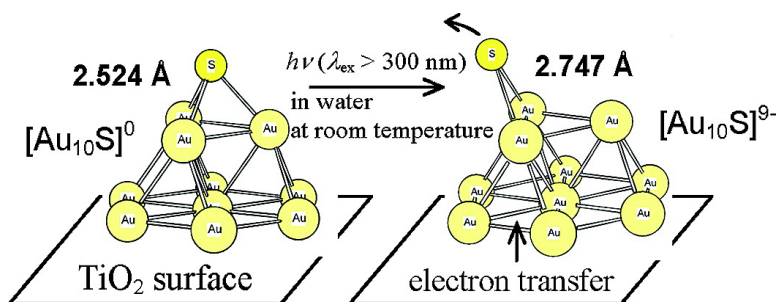


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Photoinduced Desorption of Sulfur from Gold Nanoparticles Loaded on Metal Oxide Surfaces

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The prediction of soon-to-be-depleted resources has led us to develop “chemistry for regeneration” together with chemistry for creating new functional materials. Metal nanoparticle catalysts with high performance for various chemical reactions are indispensable to the production of many useful chemicals, reductions in the emissions of harmful products,¹ and energy conversion.² However, because of great affinity of these catalysts to sulfur, they commonly undergo sulfur-poisoning from sulfur contained in the feed on the ppm order.³ The dissociation energies of metal–sulfur diatomic molecules are comparable to those for typical chemical bonds of H–H (436 kJ mol⁻¹) and C–C (348 kJ mol⁻¹), and notably, the Au–S bond (418 ± 25 kJ mol⁻¹) is very strong.⁴ It has recently been found that gold, which had so far been believed to be chemically inert, exhibits extraordinarily high activity in many important reactions, including low-temperature oxidation of carbon monoxide, partial oxidation of hydrocarbons, water–gas shift reaction, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides when dispersed as ultrafine particles smaller than ca. 10 nm on metal oxide supports such as TiO₂.⁵ Thus, from both a scientific and technological perspective, metal oxide-supported Au nanoparticles are an important and interesting object of study with regard to sulfur poisoning. Although heat cleaning is employed to clean the surfaces of sulfur-poisoned metal nanoparticles, the high-temperature heating causes a reduction in the catalytic activity due to the sintering and surface oxidation. Hence, the development of a low-temperature method for cleaning the metal surfaces is strongly required. We now report photoinduced sulfur desorption from the surfaces of Au nanoparticles loaded on metal oxides. This reaction occurs in water at ordinary temperature and pressure.

Au particles were loaded on various metal oxides [anatase (A-) and rutile (R-) TiO₂, SrTiO₃, ZnO, Fe₂O₃, and SnO₂] by the deposition–precipitation method using HAuCl₄ as a raw material.⁶ Transmission electron microscopic (TEM) observations confirmed that Au particles of comparable size (3.5 ± 0.3 nm) are highly dispersed onto each metal oxide. The characterization results of the Au nanoparticles loaded on various metal oxides (Au/oxides) are provided as Supporting Information (Table S1).

Because the persistent adsorption of sulfur-containing compounds to the Au surface results primarily from the strong Au–S bond, elemental sulfur (S₈) was used as an adsorbate. The adsorption properties of the metal oxides with and without metal clusters for S₈ were examined at 25 ± 1 °C. The adsorption selectivity for Au defined as $n_s^{\text{Au}}/(n_s^{\text{Au}} + n_s^{\text{O}})$ is also listed in Table S1, where n_s^{Au} and n_s^{O} denote the number of S atoms adsorbed on the unit surface areas of Au and metal oxide, respectively. In every system, the adsorption selectivity exceeds 99.5%, indicating that S₈ molecules are adsorbed highly selectively on the surfaces of Au nanoparticles of Au/oxides. The adsorption isotherm for Au/A-TiO₂ provides a

saturated adsorption amount of $n^{\text{Au}}_s \approx 10.8 \pm 0.4$ atoms nm⁻² with a step near $n^{\text{Au}} = 6.7 \pm 0.3$ atoms nm⁻².⁷ Figure 1A-b shows the S_{2p}-XPS spectrum for Au/A-TiO₂ with saturated adsorption of S₈ (S–Au/A-TiO₂). Two signals are situated at 160.0–161.3 and 161.3–162.9 eV assignable to the sulfurs atomically adsorbed on the Au cluster surfaces with an ionic character (Au^{δ+}–S^{δ-}) and the sulfurs adsorbed with a S₈ structure, respectively.⁸ These findings indicate that S₈ is adsorbed on the Au nanoparticle surfaces with cleavage of the S–S bond at $\theta < 1/3$, while the molecular adsorption takes place concurrently with the atomic adsorption at $\theta > 1/3$.

