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Enhancement of plasmon-induced charge separation efficiency by coupling silver nanocubes with a thin gold film

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Abstract. Plasmon-induced charge separation (PICS), in which an energetic electron is injected from a plasmonic nanoparticle (NP) to a semiconductor on contact, is often inhibited by a protecting agent adsorbed on the NP. We addressed this issue for an Ag nanocube-TiO_2 system by coating it with a thin Au layer or by inserting the Au layer between the nanocubes (NCs) and TiO_2. Both of the electrodes exhibit much higher photocurrents due to PICS than the electrodes without the Au film or the Ag NCs. These photocurrent enhancements can be explained in terms of PICS with accelerated electron transfer, in which electron injection from the Ag NCs or Ag@Au core-shell NCs to TiO_2 is promoted by the Au film, or PICS enhanced by a nanoantenna effect, in which the electron injection from the Au film to TiO_2 is enhanced by optical near field generated by the Ag NC. [DOI: 10.1117/1.JPE.6.042505]

Keywords: plasmon-induced charge separation; localized surface plasmon resonance; electron transfer; nanoantenna effect; silver nanocube.

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1 Introduction

Plasmonic light harvesting based on localized surface plasmon resonance (LSPR) of noble metal nanoparticles (NPs) has attracted much attention recently and is applied to photovoltaics and photocatalysis. There are two different ways of plasmonic light harvesting: (1) that based on a nanoantenna effect,[1] in which a metal NP entraps a photon and transfers the obtained energy to a dye molecule or semiconductor via the optical near field generated in its vicinity, and (2) that based on plasmon-induced charge separation (PICS),[2] in which an energetic electron is injected from a resonant NP to a semiconductor on contact. We reported PICS for the first time[2] and indicated that it involves electron transfer from the plasmonic NPs to the semiconductor.[2–7] The electron transfer involved is explained in terms of external photoelectric effect, hot electron injection, or interfacial electron transition, and recently some groups call it plasmonic hot electron (or carrier) injection. PICS has been widely applied to photovoltaics,[2,8–12] photocatalysis,[2,13,14] photochromism,[15–17] photoactuation,[18] and chemical sensing.[19]

A wide variety of plasmonic NPs have been used for PICS such as nanospheres,[20] nanoplates,[7] and halfshell arrays.[21] NPs prepared by photocatalytic deposition[2] or thermal dewetting of an evaporated film[9] are suitable for PICS because of direct contact with the semiconductor, while chemically synthesized NPs may exhibit lower charge separation efficiency since they are covered with a protective agent. In the case of Au nanorods (NRs) protected with cetyltrimethylammonium bromide in contact with a TiO_2 thin film, we addressed the issue by photoelectrochemical deposition of Au from aqueous $HAuCl_4$ at both ends of the NRs under UV irradiation for excitation of TiO_2.[22] The Au NRs were thus converted to nanodumbbells (NDs), and NDs exhibited improved efficiency of PICS-based electron transfer to TiO_2 via the two spherical caps at both ends of NDs. Here, we propose an easier method to improve

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the PICS-based photocurrents. We use plasmonic Ag nanocubes (NCs) protected by poly(vinylpyrrolidone) (PVP) in this work. Although Ag NCs exhibit nanoantenna effects[23–25] and various interesting optical properties,[26–29] their PICS efficiency when they are in contact with TiO_2 is low because of the insulating PVP layer. In the present work, in order to improve the PICS efficiency, we coupled the Ag NCs simply with an evaporated Au thin film, which is coated on the Ag NCs placed on TiO_2 or coated directly on TiO_2 as the underlayer of Ag NCs.

2 Experiment

2.1 *Preparation of Electrodes*

Ag NCs were synthesized by the method reported by Im et al.[30] with slight modifications[28] [Fig. 1(a)]. The average edge length of the synthesized Ag NCs is about 80 nm. A transparent indium tin oxide (ITO) electrode was coated with a thin anatase TiO_2 film (60-nm thick, observed by scanning electron microscopy, SEM) by a spray pyrolysis method at 500°C from 2-propanol containing 0.028 M titanium diisopropoxide bis(acetylacetonate) as a TiO_2 precursor. The TiO_2 film was irradiated with UV light in order to make the surface sufficiently hydrophilic. The synthesized Ag NCs were drop-cast onto the TiO_2 surface (coverage $\sim 9 \times 10^8$ particles cm^{-2}). If necessary, the substrate was coated with an Au film (*ca.* 5-nm thick, measured by quartz crystal microbalance) by vacuum evaporation before or after the drop-casting [Fig. 1(b)]. Thus, we prepared four different electrodes: $ITO/TiO_2/Ag$ NC, $ITO/TiO_2/Ag$ NC/Au, $ITO/TiO_2/Au$, and $ITO/TiO_2/Au/Ag$ NC (active area $= 12 \times 20$ mm).

