)53 |
|        |         |                        |          |            |
| PET    | Reduced | 0.1 M KOH aq           | Au25(PET)38 > Au38(PET)24 > Au133(TBBT)52 |
|        | graphene oxide |            |          | [112] |
|        |         |                        | Au279(TBBT)84 > Au28(TBBT)20 |
| TBBT   | SWNTs   | 0.1 M KOH aq           | Au56(S-Bu)20 > Au66(S-Bu)24 |
|        |         |                        |          | [113] |
|        |         |                        | Au36(TBBT)24 > Au30(S-Bu)18 |
|        |         |                        |          | [114] |
| S-Bu   | SWNTs   | 0.1 M KOH aq           | [Au25(SC12H25)18] > [Au25(SC12H25)18]** > [Au25(SC12H25)18]** |
|        |         |                        | [Au25(SC12H25)18]** > [Au25(SC12H25)18]** |
| SC12H25| –       | 0.1 M KOH aq           | [Au25(SC12H25)18]** > [Au25(SC12H25)18]** |
|        |         |                        | [Au25(SC12H25)18]** > [Au25(SC12H25)18]** |

*a* WE: GCE. *b* WE; Containing Nafion. *c* Tow-electron reduction.

In 2009, Chen et al. evaluated the ORR catalytic activity of Au11(PPh3)Cl3, Au25(PET)18, Au55(PPh3)12Cl6, and Au140(SC6H13)53 (Cl = chlorine) [111]. In this experiment, after a series of Au NCs were loaded on the GCE, the ORR activity was measured by scanning the potential using the RDE...
method in a 0.1 M KOH aqueous solution filled with O₂. When Au₉(PPh₃)Cl was used as the Au₉ NCs, the onset potential of the ORR (Figure 1B(c)) was about ~0.08 V, and the peak current density was 2.4 mA cm⁻² (Figure 7A). However, when Au₁₄(SC₆H₁₃)₃ was used as the Au₉ NCs, the onset potential shifted to the more cathodic ~0.22 V and the reduction peak current decreased to less than 1.0 mA cm⁻². These results and those for the other two Au₉ NCs indicated that the ORR activity increased with decreasing Au core size (Au₁₁(PPh₃)Cl > Au₂₅(PET)₁₈ > Au₅₅(PPh₃)₁₂Cl₆ > Au₁₄₀(SC₆H₁₃)₅₃) (Figure 7A,B and Table 3). From estimation of the number of electrons for the ORR from a Koutecky–Levich plot [85], it was observed that the relatively small size of Au₉ NCs (Au₁₁(PPh₃)Cl, Au₂₅(PET)₁₈, and Au₅₅(PPh₃)₁₂Cl₆) resulted in the occurrence of the four-electron reaction, whereas Au₁₄₀(SC₆H₁₃)₅₃ tended to follow the two-electron reaction pathway (Figures 7C,D). Later, these researchers also synthesized a series of Auₙ(SR)ₘ NCs (Au₅₅(PET)₁₈, Au₄₄(PET)₁₆, and Au₁₄₄(PET)₁₆) with PET ligands and measured their ORR activities. The results revealed that a smaller core size was associated with higher ORR activity: Au₅₅(PET)₁₈ > Au₄₄(PET)₁₆ > Au₁₄₄(PET)₁₆ (Table 3) [112]. As the core size decreased, the ratio of low-coordinated surface atoms increased and the d-band center of the Fermi level changed. It was interpreted that smaller Auₙ(SR)ₘ NCs exhibited higher ORR activity because the promotion of oxygen adsorption on the gold core surface was accelerated by miniaturization of the metal core.

Figure 7. (A) Cyclic voltammograms of Auₙ(SR)ₘ/GCE (n = 11, 25, 55, and 140) saturated with O₂ and Au₁₁(PPh₃)Cl/GCE saturated with N₂ (thin solid curve). (B) Current density and overpotential of ORR activity with each size of Auₙ NCs. (C) Koutecky–Levich plots at different applied potentials of a GCE modified with Au₁₁(PPh₃)Cl. (D) Rotating-disk voltammograms (rotation rate: 3600 rpm) of various Auₙ(SR)ₘ/GCE (n = 11, 25, 55, and 140). Panels (A–D) are reproduced with permission from reference [111]. Copyright Wiley-VCH, 2009.