As shown in Figure 1A-c, irradiation ($\lambda_{\text{ex}} > 300$ nm) of the S–Au/A-TiO₂ particles in deaerated water leads to a significant decrease in the intensities of the two S_{2p}-XPS signals. Further, when ethanol was added to the system (Figure 1A-d), the signals completely disappear after irradiation. Figure 1B shows the electronic absorption spectra of the supernatants separated by centrifugation from the S–Au/A-TiO₂ suspensions after irradiation. The spectrum of the supernatant of the S–Au/A-TiO₂ suspension stirred in the dark for 20 min has no absorption in the wavelength range between 200 and 260 nm ($t_p = 0$). Upon irradiation, an absorption peak appears at 230 nm, and its intensity increases with increasing irradiation time. This peak position was in agreement with that of the S²⁻ ion. Under these conditions, only A-TiO₂ with a band gap of 3.2 eV is excited in the system. Au/A-TiO₂ has a surface plasmon absorption band around 530 nm; however, no sulfur desorption occurred with visible-light irradiation ($\lambda_{\text{ex}} > 450$ nm). Evidently, the sulfurs adsorbed on the Au cluster surfaces are reductively desorbed in water at room temperature by the band gap excitation of the support or A-TiO₂.

Previously, efficient and selective reduction of (2,2'-dipyridyl)-disulfide (RSSR) to 2-mercaptopyridine has been found to proceed when using a Au/A-TiO₂ photocatalyst.⁹ The rate of the RSSR reduction (R_{RSSR}) and the ratio of the sulfur desorbed after 20-min irradiation (R_S) were measured for Au/oxides. Figure 2A shows the R_{RSSR} and R_S values as a function of the energy levels of the conduction band (E_{cb} vs vacuum) of the metal oxide supports. In the systems having E_{cb} greater than ca. -4.6 eV, both R_S and R_{RSSR} increase as E_{cb} increases, while the reactions hardly occur at $E_{\text{cb}} \leq -4.6$ eV. Because the edge position of the valence band (vb) mainly consisting of O_{2p} orbitals is insensitive to the type of metal oxide, larger E_{cb} means a larger band gap. Thus, the key in the photoinduced desorption of sulfur is not the number of photons absorbed by the metal oxide support, but the potential of the excited electrons in the support.

The E_{cb} in Figure 2A only indicates the upper limit of the electronic energy in the photostationary state for n-type semiconductors. To estimate the Fermi energies of Au/A-TiO₂ in the dark (E_F) and under irradiation (E_F'), the potential of the SnO₂ electrode

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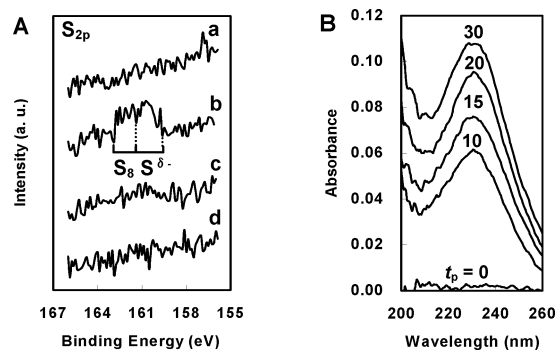


Figure 1. (A) S_{2p} -XPS spectral change of S_8 -preadsorbed Au/A-TiO₂ particles (S–Au/A-TiO₂) with irradiation ($\lambda_{\text{ex}} > 300$ nm, light intensity integrated from 320 to 400 nm, $I_{320-400} = 5.4$ mW cm⁻²): a, Au/A-TiO₂; b, S–Au/A-TiO₂; c, sample b (1 g) recovered after 5-h irradiation in deaerated water (250 mL); d, sample b recovered after 15-h irradiation in a deaerated ethanol aqueous solution (C₂H₅OH/H₂O = 150 mL/100 mL). (B) Irradiation-time dependence of electronic absorption spectra of the supernatants separated from a deaerated aqueous suspension of the S_8 -preadsorbed Au/A-TiO₂ (0.25 g) after irradiation ($I_{320-400} = 2.0$ mW cm⁻²): t_p denotes irradiation time. Before irradiation, argon bubbling was carried out for 30 min and continued throughout the irradiation. The reaction temperature was kept at 25 ± 1 °C.

