Abstract: Recently, the creation of new heterogeneous catalysts using the unique electronic/geometric structures of small metal nanoclusters (NCs) has received considerable attention. However, to achieve this, it is extremely important to establish methods to remove the ligands from ligand-protected metal NCs while preventing the aggregation of metal NCs. In this study, the ligand-desorption process during calcination was followed for metal-oxide-supported 2-phenylethanol-protected gold (Au) 25-atom metal NCs using five experimental techniques. The results clearly demonstrate that the ligand-desorption process consists of ligand dissociation on the surface of the metal NCs, adsorption of the generated compounds on the support and desorption of the compounds from the support, and the temperatures at which these processes occurred were elucidated. Based on the obtained knowledge, we established a method to form a metal-oxide layer on the surface of Au NCs while preventing their aggregation, thereby succeeding in creating a water-splitting photocatalyst with high activity and stability.

Introduction

Recently, ligand-protected metal nanoclusters controlled by atomic accuracy (atomically precise metal NCs)\(^{[1]-[14]}\) have been actively applied in heterogeneous catalysts (thermal-, photo-, and electro-catalysts).\(^{[15]-[24]}\) Metal NCs exhibit physicochemical properties and functions that differ from those of the corresponding bulk metals and metal nanoparticles (NPs). Furthermore, their properties are dramatically affected by the number of constituent atoms and heteroatom substitutions.\(^{[1]-[14]}\) Therefore, novel heterogeneous catalysts with unique catalytic properties can be created using precise metal NCs. In addition, it is difficult to identify highly active particles in conventional heterogeneous catalysts because the metal NPs are loaded with a relatively large size distribution. In contrast, for heterogeneous catalysts loaded with atomically precise metal NCs, the chemical composition of the loaded metal NCs is defined, facilitating the identification of highly active metal NCs and their selective loading. For such heterogeneous catalysts, it is also easy to obtain a deep understanding of the correlation between the geometric/ interface structure, catalytic activity and the reaction mechanism.\(^{[15,16,25]}\) Thus, the use of precise metal NCs in heterogeneous catalysis has many advantages for both the development of practical catalysts and the understanding of the mechanism of catalytic reactions.

When creating such heterogeneous catalysts, generally, 1) metal NCs are first precisely synthesized using ligands. Then, 2) the obtained atomically precise metal NCs are adsorbed onto the support. Typically, the presence of ligands in a heterogeneous catalyst leads to a decrease in catalytic activity because it inhibits the approach of the reactant to the surface of the metal NCs and induces a modification of the electronic structure of the metal NCs (Scheme 1(a)).\(^{[26,27]}\) Therefore, in many cases, 3) some or all of the ligands are removed by calcination or other pretreatments to attain higher activity (Scheme 1(b)).\(^{[15-24,28,29]}\) However, ligand removal also induces aggregation of metal NCs. When such...
aggregation occurs, the catalytic activity specific to metal NCs is diminished (Scheme 1(c)). Therefore, in ligand removal, it is extremely important to select conditions that remove only the ligands while maintaining the number of constituent atoms of the metal NCs. However, a clear understanding of the ligand-desorption mechanism during calcination has not yet been attained. To perform calcination under appropriate conditions and therefore create a highly functional heterogeneous catalyst, it is essential to attain a deep understanding of this mechanism.

In this study, for metal-oxide-adsorbed 2-phenylethethylthiolate (PET; Scheme S1(a)) protected gold (Au) 25-atom NCs ([Au25(PET)18]/C0; Scheme S2(a)), which is a commonly used catalyst in heterogeneous catalytic applications,[18,20–33] the ligand-desorption process during calcination was followed using five experimental techniques. The results clearly demonstrate that the ligand-desorption process consists of ligand dissociation on the surface of the metal NCs, adsorption of the generated compounds on the support and desorption of the compounds from the support, and elucidate the temperatures at which these processes occur. Based on the obtained knowledge, we have established a method to load Au NCs while preventing their aggregation, thereby succeeding in creating a water-splitting photocatalyst with high activity and stability.

Results and Discussion

Ligand-Desorption Mechanism

Flow of the Experiments

The flow of the experiments is illustrated in Scheme 2. Further details for each experiment and measurement are provided in the Supporting Information.