On the other hand, Dass et al. studied the dependence of the ORR activity on the core size using Auₙ NCs protected by 4-tert-butylbenzenethiolate (TBBT), whose structure differs significantly from that of PET [113]. In this experiment, single-walled carbon nanotubes (SWNTs) carrying Auₙ(TBBT)ₘ NCs (n = 28, 36, 133, and 279; Figure 8A; Auₙ(TBBT)ₘ NCs/SWNTs) were loaded onto the GCE. The ORR actives were measured by scanning the potential using the RDE method in a 0.1 M KOH aqueous solution filled with O₂ (Figure 8B). The overvoltage of the ORR was smaller in the order of Au₅₅(TBBT)₇₄ > Au₁₃₃(TBBT)₅₂ > Au₂₇₉(TBBT)₃₄ > Au₂₈(TBBT)₂₀. However, the selectivity of the four-electron reduction reaction was superior in the order of Au₅₅(TBBT)₇₄ > Au₁₃₃(TBBT)₅₂ > Au₂₇₉(TBBT)₃₄ > Au₂₈(TBBT)₂₀ [113] (Figure 8C). Notably, this trend was similar to that of the size dependence of the stability of Auₙ(TBBT)ₘ NCs itself. The same group performed similar studies using tert-butylthiolate
(S-Bu) instead of TBBT as a ligand [114]. S-Bu has a bulky framework and when this ligand is used in the synthesis of Au\(n\)(SR)\(m\) NCs, the ratio of the metal atom and the ligand in the generated Au\(n\)(SR)\(m\) NCs is different from that in Au\(n\)(SR)\(m\) NCs synthesized using another ligand. Such Au\(n\)(S-Bu)\(m\) NCs exhibit a unique size dependency for ORR activity (Au\(_{65}\)(S-Bu)\(_{29}\) > Au\(_{46}\)(S-Bu)\(_{24}\) > Au\(_{30}\)(S-Bu)\(_{18}\) > Au\(_{23}\)(S-Bu)\(_{16}\)) [114].

Figure 8. (A) X-ray crystal structures of Au\(n\)(TBBT)\(m\) NCs (\(n = 28, 36, 133, \) and 279). (B) Rotating-disk voltammograms recorded for the ORR activity of Au\(_{36}\)(TBBT)\(_{24}\)/GCE at different rotation rates. (C) Reaction rate constant \(\ln(k)\) vs. overpotential E plots with each size of Au\(n\)(TBBT)\(m\) (\(n = 28, 36, 133, \) and 279). Panels (A–C) are reproduced with permission from reference [113]. Copyright American Chemical Society, 2018.

In addition to these effects of core sizes and ligands, the ORR activity also depended on the charge state of Au\(n\)(SR)\(m\) NCs. Chen et al. carried [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{-}\), [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{0}\), and [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{+}\) (SC\(_{12}\)H\(_{25}\) = 1-dodecanethiolate) on the GCE, and their ORR activities were evaluated by scanning the potential in a 0.1 M KOH aqueous solution using a rotating ring-disk electrode (RRDE) filled with O\(_2\) [115]. In addition, the generation of H\(_2\)O\(_2\) was evaluated from the RRDE current at a fixed ring potential (0.5 V vs. saturated calomel electrode (SCE)). When [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{-}\), [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{0}\), and [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{+}\) were used, the efficiencies of H\(_2\)O\(_2\) were 86%, 82%, and 72%, respectively. In addition, the number of electrons for the ORR was estimated to be 2.28 ([Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{-}\)), 2.35 ([Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{0}\)), and 2.56 ([Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{+}\); Figure 9A–C). For [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{-}\), which showed the highest production rate of H\(_2\)O\(_2\), the activity decreased only 9% even after 1000 cycles (Figure 9D). These results indicate that [Au\(_{25}\)(SC\(_{12}\)H\(_{25}\))\(_{18}\)]\(^{-}\) has high H\(_2\)O\(_2\) generating ability (Table 3) [115]. Since H\(_2\)O\(_2\) is a useful raw material for chemical products, the development of their highly selective production reactions is important. Jin et al. also studied the dependence of the ORR activity on the charge state of Au\(n\)(SR)\(m\) NCs using [Au\(_{25}\)(PET)\(_{18}\)]\(^{-}\), [Au\(_{25}\)(PET)\(_{18}\)]\(^{0}\), and [Au\(_{25}\)(PET)\(_{18}\)]\(^{+}\). They reported that too strong of an OH\(^{-}\) adsorbing ability of [Au\(_{25}\)(PET)\(_{18}\)]\(^{-}\) reduces the ORR activity [77]. Thus, it has been clarified that the charge state of Au\(n\)(SR)\(m\) NCs also has a significant effect on the ORR activity of Au\(n\)(SR)\(m\) NCs.
Figure 9. (A) Cyclic voltammograms, (B) electron transfer number \(n\), and (C) percentage of \(\text{H}_2\text{O}_2\) of the ORR on \(\text{Au}_{25}(\text{SCl}_{12}\text{H}_{25})_{18}\) with different charge states \([\text{Au}_{25}(\text{SCl}_{12}\text{H}_{25})_{18}]^{-}\), \([\text{Au}_{25}(\text{SCl}_{12}\text{H}_{25})_{18}]^{0}\), and \([\text{Au}_{25}(\text{SCl}_{12}\text{H}_{25})_{18}]^{+}\) in 0.1 M KOH aq saturated with \(\text{O}_2\). (D) Accelerated durability tests of \([\text{Au}_{25}(\text{SCl}_{12}\text{H}_{25})_{18}]^{-}\) performed for 1000 cycles. Panels (A–D) are reproduced with permission from reference [115]. Copyright Royal Society of Chemistry, 2014.