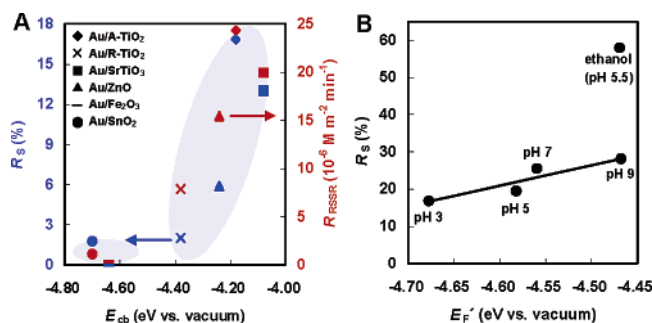


Figure 2. (A) Plots of R_S and R_{RSSR} for the Au/oxide systems vs energy level of the conduction band of the metal oxide support. The pH of the solution was adjusted to 3.0 with HNO₃, and irradiation ($\lambda_{\text{ex}} > 300$ nm, $I_{320-400} = 2.0$ mW cm⁻²) was carried out at 298 K under deaerated conditions. The sulfurs adsorbed on Au/oxides before and after 20-min irradiation were completely oxidized to SO₄²⁻ ions with a H₂O₂ solution to be quantified by ion chromatography. The E_{cb} was calculated from the literature value of flat band potential.^{10,11} (B) Dependence of R_S on the Fermi energy in the photostationary state of Au/A-TiO₂-film coated SnO₂ electrode (E_F'). A-TiO₂ films with a thickness of 65 ± 5 nm were formed on SnO₂-film coated glass plates by a sol-gel method.¹² The photopotential was measured as a function of the pH of the solutions containing 0.1 M Na₂SO₄ electrolyte under deaerated conditions: $\lambda_{\text{ex}} > 300$ nm, $I_{320-400} = 10$ mW cm⁻².

overcoated with an Au cluster-loaded A-TiO₂ film was measured in the dark and under irradiation as a function of the solution pH. In the dark, the E_F increased linearly against pH with a slope of 48 ± 3 meV/pH, and irradiation caused an increase in E_F of 0.33 eV relative to the dark value. These upward shifts of E_F are likely induced by an accumulation of the excited electrons in the cb of TiO₂ as a result of the oxidation of water by the vb holes. Figure 2B shows plots of the R_S values for Au/A-TiO₂ particles in aqueous solutions with varying pH vs E_F' in the corresponding solvent. In a similar manner as in Figure 2A, a positive correlation is observed between R_S and E_F' . As A-TiO₂ and Au clusters are in contact with each other in Au/A-TiO₂, the Fermi energies are nearly equal in the photostationary state. As such, the photoinduced upward shift of E_F originating from the excited A-TiO₂ can lead to the reductive desorption of sulfur via the electron transfer from A-TiO₂ to Au.¹³ When ethanol was added (1.1 M), the photoinduced shift of E_F reached 0.40 eV. Ethanol can inject two electrons per molecule into excited TiO₂ to induce a large E_F' , even in acidic solution.¹⁴

The large R_S value of 58% in the ethanol-added system is attributable to the synergy of the enhancement of the sulfur desorption and the restriction of the readsorption of desorbed sulfurs that partly pass over to the gas phase as H₂S at pH = 5.5. Further, the photoinduced sulfur desorption from Au/A-TiO₂ (Au = 0.38 wt %) was enhanced with increasing Au cluster size (d^{Au}) at $d^{\text{Au}} < 11$ nm: $R_S = 16\%$ for $d^{\text{Au}} = 3.2$ nm, $R_S = 17\%$ for $d^{\text{Au}} = 6.6$ nm and $R_S = 39\%$ for $d^{\text{Au}} = 11$ nm at pH = 3.

The catalytic activities of various Au/A-TiO₂ samples for the partial oxidation of benzyl alcohol were studied (Supporting Information, Table S2). The Au/A-TiO₂ catalyst system yields benzyl aldehyde with a conversion of 40% and selectivity of 71%. When S–Au/A-TiO₂ is used as a catalyst, the conversion is reduced to 11%. The photocleaned S–Au/A-TiO₂ exhibits activity comparable to that of the original Au/A-TiO₂, whereas the activity is lost for the heat-cleaned S–Au/A-TiO₂. In the Au/TiO₂-catalyzed low-temperature oxidation of CO, it has been shown that activity reaches a maximum at $d^{\text{Au}} \approx 3$ nm, then disappears at $d^{\text{Au}} > 4.5$ nm.¹⁵ In the present system, the d^{Au} slightly increases after the S_8 adsorption, but the d^{Au} is invariant before and after photocleaning. On the other hand, the value for the sample heat-cleaned at 873 K exceeds 10 nm. This finding indicates that the catalytic activity for the Au/A-TiO₂-catalyzed oxidation of benzyl alcohol also strongly depends on the Au cluster size.

In conclusion, we have identified the presence of photoinduced sulfur desorption from the surfaces of the metal oxide-supported Au nanoparticles in water at room temperature. This reaction was found to be driven by an upward shift of the Fermi energy of the metal oxide-loaded Au nanoparticles with irradiation. It has also been demonstrated that this phenomenon is applicable to the low-temperature cleaning of sulfur-poisoned metal catalysts.

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Supporting Information Available: The characterization results of the Au clusters loaded on various metal oxides (Au/oxides); catalytic activity of Au/A-TiO₂ for oxidation of benzyl alcohol. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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