For metal NCs, [Au25(PET)18] (counter ion is tetraoctylammonium ion = TOA+; hereinafter described as Au25(PET)18) was used. Au25(PET)18 was synthesized with atomic precision using a reported[34] method with slight modification (Scheme 2(a), Scheme S3, and Figure S1A(a)). For metal oxides, to apply the obtained heterogeneous catalysts as water-splitting photocatalysts (Scheme 3)[35–38] BaLa4Ti4O15 (Scheme S2(b) and S4)[39–42] which is one of the most advanced photocatalysts, was used. When metal oxides are placed in water, hydroxyl groups (-OH) are generally formed on their surfaces. Metal NCs protected by hydrophobic ligands, such as PET, are barely adsorbed on such hydrophilic surfaces.[43] However, to estimate the metal loading weight with high accuracy, it is necessary to adsorb the metal NCs on the support with a high adsorption efficiency. Therefore, some of the PET in Au25(PET)18 was replaced with hydrophilic p-mercaptobenzoic acid (p-MBA; Scheme S1(b)) [44] (Scheme 2(b) and Figure S1B(a)).[43] The obtained Au25(PET,p-MBA)x (x = 5–12; hereinafter described as Au25(PET,p-MBA)x) was stirred with BaLa4Ti4O15 in acetone solution for 1 h at a weight ratio of 0.1 wt % Au, which gave the best water-splitting photocatalytic activity in our previous study.[40]
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**Mechanism for Au_{25}(PET, p-MBA)_{18}**

To better understand the phenomena occurring on the metal oxide during calcination, we first examined the ligand-desorption pattern of Au_{25}(PET, p-MBA)_{18}, which was not loaded on the metal oxide. Figure 1A presents the DIP-MS spectrum of Au_{25}(PET, p-MBA)_{18}. This MS spectrum contains peaks derived from all the compounds desorbed from the sample from 80°C to 500°C (Table S1). The main peaks appeared at m/z = 91, 105, 137, 154, 254, 274, and 290. The peak at m/z = 254 is attributed to a compound derived from TOA⁺ (Figure S2), which is the counter cation of Au_{25}(PET, p-MBA)_{18}. Comparison of the DIP-MS spectra with Au_{25}(PET, 3-MPA)_{18} and Au_{25}(SC4, 3-MPA)_{18} (3-MPA = 3-mercaptopyrrolic acid; SC4 = 1-buthanethiolate; Scheme S1(c)/(d) and Figure S1) with different ligand combinations revealed that the peaks at m/z = 91, 105, and 274 correspond to PET-derived compounds, and the peak at m/z = 290 can be obtained only when both PET and p-MBA are present (Figure S3–S5). It can be interpreted that the peak at m/z = 91 is caused by EI dissociation of PET, and the peak at m/z = 137 is caused by EI dissociation (Figure S6) of p-MBA (M_w = 154) (Figure 2(a) and Figure S7). These results indicate that 1) calcination of Au_{25}(PET, p-MBA)_{18} yields phenylethane (PET; m/z = 105), p-MBA (m/z = 154; in this case, thiol rather than thiolate), (PET); (m/z = 274), and PET-p-MBA (m/z = 290) as the major desorbates, and 2) therefore, in the calcination of Au_{25}(PET, p-MBA)_{18}, S–C and Au–S bond dissociations in Au–PET and Au–S bond dissociation in Au–p-MBA occur as the main dissociation channels (Figure 2(a)). Although these results are overall consistent with previous reports,[54] the fact that p-MBA is desorbed from the surface of the Au NCs as a thiol rather than a thiolate was first demonstrated in this report.[49]
Next, DIP-MS measurements of Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$ were performed. Figure 3A presents the mass spectra of the compounds desorbed at temperatures ranging from 80 to 500°C. Surprisingly, the peaks attributed to PE ($m/z$ = 105), p-MBA ($m/z$ = 154), (PET)$_2$ ($m/z$ = 274), and PET/p-MBA ($m/z$ = 290) were negligibly observed in the mass spectra. On the other hand, carbon dioxide (CO$_2$; $m/z$ = 44), which is one of the final products of calcination, benzene ($m/z$ = 78), and styrene ($m/z$ = 104) were strongly observed in the mass spectra. Benzene is interpreted to form from the EI dissociation of styrene (Figure S9). Figure 3B shows the correlation between the desorption temperature and ion intensity for CO$_2$ (Figure 3B(a)) and styrene (Figure 3B(b)). The main desorption temperatures of CO$_2$ (320–450°C) and styrene (225–310°C) were shifted to higher values compared with those for PE (195–235°C), p-MBA (200–295°C), (PET)$_2$ (195–235°C), and PET/p-MBA (210–240°C) desorbed from unsupported Au$_{25}$(PET, p-MBA)$_{18}$ (Figure 1B and S10). These results imply that the PE, p-MBA, (PET)$_2$, and PET/p-MBA thermally dissociated from Au$_{25}$(PET, p-MBA)$_{18}$ were once adsorbed on the BaLa$_4$Ti$_4$O$_{15}$ surface and then desorbed from the surface of BaLa$_4$Ti$_4$O$_{15}$ in the form of styrene or CO$_2$ (Figure 2(b)).

