

Plasmon-Induced Photoelectrochemistry at Metal Nanoparticles supported on Nanoporous TiO₂

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Metal nanoparticles, which show various colors based on size- and shape-dependent plasmon resonance, have a wide variety of applications. Plasmon-based photochemical and photothermal reactions have been used for the preparation of Ag nanoprisms and Au nanorods and irreversible and reversible photoimaging. Here we report the plasmon-induced photoelectrochemistry at gold and silver nanoparticles incorporated in a nanoporous TiO₂ film. One would employ the composite materials for the devices of which sensitive wavelength can be tuned or broadened by selecting appropriate nanoparticles. Cost of photovoltaic cells with expensive dyes will be reduced. Visible light-sensitive photocatalysts and simple surface plasmon resonance biosensors without photodiodes are additional potential applications. In the present work, the plasmon-induced photoelectrochemistry was studied for photoelectrochemical conversion of energy as well as information.

In a typical experiment, a Au-TiO₂ or Ag-TiO₂ film was prepared as follows: an ITO coated glass plate was coated with a nanoporous TiO₂ film prepared from an anatase TiO₂ sol (Ishihara Sangyo Kaisha, STS-21, 20 nm particle diameter) by spin-coating (sintered at 723 K for 1 h). Au or Ag nanoparticle suspended in ethanol (AuE-101, 5-20 nm diameter, 20wt%-Au, 3wt%-protective polymer or AgE-102, 5-20 nm diameter, 30wt%-Ag, 2wt%-protective polymer, Nippon Paint) was diluted with ethanol (1 000-fold). The substrate was immersed in the suspension for 12-15 h and was rinsed. The resulting Au-TiO₂ exhibited an absorption band characteristic of the plasmon absorption of Au nanoparticles (542 nm), although it was red-shifted compared to that of the suspension (530 nm) due to high refractive index of TiO₂ (2.52).

The photopotential action spectra of TiO₂ and Au-TiO₂ films in N₂-saturated 0.05 M aqueous NaOH are shown in Fig. 1A. The substrate was irradiated with a 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 TiO₂ film because TiO₂ absorbs no visible light. In contrast, a significant negative potential shift was obtained at the Au-TiO₂ 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⁻/I₃⁻ 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-TiO₂ film under illumination and the photocurrent ceased as the light was turned off (inset of Fig. 1B). The photocurrent was reproducible and stable.

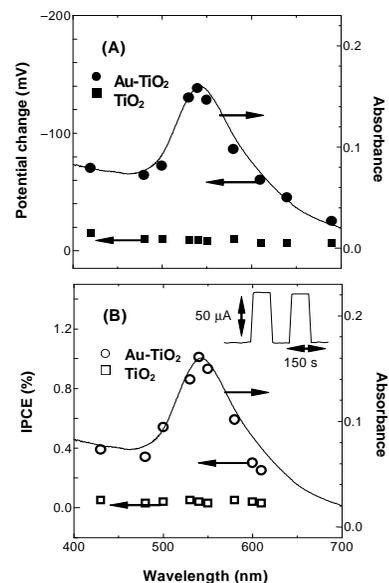


Fig. 1 Action spectra for changes in open-circuit potential (A) and IPCE (B) of the Au-TiO₂ film in N₂-saturated 0.05 M NaOH aqueous solution (containing 0.5 M KI and 50 mM iodine for (B)) in response to light irradiation (1.36×10^{15} photons cm⁻²). Absorption spectra of Au nanoparticles in the TiO₂ film are also depicted (solid curves). (B, inset) Photocurrent changes in response to switching of the illumination (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-TiO₂ interfacial region, where bands of TiO₂ may bend in the space charge layer, the oscillating electrons may be influenced by the electric field of the layer. This should cause the transport of the electron(s) to TiO₂ bulk. Simultaneously, the Au nanoparticle, which is being charged positively, takes electron(s) from a coexisting donor, I⁻. In the present case, Au nanoparticles, similar to dyes, play a role as sensitizers.

Next, we studied the photoresponse of Ag nanoparticles confined in a TiO₂ film. Although the maximum potential change (~150 mV) was comparable to that for the Au-TiO₂ film, 4-fold enhancement in IPCE (4.1%) was observed. Although Ag nanoparticles are not necessarily stable in the presence of I⁻/I₃⁻ in general, the protective polymer 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, have passed through the cell.

Thus, it is of great importance to select more appropriate redox couples, not only for improving stability of the composite film, but also for increasing the photoelectrochemical conversion of energy. Then, we investigated the relationship among open-circuit photovoltage, anodic photocurrent, and the redox potential of various redox couples. The more positive redox potential, the higher photovoltage and anodic photocurrent were obtained. A strikingly high open-circuit photovoltage of 0.75 V, which is comparable with dye-sensitized solar cells, was obtained for the Au-TiO₂ when the most suitable redox couple was employed.