Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO$_2$

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Nanoporous TiO$_2$ films loaded with gold and silver nanoparticles exhibit negative potential changes and anodic currents in response to visible light irradiation, so that the films would potentially be applicable to inexpensive photovoltaic cells, photocatalysts and simple plasmon sensors.

Metal nanoparticles, which show various colors on the basis of size- and shape-dependent plasmon resonance,[1–3] have a wide variety of applications.[4–7] Plasmon-based photochemical and photothermal reactions have been used for preparation of Ag nanoprisms[2,3,8] and Au nanorods[9] and irreversible[10] and reversible[11,12] photo-imaging. In the present work, plasmon-induced photoelectrochemistry was studied for energy conversion. Although metal nanoparticles have been employed in photocatalysts[13] and photovoltaic cells,[14] these have not been based on the plasmon absorption. Recently, laser-induced temperature jump electrochemistry[15] has been reported for Au nanoparticle-coated indium tin oxide (ITO) electrodes. Although this phenomenon might be based on the plasmon absorption, the photopotential and photocurrent responses were too small to apply the system to energy conversion.

Here we report the plasmon-induced photoelectrochemistry at gold and silver nanoparticles incorporated in a nanoporous TiO$_2$ film. The system would be applied to photoelectrochemical conversion of energy as well as information. One would apply the composite materials to devices for which a sensitive wavelength can be tuned or broadened by selecting appropriate nanoparticles. The cost of photovoltaic cells[16] with expensive dyes would be reduced. Visible light-sensitive photocatalysts[17] and simple surface plasmon resonance biosensors without photodiodes are additional potential applications.

In a typical experiment, a Au–TiO$_2$ or Ag–TiO$_2$ film was prepared as follows: an ITO coated glass plate was coated with a nanoporous TiO$_2$ film prepared from an anatase TiO$_2$ sol (Ishihara Sangyo Kaisha, STS-21, 20 nm particle diameter) by spin-coating (sintered at 723 K for 1 h). A suspension of Au or Ag nanoparticles in ethanol (AuE-101, 5–20 nm diameter, 20 wt%-Au, 3 wt%-protective polymer or AgE-102, 5–20 nm diameter, 30 wt%-Ag, 2 wt%-protective polymer, Nippon Paint) was diluted with ethanol (1000-fold). The substrate was immersed in the suspension for 12–15 h and was rinsed. The resulting Au–TiO$_2$ exhibited an absorption band characteristic of the plasmon absorption of Au nanoparticles (542 nm), although it is red-shifted compared to that of the suspension (530 nm) due to the high refractive index of TiO$_2$ (2.52).

The photopotential action spectra of TiO$_2$ and Au–TiO$_2$ films in N$_2$-saturated 0.05 M aqueous NaOH are shown in Fig. 1A. The substrate was irradiated with visible light using a xenon lamp with an ultraviolet-cut filter and a bandpass filter (fwhm, 10 nm) from the back (1.36 × 10^{15} photons cm^{-2}). No obvious change in the open-circuit potential was observed at the TiO$_2$ film because TiO$_2$ absorbs no visible light. In contrast, a significant negative potential shift was obtained at the Au–TiO$_2$ film under illumination. The photopotential action spectrum coincided very well with the absorption spectrum of the Au nanoparticles in the film. The maximum potential response (~ 140 mV) was obtained at around the absorption peak wavelength. In addition, the protective polymer absorbs no visible light. Thus, the photo-induced potential shifts were attributed to plasmon absorption of the Au nanoparticles.

Short-circuit photocurrents were also measured in the presence of I$^-$/I$_3^-$ redox couple. The incident photon to current conversion efficiency (IPCE, flux of collected electrons per flux of incident photons) was evaluated from the short-circuit photocurrent (Fig. 1B). A remarkable anodic current enhancement was observed at the Au–TiO$_2$ film under illumination and the photocurrent ceased as the light was turned off (inset of Fig. 1B). The photocurrent was reproducible and stable. Even after 0.2 C of charges, which are sufficient to oxidize almost all of the deposited Au to Au^{3+}, had passed, the absorbance of the Au particles in the film was not changed. Therefore, the current cannot be ascribed to the oxidation of Au. The IPCE–wavelength relationship tightly fits the absorption spectrum of the Au nanoparticles in the TiO$_2$ film and shows the maximum IPCE (~ 1.0%) at around 540 nm.