**Mechanism for Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$**

Au L$_3$-edge FT-EXAFS analysis was performed on unsupported Au$_{25}$(PET, p-MBA)$_{18}$ and calcined samples to attain a deeper understanding of the temperature at which each step occurs (Figure 4 and S11). The peaks at ca. 1.8 Å$^{[45,47,48]}$ attributed to the Au–S bond were clearly observed in the spectra of Au$_{25}$(PET, p-MBA)$_{18}$ (Figure 4(a)) and the sample after calcination at 250°C (Figure 4(b)). On the other hand, for the sample calcined at 300°C (Figure 4(c)), the intensity of this peak was significantly reduced. This finding indicates that almost all the Au–S bonds dissociate in the temperature range of 250–300°C in Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$, which is consistent with the results in Figure 1B(b)–(d).

As for the behavior of the compounds transferred onto BaLa$_4$Ti$_4$O$_{15}$, it can be judged from Figure 3B that the organic compounds start to be removed from the BaLa$_4$Ti$_4$O$_{15}$ surface at 225°C. Since the desorption of the compound from Au$_{25}$(PET, p-MBA)$_{18}$ continues up to a temperature of ca. 300°C (Figure 1B and Figure 4), it can be interpreted that the migration of the compounds from Au$_{25}$(PET, p-MBA)$_{18}$ onto BaLa$_4$Ti$_4$O$_{15}$ and the desorption of organic compounds from the BaLa$_4$Ti$_4$O$_{15}$ surface proceed in parallel at temperatures above 225°C. With respect to S compounds, it was observed that the S compounds remain on the surface of BaLa$_4$Ti$_4$O$_{15}$ in the form$^{[49]}$ of SO$_3^-$ or SO$_4^{2-}$ even at 500°C (Figure 5).
Figure 4. Au $L_3$-edge FT-EXAFS spectra of a) $\text{Au}_{25}(\text{PET}, p\text{-MBA})_{18}$, $\text{Au}_{25}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ obtained by calcination at b) 250$^\circ$C and c) 300$^\circ$C, and d) Au foil. The purple and yellow regions indicate the Au–S and Au–Au bond regions, respectively. In (a), only weak peaks appear in the Au–Au bond region because the Au$_{15}$ core (Scheme 52(a)) fluctuates at room temperature.

Figure 5. Comparison of S 2p XPS spectra: a) $\text{Au}_{25}(\text{PET}, p\text{-MBA})_{18}$, b) $\text{Au}_{25}(\text{PET}, p\text{-MBA})_{18}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$, $\text{Au}_{25}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ obtained by calcination at c) 300$^\circ$C and d) 500$^\circ$C. In the spectra, the green and purple lines indicate the baseline and fitting result, respectively. The peak at ca. 162.8 eV is assigned to S in Au–S, whereas the peaks at ca. 167.2 eV and ca. 167.3 eV are assigned to S oxides, such as $\text{SO}_3^2$ and $\text{SO}_4^{2-}$.

Figure 6(a)–(h) present TEM images of $\text{Au}_{25}(\text{PET})_{18}$, $\text{Au}_{25}(\text{PET}, p\text{-MBA})_{18}$, the sample before calcination, the sample after calcination at 250$^\circ$C, 300$^\circ$C, 350$^\circ$C, 400$^\circ$C, and 500$^\circ$C, respectively. In Figure 6(a)–(e), only fine particles of approximately 1 nm are observed. On the other hand, in Figure 6(f)–(h), particles with a size over 2 nm are observed.

These results indicate that calcination up to 300$^\circ$C causes almost no aggregation of $\text{Au}_{15}$; however, calcination at a higher temperature causes $\text{Au}_{15}$ aggregation.

