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## Photoelectrochemical etching and energy gap control of silver clusters

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**Energy gap of Ag clusters is controlled on the basis of photoinduced electron transfer from the clusters to TiO<sub>2</sub>. With 2.6-eV light irradiation, Ag<sub>32</sub> clusters on TiO<sub>2</sub> are oxidized and disappear. With <1.6-eV light, the energy gap of Ag<sub>32</sub> is changed from ~1.4 to ~1.7 eV because of the photoetching.**

Quantum-sized metal clusters (CLs), which are smaller than ~2 nm in diameter and consist of less than ~250 atoms, have discrete electron levels due to a quantum size effect. Based on such discrete levels, metal CLs exhibit some unique properties such as photoabsorption<sup>1,2</sup> and fluorescence,<sup>2,3</sup> magnetism,<sup>4,5</sup> catalysis,<sup>6,7</sup> photosensitization,<sup>8-10</sup> and electroluminescence.<sup>11</sup> In particular, their optical, photochemical, and photoelectrochemical properties strongly depend on the HOMO-LUMO energy gap of the CL. Metal CLs with a wide energy gap can make efficient use of photons of high energy (i.e. short wavelength) and the excited CLs are advantageous for electron exchange with wide variety of electron donors and acceptors. On the other hand, narrow gap CLs can absorb photons over a wide range of wavelengths, because they can even absorb photons of low energy (i.e. long wavelength). Control of the energy gap of metal CLs is therefore an important issue.<sup>10</sup>

The energy gap is basically dependent on the CL size. As the CL size increases, the electron levels are more densely distributed and the HOMO-LUMO gap decreases.<sup>2,12</sup> At present, a size-focusing method is used to control the size of metal CLs. Heating<sup>13-16</sup> or aging<sup>17-19</sup> of size-polydisperse CLs selectively gives highly stable CLs such as Au<sub>25</sub>,<sup>13,18,19</sup> Au<sub>38</sub>,<sup>14,15</sup> Au<sub>102</sub>,<sup>17</sup> and Au<sub>144</sub>.<sup>16</sup> On the other hand, we can simultaneously obtain many different CLs separated by size on the basis of electrophoresis,<sup>2,20-22</sup> although their yields are relatively low.

In this study, we control the energy gap of Ag CLs by photoelectrochemical etching. Recently, we have found that

metal CLs can be used as a photosensitizer of TiO<sub>2</sub>. The metal CL-modified TiO<sub>2</sub> (CL/TiO<sub>2</sub>) works as a photoanode of wet<sup>8,10,23-27</sup> or solid-state<sup>28</sup> solar cells and as a photocatalyst<sup>9,29</sup> driven by visible and near infrared light. In the presence of an appropriate electron donor, an electron excited from HOMO to LUMO of the CL is injected into the TiO<sub>2</sub> conduction band, accompanied by electron transfer from the donor to HOMO of the CL. However, in the absence of a good electron donor, positive charges would accumulate in the metal CL, and the CL could eventually be oxidized to corresponding metal cations. The oxidation would result in a decrease in the CL size and an increase in the energy gap. The photooxidation ends when the energy gap of the CL becomes smaller than the energy of irradiated photons (i.e. absorption edge wavelength < irradiation wavelength, Fig. 1). Here we employ a glutathione (GSH)-protected Ag CL, Ag<sub>32</sub>(SG)<sub>19</sub> (Ag<sub>32</sub>),<sup>30</sup> and control its energy gap on the basis of photoinduced charge separation between Ag<sub>32</sub> and TiO<sub>2</sub>.