4. Conclusions

A system for the generation of a fuel such as hydrogen or methanol using natural energy (e.g., solar cells or photocatalytic water splitting) and the production of electricity by fuel cells using these fuels would be one of the ultimate energy conversion systems for our society. To realize such a system, high activation of the HER, OER, HOR, and ORR is indispensable. Recently, \(\text{Au}_n\) NCs have attracted considerable attention as model catalysts for these reactions. In this review, recent works on these materials were summarized. The overall characteristics of the HER, OER, and ORR can be summarized as follows.

1) Since the core size, doping metal, ligand structure, and charge state affect the electronic and geometrical structures of \(\text{Au}_n\) NCs, these parameters also have a great effect on the catalytic activity of \(\text{Au}_n\) NCs.

2) Although these three reactions proceed via different mechanisms, reducing the core size of \(\text{Au}_n\) NCs and improving the ligand conductivity tend to improve the activities.

3) When \(\text{Au}_n\) NCs are carried on a conventional catalytic support, their electronic structure changes and thus their catalytic activity also changes. Therefore, \(\text{Au}_n\) NCs are also useful for improving the catalytic activity of conventional catalytic materials.

5. Perspectives

Until recently, the materials with relatively high activity for all of HER, OER, and ORR are considered to be limited to Ir, Rh, Ru, and Pt [84,85]. However, the recent studies demonstrated that these properties could also be caused in Au by the discretization of the band structure (e.g., shift of d-band center [107,111]). For \(\text{Au}_n\) NCs, it is possible to precisely control the electronic/geometrical structures and thereby to elucidate the correlation between catalytic activity and electronic/geometrical structure. In addition, the use of fine \(\text{Au}_n\) NCs as a catalyst is effective in reducing the consumption of expensive noble metals. It is expected that the studies on the catalytic
activities of Au\textsubscript{n} NCs lead to solve the mechanism in catalytic reactions on the metal surface and create the amazing catalysts we have never seen.

However, to create such HER, OER, and ORR catalysts using Au\textsubscript{n} NCs and their alloy NCs, further studies are required. Previous studies have shown that doping with Group 10 elements (Pt and Pd) induces high activation. Thus, a method for increasing the doping concentration of these elements is expected to be developed in the future. In addition, regarding the HER and OER, in spite of decomposing water, most studies thus far have used hydrophobic ligands that are not compatible with water. This may be related to the fact that the synthesis of hydrophobic Au\textsubscript{n} NCs is easier than that of hydrophilic Au\textsubscript{n} NCs. In particular, it is difficult to selectively synthesize a group-10-element-doped cluster using a hydrophilic ligand using the conventional synthesis method. However, as shown in this review, it is more appropriate to use hydrophilic Au\textsubscript{n} NCs as HER and OER catalysts. Therefore, in the future, additional research on hydrophilic Au\textsubscript{n} NCs is expected to increase the types of ligands and core sizes of hydrophilic Au\textsubscript{n} NCs. Such studies are expected to lead to the creation of highly active HER, OER, and ORR catalysts and eventually to the development of design guidelines for establishing ultimate energy conversion systems.

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