Based on all the above results, the phenomena that occurs during calcination of $\text{Au}_{25}(\text{PET}, p\text{-MBA})_{18}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ can be described as follows (Figure 7):

1) The S–C and Au–S bond dissociation of Au–PET starts to occur at approximately 195$^\circ$C, followed by the Au–S dissociation of Au–p-MBA at approximately 200$^\circ$C. These dissociations are complete by 295$^\circ$C. The compounds produced by the dissociation (PE, p-MBA, PET, and PET–p-MBA) migrate to the BaLa$_4$Ti$_4$O$_{15}$ surface (Figure 7(b)).

2) At temperatures above 225$^\circ$C, in parallel with 1), the adsorbates on BaLa$_4$Ti$_4$O$_{15}$ start to desorb from the
surface of BaLa₄Ti₄O₁₅ in the form of styrene and/or CO₂ (Figure 7(c)).

3) At ca. 300°C, most of the ligands are desorbed from the surface of the Au NCs; the Au₂₅ maintains its size even at this temperature (Figure 7(d)). However, based on our previous work, the geometric and electronic structures of Au₂₅ is considered to change, largely due to elimination of the ligands; for example, the gold core geometry changes from a spherical structure (Scheme S2(a)) to a flat structure.

4) A further increase of the calcination temperature causes significant aggregation of Au₂₅ (Figure 7(e)). Organic (Figure 3 B(a)) and S compounds (Figure 5(d)) continue to remain on BaLa₄Ti₄O₁₅ and cannot be completely eliminated even at 500°C (Figure 7(e)).

In addition to the strength of the Au–S and S–C bonds, the interaction between the ligands on the surface of the Au NCs also significantly affects the temperature of the ligand desorption from the surface of the Au NCs (Figure S12). It is also presumed that the temperature at which the compound is desorbed from the support is related to the magnitude of the compound-support interaction. In addition, the ease of dissociation/desorption of the ligands and the resulting aggregation of Au NCs appears to slightly vary depending on the calcination atmosphere (Figure S13). However, the results suggesting 1)–4) have often been observed during previous calcinations performed with thiolate (SR) functional groups, supports, and atmospheres different from this study for example, Au₂₅(SG)₁₈/BaLa₄Ti₄O₁₅ (SG = glutathionate) and Au₃₈(PET)₂₄/CeO₂ (CeO₂ = cerium(IV) oxide). Therefore, although there are differences in the required temperatures, it is inferred that behavior similar to that described in 1)–4) occurs during the calcination of any SR-protected Au NCs (Auₙ(SR)ₘ NCs; n = number of Au, m = number of SR ligands)/metal oxide. To date, a unified view has not been presented for the behavior of these Auₙ(SR)ₘ NCs/metal oxides during calcination. In this study, we succeeded in elucidating the details of the phenomena occurring during the calcination of Au₂₅(PET, p-MBA)₁₈/BaLa₄Ti₄O₁₅ by combining multiple experimental techniques (DIP-MS, EXAFS spectroscopy, XPS, and TEM observation).

**Figure 7.** Proposed phenomenon occurring at each temperature during calcination of Au₂₅(PET, p-MBA)₁₈/BaLa₄Ti₄O₁₅; at a) room temperature, b) ca. 195°C, c) ca. 225°C, d) ca. 300°C, and e) 500°C.