2.2 *Measurement of Photocurrents*

One of the four electrodes was used as the working electrode. This electrode was connected to a potentiostat (SI 1280 B, Solartron) with an Ag|AgCl reference electrode and a Pt counter electrode and soaked in 0.1 M aqueous KNO_3 containing 0.5 M ethanol as an electron donor. The working electrode was polarized at +0.5 V versus Ag|AgCl and irradiated with monochromatic light (full width at half maximum = 20 nm, 5.0×10^{15} photons $cm^{-2}\,s^{-1}$, and light irradiation area = 1.8 cm^{-2}) using an optospectrum generator (Hamamatsu Photonics), and a steady-state photocurrent was measured at each wavelength. Virtually, the same photocurrents were observed even if the photoanode was short circuited to the counter electrode.

3 Results and Discussion

3.1 *Photocurrent Responses of the $ITO/TiO_2/Ag$ NC Electrode*

Ag NCs dispersed in ethanol exhibit the main extinction peak based on dipolar LSPR at 506 nm. When an Ag NC is adsorbed onto a substrate with a high refractive index, the LSPR peak splits into two peaks due to the distal and proximal modes.[26] In the distal mode, electron oscillation is

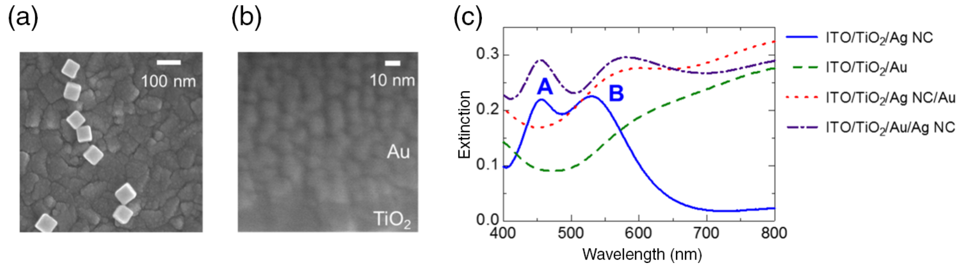

Fig. 1 Scanning electron micrographs of (a) the Ag NCs and (b) the Au films. (c) Extinction spectra of the $ITO/TiO_2/Ag$ NC, $ITO/TiO_2/Ag$ NC/Au, $ITO/TiO_2/Au$, and $ITO/TiO_2/Au/Ag$ NC electrodes in water.

localized at the top of the NC away from the substrate, and in the proximal mode, the oscillation is localized at the bottom of the NC in contact with the substrate. The Ag NCs on TiO_2 show two peaks [Fig. 1(c)], namely peak A at 456 nm due to the distal mode and peak B at 530 nm due to the proximal mode.

First, we measured photocurrent responses from the $ITO/TiO_2/Ag$ NC electrode irradiated from the backside with monochromatic light of different wavelengths in the electrolyte solution. Three independently prepared electrodes were examined and the average currents were plotted against the irradiation wavelength (Fig. 2). Small anodic photocurrents were observed in the wavelength range examined (430 to 670 nm). Conduction electrons in an Ag NC oscillate in resonance with electric field oscillation of the incident light, and an electron is injected from the resonant NC to the conduction band of TiO_2, resulting in PICS.[2] As a result, the anodic photocurrent flows [Fig. 3(a)]. However, the photocurrents were very low and no obvious current peaks corresponding to the distal and proximal modes were obtained. The low currents could be explained in terms of a blocking effect of insulating PVP, which covers and protects the NC surface. Capping agents like PVP are known to block access of reactant molecules.[31,32] Likewise, the PVP layer should also inhibit the electron transfer from the Ag NC to TiO_2.

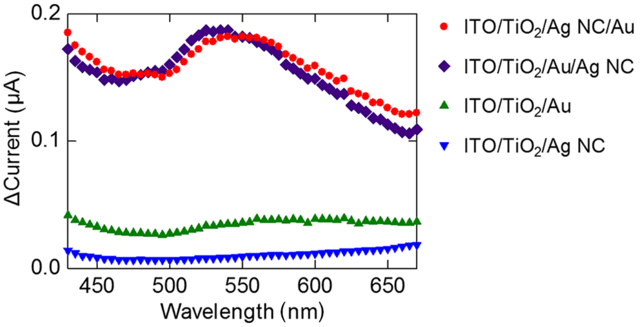

Fig. 2 Photocurrent action spectra of the $ITO/TiO_2/Ag$ NC, $ITO/TiO_2/Ag$ NC/Au, $ITO/TiO_2/Au$, and $ITO/TiO_2/Au/Ag$ NC electrodes in 0.1-M aqueous KNO_3 containing 0.5-M ethanol. Each datapoint shows the average of photocurrent responses from three independently prepared electrodes.