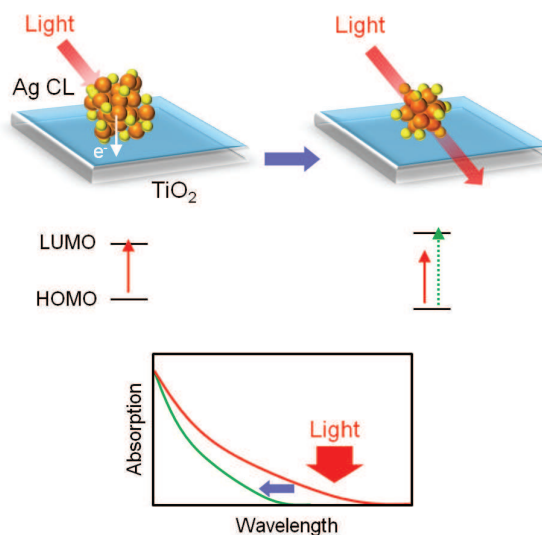


Fig. 1 Concept of the energy gap control of a Ag CL adsorbed on TiO<sub>2</sub> on the basis of photoelectrochemical etching.

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$\text{Ag}_{32}$  was synthesized and separated according to the literature.<sup>20,22</sup> In short, 0.25 mmol GSH and 0.25 mmol  $\text{AgNO}_3$  dissolved in water (2 and 0.5 mL, respectively) were sequentially added to ice-cold methanol (47.5 mL) and mixed for 5 min. An ice-cold 0.2 M aqueous  $\text{NaBH}_4$  (12.5 mL) was added under vigorous stirring and aged for 1 h. All the solutions were deaerated by  $\text{N}_2$ . The obtained precipitates were centrifuged at 3000g for 5 min and dried in vacuum at room temperature. The powders thus obtained (5 mg) were dissolved in deaerated water containing 5 vol% glycerol (1.5 mL), and  $\text{Ag}_{32}$  was separated from the Ag CLs in the solution by polyacrylamide gel electrophoresis (PAGE).

The PAGE pattern and the absorption spectrum of the separated  $\text{Ag}_{32}$  aqueous solution are shown in Fig. 2. The spectrum is virtually identical with that of  $\text{Ag}_{32}$ .<sup>30</sup> The PAGE-separated  $\text{Ag}_{32}$  sample should essentially be free from other Ag CLs, Ag compounds, or Ag ions. The concentration of  $\text{Ag}_{32}$  in the solution was calculated to be  $5.2 \times 10^{-6}$  M from the content of Ag atoms ( $1.7 \times 10^{-4}$  M) determined by inductively coupled plasma mass spectrometry (SPQ9000, Hitachi). Therefore, absorption coefficient of  $\text{Ag}_{32}$  at 480 nm is calculated to be  $6.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . This is comparable to the values of thiol-protected Au CLs ( $\sim 1 \times 10^4 - 2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  in the visible region).<sup>2,31</sup>

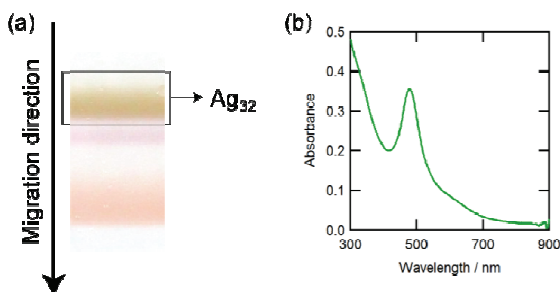


Fig. 2. (a) An electrophoretic pattern of the polydisperse Ag CLs (bias voltage of 150 V was applied for 10 h). (b) An absorption spectrum of an aqueous solution of  $\text{Ag}_{32}(\text{SG})_{19}$  ( $5.2 \times 10^{-6}$  M).