**Toward the Creation of High-Performance Water-Splitting Photocatalysts**

As described above, the behavior of Au₂₅(PET, p-MBA)₁₈/BaLa₄Ti₄O₁₅ during calcination was elucidated, and most of the ligands were successfully removed from Au₂₅ with almost no aggregation (Figure 6(e)). However, Au NCs with exposed surfaces are prone to aggregation when left untended (Figure S14) and during catalytic reactions. Therefore, to create...
a highly durable heterogeneous catalyst, it is essential to apply some type of treatment to the catalyst to suppress the aggregation of Au NCs. In our previous study, we showed that when Au$_{25}$/Cr$_2$O$_3$/BaLa$_4$Ti$_4$O$_{15}$, which was obtained by the calcination of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$, was irradiated with UV light, Au$_{25}$ was embedded in the Cr$_2$O$_3$ layer (Cr$_2$O$_3$/Au$_{25}$/BaLa$_4$Ti$_4$O$_{15}$; Scheme 2(e)), and the stability of Au$_{25}$ against aggregation was greatly improved.$^{[43]}$ Furthermore, the formation of such a Cr$_2$O$_3$ film suppressed the reverse reaction on the surface of the Au NCs, resulting in higher water-splitting activity.$^{[43]}$ In the precursor, Au$_{25}$(PET, p-MBA)$_{18}$, the ligand was strongly bound to the surface of the Au NCs. However, in Cr$_2$O$_3$/Au$_{25}$/BaLa$_4$Ti$_4$O$_{15}$, it is assumed that the amorphous structure of Cr$_2$O$_3$ is weakly bound to Au NCs and forms an overlying structure on Au NCs because Au does not form bonds with O easily.$^{[43,55]}$ This appears to be the reason why Cr$_2$O$_3$/Au$_{25}$/BaLa$_4$Ti$_4$O$_{15}$ showed high water-splitting activity without losing the high H$_2$-generation activity of small Au NCs. It has been reported by other groups that the formation of such metal/semiconductor oxide films on the surface of metal NCs improves the stability of metal NCs against not only photocatalytic water-splitting reactions but also thermocatalytic reactions.$^{[17,56,57]}$ Therefore, the establishment of a method to form a metal oxide film on the Au$_{25}$ surface while suppressing the aggregation of Au$_{25}$ is expected to be extremely useful not only for the creation of high-performance water-splitting photocatalysts but also for the creation of high-performance heterogeneous catalysts. In our previous study, the aggregation of Au$_{25}$ occurred in the Cr$_2$O$_3$ layer.$^{[43]}$ In the current study, we attempted to elucidate the behavior of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ during calcination and light irradiation using six experimental techniques (DIP-MS, EXAFS spectroscopy, FT-IR spectroscopy, XPS, TEM observation, and HAADF-STEM EDX element mapping), and then, based on the obtained knowledge, we sought to establish a method to better control the particle size of Au NCs.

First, we investigated the behavior of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ during calcination. Figure 8A presents the DIP-MS spectrum of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ obtained by increasing the temperature from 80°C to 500°C. The observed compounds were overall very similar to those observed for Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$ (Figure 3A). This result indicates that the overall mechanism of ligand removal during the calculation of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ is similar to that of Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$ described in Figure 7. Indeed, the Au L$_3$-edge FT-EXAFS (Figure S15) and S 2p XPS (Figure S16) results strongly support this interpretation.

However, there are also some differences in the calculation mechanism between Au$_{25}$(PET, p-MBA)$_{18}$/BaLa$_4$Ti$_4$O$_{15}$ and Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$. For example, during the calculation of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$, styrene desorption started at a lower temperature (150°C; Figure 8B(b)) than that at which bond dissociation started on the surface of the Au NCs (195°C; Figure 1B). The study using FT-IR spectroscopy (Figure S17 and S18) revealed that some of the ligands in Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ migrated from Au$_{25}$(PET, p-MBA)$_{18}$ to Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ without heating. Such ligand migration is interpreted to be related to the start of the styrene desorption at 150°C in Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$ (Figure S19 and S20).

The Au L$_3$-edge FT-EXAFS (Figure S15) and diffuse reflectance spectra (Figure S21) of a series of samples indicate that the Au NCs change their geometric and electronic structures following ligand elimination, similar to the case of Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$.$^{[43]}$ Figure 9A(a) presents a TEM image of the sample after calcination at 300°C, revealing the presence of particles with an average size of 2.9 ± 0.9 nm. There are two possible explanations for this finding: 1) in Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$, significant aggregation of Au$_{25}$ occurs upon calculation with ligand removal and 2) in Au$_{25}$(PET, p-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$, the aggregation of Au$_{25}$ is also relatively suppressed during calcination but starts to occur soon thereafter.

In order to clarify the reason for the observed 2.9 ± 0.9 nm particles, we initiated UV-light irradiation within a few minutes after calcination. The average particle size of the Au NCs was suppressed to 1.5 ± 0.5 nm (Figure 9A(b)). According to HAADF-STEM EDX elemental mapping, these Au NCs were embedded in the Cr$_2$O$_3$ film (Figure 9B and S22 and Table S2). These results indicate that the aggregation of Au$_{25}$ is relatively suppressed upon heating.
Based on this understanding, it is extremely important to reduce the time between calcination and light irradiation as much as possible to create highly functional water-splitting photocatalysts with fine and stable Au NCs. In fact, the sample in Figure 9A(b) exhibited a higher water-splitting activity than the sample with more aggregation (Figure S24 and S25 and Scheme S8). In addition, further aggregation of Au NCs was suppressed even after long-term exposure to air for this sample, and this sample exhibited high durability during the water-splitting photocatalysis (Figure 11 and S26). Currently, Cr2O3 film formation by UV-light irradiation is performed in pure water (Figure S23). However, the addition of a suitable sacrificial agent to the water would increase the consumption rate of the holes generated by the UV-light irradiation,[43,58,59] thereby allowing the reduction reaction on the surface of the Au NCs, i.e., Cr2O3 film formation, to occur in a shorter time. It is expected that photocatalysts with even less aggregation of Au NCs can be created in the future by improving the Cr2O3 film formation method.