A possible mechanism of the photoelectrochemical response is plasmon-induced charge separation. At the Au nanoparticle surface, collective oscillation of electrons is induced by incident light. In the Au–TiO$_2$ interfacial region, where bands of TiO$_2$ may bend in the space charge layer,[18] the oscillating electrons may be influenced by the electric field of the layer. This should cause the transport of the electron(s) to TiO$_2$ bulk. Simultaneously, the Au nanoparticle, which is being charged positively, takes electron(s) from a coexisting donor, I$^-$. This possible mechanism is similar to the dye-sensitized nanoporous TiO$_2$.[16] Since the currents did not necessarily require the presence of the electron acceptor, iodine, but the electron donor, I$^-$, mediated electron transfer from the excited Au particles to the electrode is excluded from the possible mechanisms.
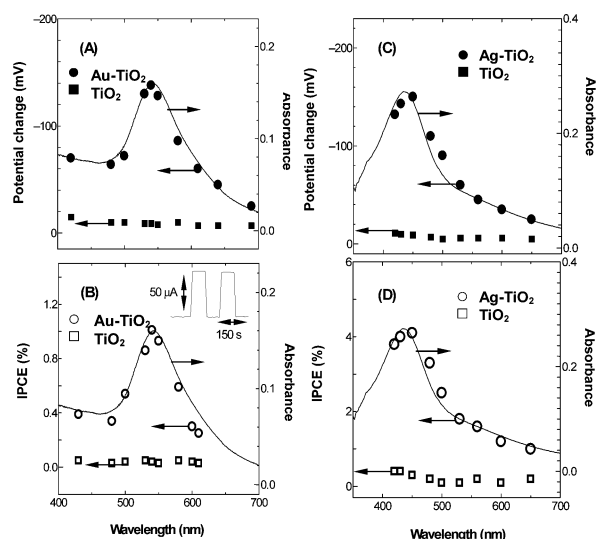
Fig. 1 Action spectra for changes in open-circuit potential (A, C) and IPCE (B, D) of the Au–TiO$_2$ (A, B) and Ag–TiO$_2$ (C, D) films in N$_2$-saturated 0.05 M NaOH aqueous solution (containing 0.5 M KI and 50 mM iodine for (B, D)) in response to light irradiation (1.36 × 10^{15} photons cm^{-2}). Absorption spectra of Au and Ag nanoparticles in the TiO$_2$ film are also depicted (solid curves). (B, inset) Photocurrent changes in response to switching of the illumination (540 nm).

This is a completely different phenomenon from those reported previously for semiconductor–metal nanocomposites. In the case of photocatalysts, metal nanoparticles have been used as a sink for charge carriers photoexcited in the semiconductor.[13] As for dye-sensitized photovoltaic cells, metal nanoparticles have been employed to improve hole transfer efficiency.[14] In either case, nanoparticles do not serve as sensitizers.

The plasmon-induced temperature increase might be another possible mechanism. As for the reported Au–ITO system,[15] however, both open-circuit voltage (< 10 mV) and current density (< 50 nA) were much smaller in spite of very strong incident light (8.7×10^{17} photons cm^{-2}) in comparison with our system. Actually, when we replaced the TiO_2 film with a nanoporous ITO film, both photopotential and photocurrents were too small (6 mV and 35 nA, respectively), although the amount of loaded Au nanoparticles was almost the same. This suggests that the temperature effect or the charge separation is suppressed on ITO. The latter could be explained in terms of a very thin space charge layer in ITO, which should not effectively contribute to the charge separation. Other results supporting the charge separation mechanism are described below.