Next, we observed morphology of the  $\text{Ag}_{32}$ -adsorbed single-crystalline  $\text{TiO}_2$  surface and its change under visible light irradiation. Although transmittance electron microscopy (TEM) is the most widely used method for observation of CLs, a strong electron beam causes reactions of  $\text{Ag}_{32}$ , including the electron transfer from  $\text{Ag}_{32}$  to  $\text{TiO}_2$ . In addition, observation of the same CLs before and after visible light irradiation under ambient conditions is almost impossible. We therefore carried out atomic force microscopy (AFM, NanoNavi, Hitachi). A rutile  $\text{TiO}_2(110)$  single-crystal substrate ( $10 \times 10 \times 0.5$  mm, Shinkosha) was etched in 20 vol% aqueous HF for 10 min, rinsed with water and dried, followed by annealing at 900 °C for 1 h. The aqueous  $\text{Ag}_{32}$  was diluted to  $4.4 \times 10^{-11}$  M with 0.01 M sodium acetate buffer (pH 4, deaerated with  $\text{N}_2$ ). A 150- $\mu\text{L}$  aliquot of the solution was cast on the single crystal and left for 2 h. Then the substrate was rinsed thoroughly with water and dried. The surface was subjected to AFM observation ( $500 \times 500$  nm,  $512 \times 512$  datapoints). Since the

scan interval is 0.98 nm, underestimation of the CL height should be less than 0.013 nm taking the tip curvature radius (10 nm) into account.

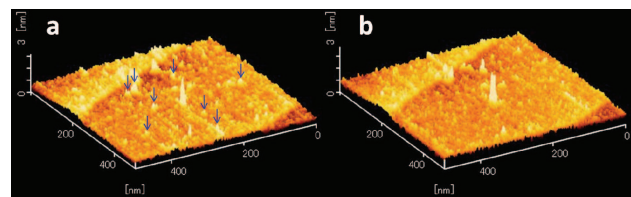
So far, there are no reports on the structure of  $\text{Ag}_{32}(\text{SG})_{19}$ . In the case of  $\text{Au}_{25}(\text{SG})_{18}$ , an icosahedral  $\text{Au}_{13}$  core is covered with 6  $\text{Au}_2(\text{SG})_3$  staple motifs.<sup>1,32</sup> Similarly,  $\text{Au}_{38}(\text{SG})_{24}$  has an anisotropic  $\text{Au}_{23}$  core surrounded by 6  $\text{Au}_2(\text{SG})_3$  and 3  $\text{Au}(\text{SG})_2$  motifs.<sup>33,34</sup> Heights of  $\text{Au}_{13}$  and  $\text{Au}_{23}$  cores are calculated to be 0.725 nm and 0.754 nm from the atomic radius of Au, 0.144 nm. Since the atomic radius of Ag is equal to that of Au, heights of  $\text{Ag}_{13}$  and  $\text{Ag}_{23}$  should be close to those of  $\text{Au}_{13}$  and  $\text{Au}_{23}$ , respectively. Considering that the roughness of the  $\text{TiO}_2$  surface is about 0.3 nm, the apparent height of  $\text{Ag}_{32}$  could be 0.5–1.5 nm or so.

Surface images of the  $\text{TiO}_2$  substrate with  $\text{Ag}_{32}$  CLs before and after irradiation with 480 nm, 1  $\text{mW cm}^{-2}$  monochromatic light in humid air ( $\sim 70\%$  relative humidity, RH) for 30 min are shown in Fig. 3. More than 20 "CL-sized" particles were found before irradiation, and 8 of them (indicated with arrows) disappeared after the irradiation. On the other hand, disappearance was not significant when  $\text{TiO}_2$  substrate with  $\text{Ag}_{32}$  was left for 30 min in the dark. Some of the CL-sized particles are  $\text{Ag}_{32}$  CLs, and it is reasonable to infer that at least some of the  $\text{Ag}_{32}$  CLs disappear during the light irradiation, probably because of oxidation to  $\text{Ag}^+$  ions, which are released into adsorbed water layer on the  $\text{TiO}_2$  surface ( $\sim 5$  molecular layers at  $\sim 70\%$  RH<sup>35</sup>), as a result of injection of excited electrons to  $\text{TiO}_2$ . The injected electrons may be accepted by ambient oxygen or released  $\text{Ag}^+$  to give small Ag particles as is the case for the photooxidation of plasmonic Ag nanoparticles.<sup>36–38</sup> The oxidation of the CLs must be direct oxidation of the Ag core to  $\text{Ag}^+$  ions or two-step oxidation consisting of desorption of some ligands due to oxidation of the thiol moiety to a  $\text{SO}_2^-$  group or  $\text{SO}_4^{2-}$  ion<sup>39</sup> and following oxidation of the partially naked Ag core.