Conclusion

In this study, the calcination mechanisms of Au25(PET, pMBA)18/BaLa4Ti4O15 and Au25(PET, pMBA)18/Cr(OH)3/BaLa4Ti4O15 were investigated, and fine and stable Au NCs-loaded heterogeneous water-splitting photocatalysts were created. The following findings were obtained.

1) During the calcination of Au25(PET, pMBA)18/BaLa4Ti4O15, the dissociation of S–C and Au–S bonds of Au–PET first starts to occur and then the dissociation of the Au–S bonds of Au–p-MBA starts. The desorbed compounds are then adsorbed onto the support. As the temperature is increased, most of the compounds on the support are desorbed as styrene or CO2. At temperatures above 225 °C, the migration of the compound onto the support and the desorption of the compound from the support occur contemporaneously. Although most of the ligands can be removed from the Au25 surface by calcination at 300 °C while maintaining the size of Au25, some organic compounds and S oxides still remain on the BaLa4Ti4O15 surface even at 500 °C.

2) For the calcination of Au25(PET, pMBA)18/Cr(OH)3/BaLa4Ti4O15, the overall phenomenon is similar to that of Au25(PET, p-MBA)18/BaLa4Ti4O15. However, it differs from the case of Au25(PET, p-MBA)18/BaLa4Ti4O15 in that the compound desorption from the support surface occurs before the start of the ligand dissociation from the Au NCs (Figure 10(b)).

3) When Au25/Cr2O3/BaLa4Ti4O15 is irradiated with light, Au NCs are embedded in Cr2O3 (Figure 10(f)). This phenomenon is assumed to be caused by the transfer of excited electrons generated in the photocatalyst to Au NCs and thereby the reduction of highly oxidized Cr (+3+) to form a deposit over the surface of the Au NCs (Figure S23).
The findings obtained in this study are expected to provide clear design guidelines for the creation of highly functional heterogeneous catalysts using metal NCs, which have been reported thus far.[12,60,61]

Supporting Information: Experimental section, additional schemes, additional DIP-MS, XPS, FT-IR, FT-EXAFS spectra, TEM image, and photocatalytic activity.

Acknowledgements

We thank Dr. Jun Hirayama (Kyoto University) for technical assistance. This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant number JP16H04099, 16K21402, 20H02698, 20H02552). The authors acknowledge also the instruments and scientific and technical assistance of Ashley Slattery and Microscopy Australia at

Figure 10. Proposed phenomenon occurring at each temperature and by UV-light irradiation in Au$_{25}$(PET, $p$-MBA)$_{18}$/Cr(OH)$_3$/BaLa$_4$Ti$_4$O$_{15}$; at a) room temperature, b) ca. 150°C, c) ca. 195°C, d) ca. 300°C, e) 500°C, and f) after UV-light irradiation.

Figure 11. Time course of water-splitting activity of Cr$_2$O$_3$/Au NCs/BaLa$_4$Ti$_4$O$_{15}$ with Au NC particle-size of 1.5 ± 0.5 nm (Figure 9A(b)). The red and blue circles represent H$_2$ and O$_2$, respectively.
Conflict of interest

The authors declare no conflict of interest.

Keywords: catalysts · metal clusters · nanostructures · photocatalysts · water splitting
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Manuscript received: April 9, 2021
Revised manuscript received: May 18, 2021
Accepted manuscript online: May 26, 2021
Version of record online: 

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Heterogeneous Photocatalysis

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Creation of High-Performance Heterogeneous Photocatalysts by Controlling Ligand Desorption and Particle Size of Gold Nanocluster

The ligand-desorption process during calcination was elucidated for metal-oxide-supported thiolate-protected gold (Au) 25-atom metal nanoclusters (NCs) using five experimental techniques. Furthermore, based on obtained knowledge, a method was established to form a metal-oxide layer on the surface of Au NCs while preventing their aggregation, thereby succeeding in creating a water-splitting photocatalyst with high activity and stability.