Next, we investigated the photoresponse of Ag nanoparticles confined in a TiO_2 film (Figs. 1C and 1D). Although the maximum potential change (~ 150 mV) was comparable to that for the Au–TiO_2 film, 4-fold enhancement in IPCE (4.1%) was observed. Since the present Ag nanoparticles absorb 47% of incident photons at the peak wavelength, it might be possible to improve the IPCE value to about 9%, by increasing the number of nanoparticles. Also, selection of a more suitable redox couple might improve the open-circuit photovoltage (125 mV).

Although Ag nanoparticles are not necessarily stable in the presence of I^-/I_3^- in general, the protective polymer[19] of the metal nanoparticles might suppress the corrosion. Actually, the film exhibited the characteristic plasmon absorption peak even after 0.8 C of charges, which are required to dissolve almost all of the Ag particles, had passed through the cell. Selection of a more appropriate redox couple should improve the stability further.

We also examined a TiO_2 film loaded with both Au and Ag nanoparticles. A Au–TiO_2 film (Fig. 2A, not fully loaded with Au to leave room) was further loaded with Ag particles (Fig. 2B). The absorption peaks at around 440 nm and 540 nm indicate successful loading with Ag particles without significant loss of Au. However, the photopotential action spectrum was not in agreement with the absorption spectrum of the Au + Ag particles, but with the differential absorption spectrum for Ag particles alone (Fig. 2B). In particular, at around 540 nm, where the Au particles exhibited the maximum absorption, the potential change of the Au–TiO_2 film dramatically dropped from -35 mV to -5 mV as the film was further loaded with Ag. The short-circuit current in the presence of the I^-/I_3^- couple for the Au–TiO_2 film was also decreased from 20 μA to 0.5 μA at 540 nm while it was increased from 2 μA to 13 μA
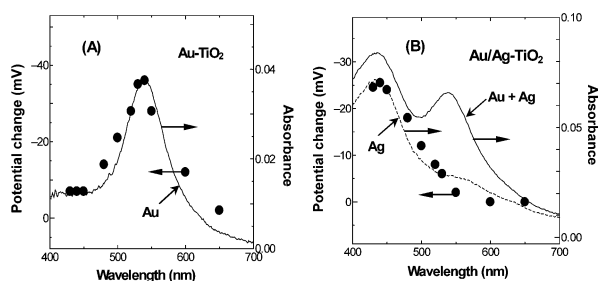
at 440 nm by the loading with Ag particles. The photoexcited electrons on a Au nanoparticle might be trapped by an adjacent Ag nanoparticle in the ground state, and following back electron transfer to the Au particle might result in charge recombination. In any event, these results support the charge separation mechanism rather than the temperature jump effect mechanism,[15] because it is difficult to explain these results in terms of the latter mechanism.

Photocatalytically deposited metal nanoparticles were also functioning. The TiO_2 film was soaked in 1 mM aqueous $HAuCl_4$ and rinsed with water. The film was irradiated with ultraviolet light (1 mW cm^{-2}) to reduce the adsorbed Au^{3+} to Au. The photo-potential action spectrum fits the absorption spectrum of the deposited Au (maximum potential change, ~ 90 mV). Under white light (5 mW cm^{-2}), the potential change was about 250 mV. After treatment with a 10 mM ethanol solution of 1-octadecanethiol (10 min) to protect the Au particles, stable photocurrents were obtained in the presence of I^-/I_3^-. Optimization of the size and density of the nanoparticles and the protective layer would improve the characteristics. As for Ag particles, the TiO_2 film treated with 1 M aqueous $AgNO_3$ was irradiated with ultraviolet light.[11] The maximum potential change was 45 mV, and stable photocurrents were observed in the presence of I^-/I_3^- after the treatment with 1-octadecanethiol.

Plasmon photoelectrochemistry might be promising in various potential applications including photo-energy conversion and transducing of optical information.

Notes and references

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Fig. 2 Action spectra for changes in open-circuit potential of the Au–TiO_2 film in N_2-saturated 0.05 M NaOH aqueous solution in response to light irradiation before (A) and after (B) the loading with Ag nanoparticles. Absorption spectra of Au and Ag nanoparticles in the TiO_2 film are also depicted. The dashed curve in (B) is obtained by subtracting the spectrum for Au in (A) from that for Au + Ag in (B).