Thus, photoelectrochemical etching of  $\text{Ag}_{32}$  is suggested to be possible, although more quantitative analysis is difficult with AFM considering the precision of the measurements and the surface roughness. So we investigated energy gap control of  $\text{Ag}_{32}$  by light irradiation. In general, the HOMO-LUMO energy gap increases and photoabsorption edge blue-shifts with decreasing metal CL size.<sup>2,12</sup> If we oxidize CLs photoelectrochemically at a certain wavelength, the CL size would decrease and the photooxidation would eventually stop when their absorption edge becomes shorter than the irradiation wavelength (Fig. 1). There are some reports on photoetching of semiconductor quantum dots (QDs) in an aqueous solution.<sup>40,41</sup> Since the absorption edge of those QDs also depends on the particle size, it can be controlled by self-oxidation of QDs at an appropriate irradiation wavelength. In the present study, although the CLs are not self-oxidized in a solution, those are oxidized as a result of photoinduced electron transfer from the CLs to  $\text{TiO}_2$ .

For evaluation of the energy gap of CLs, we fabricated  $\text{Ag}_{32}/\text{TiO}_2$  electrodes as reported in our previous paper.<sup>25</sup> A compact  $\text{TiO}_2$  layer ( $\sim 34$  nm thick) was formed on an ITO-coated glass plate by a spray pyrolysis method. The substrate

was heated at 450 °C on a hot plate and an isopropanol solution of titanium diisopropoxide bis(acetylacetonate) (0.11 M) was sprayed on it (0.12 MPaG, 1 s spray twice with interval of 60 s), followed by further heating for 30 min. After cooling down, a nanoporous TiO<sub>2</sub> layer was formed on the compact layer by spin-coating (1500 rpm, 10 s) TiO<sub>2</sub> slurry (STS-21, Ishihara Sangyo, diluted to 75 vol% with pure water) and annealing at 450 °C for 1 h. Ag<sub>32</sub> aqueous solution (~5 × 10<sup>-6</sup> M, 0.2 vol% of acetic acid was added) was cast on the TiO<sub>2</sub> electrode and left for 2 h to adsorb Ag<sub>32</sub> on TiO<sub>2</sub>. We determined the absorption edge and the energy gap of Ag CLs adsorbed on TiO<sub>2</sub> from the photovoltage action spectrum, since the absorption edge was much less clear in the absorption spectrum due to optical interference effects of the thin ITO and TiO<sub>2</sub> layers. The photovoltage was measured with a Pt wire counter electrode in 0.1 M sodium acetate buffer (pH 5, deaerated with N<sub>2</sub>), 0.5 min after the monochromatic light irradiation started (3 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup>, full width at half maximum = 10 nm).



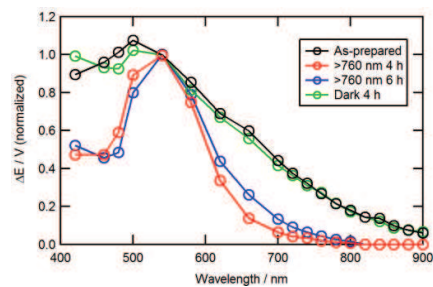
**Fig. 3.** AFM images of Ag<sub>32</sub> adsorbed on a rutile TiO<sub>2</sub>(110) single crystal (a) before and (b) after the irradiation with 480 nm, 1 mW cm<sup>-2</sup> light for 30 min in air (~70% RH). CLs indicated with arrows in Panel a disappeared after the irradiation.

