

Photoelectrochemistry of Silver Clusters Supported on TiO₂ under Visible Light Irradiation

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Metal clusters (CLs), which are smaller than 2 nm in diameter and consist of less than 250 metal atoms, have discrete electron levels due to a quantum size effect whereas bulk metals are characterized by electron band structure. Based on the discrete levels, the metal CLs exhibit molecular-like properties such as optical absorption from ultraviolet to near infrared regions. The metal CLs are also known as effective catalysts and electrocatalysts when supported on appropriate substrates.

Recently we have shown that the metal CLs can be utilized as a photosensitizer of titanium dioxide (TiO₂). We have found that TiO₂ modified with Au CLs exhibits photovoltaic [1,2] and photocatalytic [3] properties in response to visible and near infrared light. Furthermore, we have found that Pt, Pd, and Ag CLs also serve as a sensitizer of TiO₂ [4].

The photocurrent generation is likely due to photoinduced charge separation at the metal CL-TiO₂ interface, in which excited electrons transfer from the CLs to the conduction band of TiO₂ (Fig. 1). In the present work, to obtain further evidence of the photoinduced electron injection, we directly observed the behavior of Ag CLs adsorbed on TiO₂ under visible light irradiation by atomic force microscopy (AFM).

Ag CLs were synthesized as described elsewhere [5]. We obtained Ag₃₂(SG)₁₉ (GSH = glutathione) by polyacrylamide gel electrophoresis (Fig. 2) [6]. To adsorb Ag₃₂ on the surface of rutile TiO₂ (110) single crystal, Ag₃₂ aqueous solution was diluted with acetic acid-sodium acetate buffer solution (pH 4) and cast on the TiO₂ single crystal and left for 2 hours. GSH-protected Ag CLs are electrostatically bound to TiO₂ via their carboxyl groups.

Adsorbed Ag CLs were observed by AFM (Fig. 3a). The average height of the CLs were 0.89 ± 0.21 nm ($n = 23$). This suggests that Ag CLs of uniform size adsorbed on the surface of the TiO₂. The sample was irradiated with 480 nm monochromatic light (1 mW cm^{-2}) under humid condition (relative humidity ~70%) for 30 min. As a result, some of the Ag CLs disappeared and new particles (2.7 nm height) deposited (Fig. 3b). These observations can be explained in terms of the injection of the excited electrons from the Ag CLs to TiO₂. The electron injection results in oxidation of the Ag CLs to Ag⁺ ions. The Ag⁺ ions released into the adsorbed water layer on the TiO₂ surface are recombined with the electrons injected to TiO₂, resulting in the deposition of the new Ag particles.

On the other hand, most CLs (~90%) remained unchanged under 30-min irradiation of 800 nm light (1 mW cm^{-2}). As shown in Fig. 2b, the Ag CLs have strong absorption peak at 480 nm and exhibit much lower absorption at 800 nm. These results indicate that the disappearance of Ag CLs is triggered by their photoabsorption.

In conclusion, we could directly observe the dissolution of Ag CLs and redeposition of Ag particles on TiO₂ under visible light. These results strongly support the photoinduced charge separation at the interface between Ag CL and TiO₂. In the presentation, we will

also describe some applications of the charge separation.

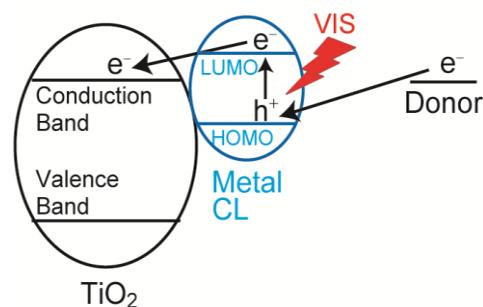


Fig. 1. Photoinduced charge separation at the metal CL-TiO₂ interface.

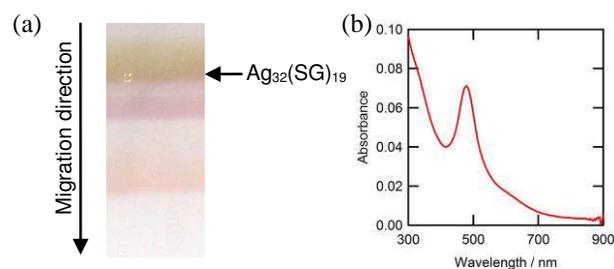


Fig. 2. (a) Electrophoretic pattern of Ag CLs and (b) an absorption spectrum of an Ag₃₂(SG)₁₉ aqueous solution.

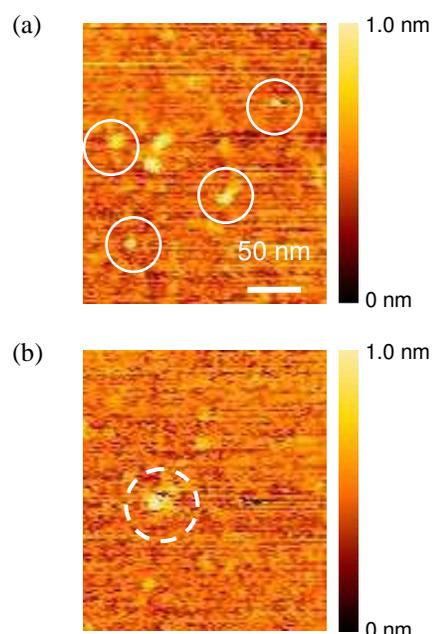


Fig. 3. AFM images of Ag₃₂-modified TiO₂ substrate (a) before and (b) after irradiation of 480 nm monochromatic light (1 mW cm^{-2} , 30 min). Disappeared CLs and deposited particles are highlighted with circles and dashed circles, respectively.

References

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