Fig. 4 shows photovoltage action spectra of an as-prepared and irradiated Ag<sub>32</sub>/TiO<sub>2</sub> electrodes. The as-prepared Ag<sub>32</sub>/TiO<sub>2</sub> electrode responded even to ~900 nm near infrared light; the energy gap was ~1.4 eV. To control the energy gap, the as-prepared Ag<sub>32</sub>/TiO<sub>2</sub> electrode was irradiated with >760 nm, 5 mW cm<sup>-2</sup> light for 4 or 6 h in the buffer solution. A photopotential action spectrum was not measured prior to the >760 nm light irradiation to avoid photooxidation of Ag<sub>32</sub> during the measurement. After the >760 nm light irradiation, the electrodes responded to light only at wavelengths shorter than 800 nm; the energy gap was around 1.6 eV.

If we define the edge wavelength as the wavelength at which the photovoltage is <5% of the maximum value, that for the as-prepared electrode is 867 ± 31 nm, whereas those for irradiated electrodes (4 and 6 h) are 733 ± 42 and 740 ± 35 nm, respectively (n = 3 for each case). On the other hand, the edge wavelength did not shift when the cell was left in the dark for 4 h (Fig. 4). Energy gap of thiol (RSH)-protected metal CLs (R = organic moiety) does not significantly depend on the structure of R but on the metal core structure.<sup>18</sup> Therefore, the photoinduced blue-shift in the edge wavelength is not due to oxidation of R. Rather, it can be explained in terms of the photoetching of Ag<sub>32</sub>. Ag<sub>32</sub> absorbs the >760 nm light and transfers electrons to TiO<sub>2</sub>, resulting in oxidation of Ag<sub>32</sub> CLs themselves by their vacant HOMO levels via one of the two possible pathways described above: the direct oxidation of the

Ag core or the two-step oxidation involving the oxidative desorption of some ligands and the following oxidation of the bared Ag core. As the size of Ag<sub>32</sub> is decreased by the oxidation, the absorption edge is gradually blueshifted, and finally the oxidation stops when the edge wavelength becomes shorter than 760 nm. The edge wavelength of the photooxidized CLs was close to the absorbance edge wavelength of a Ag CL with ca. 25 Ag atoms.<sup>25</sup>

We also irradiated the Ag<sub>32</sub>/TiO<sub>2</sub> electrode with 480 nm, 1 mW cm<sup>-2</sup> monochromatic light. After 2 h irradiation, the photoresponse (<2 mV at 540 nm) was much smaller than that of the as-prepared one (>35 mV at 540 nm). Most of the Ag CLs lost their photoactivities completely due to extensive photoetching.



**Fig. 4.** Photopotential shift ( $\Delta E$ ) action spectra of Ag<sub>32</sub>/TiO<sub>2</sub> electrodes, as-prepared one, one irradiated with 760 nm, 5 mW cm<sup>-2</sup> light, and one stored in dark. To avoid an effect of photooxidation during the photopotential measurement, different Ag<sub>32</sub>/TiO<sub>2</sub> electrodes were used.

## Conclusions

In conclusion, we demonstrated a new method for energy gap control of Ag<sub>32</sub> based on photoinduced electron transfer from Ag<sub>32</sub> to TiO<sub>2</sub>. Photoetching of Ag<sub>32</sub> on a TiO<sub>2</sub> single crystal under 480 nm light was suggested by AFM. The absorption edge (energy gap) of Ag<sub>32</sub> on nanoporous TiO<sub>2</sub> was changed from ~870 nm (~1.4 eV) to ~740 nm (~1.7 eV) by irradiation with >760 nm light. The present technique may be applied to other metal CLs. In the case of more stable metal CLs, negative shifting of the redox potential by the aid of appropriate ligands would help the etching.<sup>42</sup>

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