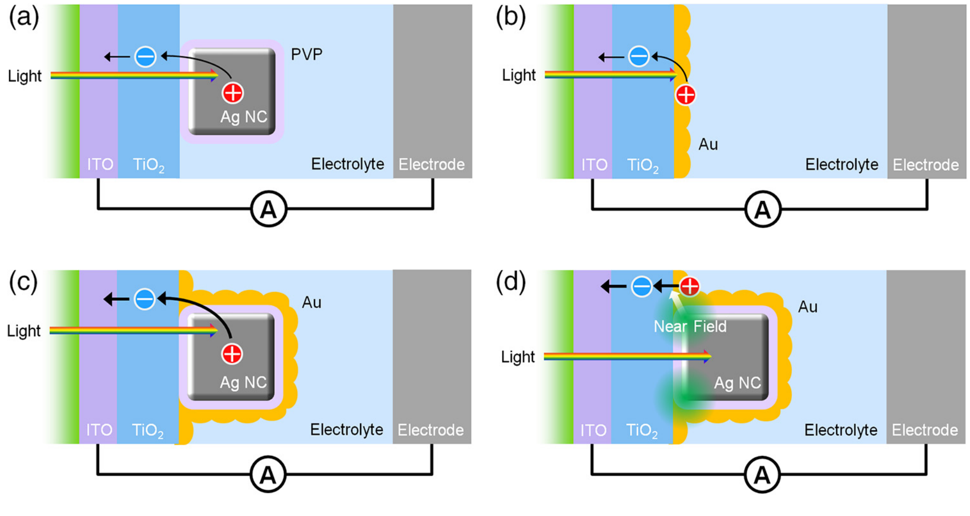

Fig. 3 Possible mechanisms of the photocurrents based on PICS for (a) $ITO/TiO_2/Ag$ NC, (b) $ITO/TiO_2/Au$, and (c and d) $ITO/TiO_2/Ag$ NC/Au electrodes [(c) PICS with accelerated electron transfer and (d) PICS enhanced by the nanoantenna effect].

3.2 *Effect of a Thin Gold Coating*

We therefore coated the Ag NCs on TiO_2 with a thin Au layer (*ca*. 5 nm thick) by evaporation, envisaging promotion of the electron transfer. The photocurrent responses from the $ITO/TiO_2/Ag$ NC/Au electrode thus prepared were measured and are shown in Fig. 2. The Au coating greatly improved the anodic photocurrents and a broad peak was obtained at around 550 nm. This electrode showed an extinction peak at 580 nm [Fig. 1(c)]. There is a possibility that the influence of the high refractive index substrate is weakened by the Au coating and therefore the distal mode is suppressed. The photocurrent response at the peak was about 20 times higher than that without the Au coating.

We also coated the Au layer directly on TiO_2 and examined its photocurrent responses for comparison. This $ITO/TiO_2/Au$ electrode also exhibited photocurrent responses that increased gradually with increasing wavelength from about 500 nm. The extinction spectrum of the Au film showed a similar trend [Fig. 1(c)]. In general, a thin Au film prepared by evaporation consists of interconnected fine Au NPs, and hence it exhibits not only the propagating surface plasmon resonance, but also LSPR.[33] Therefore, the present Au film also injects electrons into TiO_2 and exhibits photocurrents based on PICS [Fig. 3(b)]. Actually, nanoparticulate structures of 10- to 20-nm size were observed by SEM [Fig. 1(b)]. With reference to the response of this electrode, the introduction of Ag NCs under the Au thin film enhanced the photocurrents by approximately five times.

3.3 *Mechanisms of the Photocurrent Enhancement*

There are two possible reasons that the response from the $ITO/TiO_2/Ag$ NC/Au electrode is much higher than those from the $ITO/TiO_2/Ag$ NC and $ITO/TiO_2/Au$ electrodes. One of them is "PICS with accelerated electron transfer" shown in Figs. 3(c) and 4(a), in which electron injection from the Ag NC or Ag@Au core-shell NC to TiO_2 is promoted by good electronic contact between the Au film and TiO_2. The other one is "PICS enhanced by the nanoantenna effect" shown in Figs. 3(d) and 4(b), in which the electron injection from Au to TiO_2 is enhanced by optical near field generated by the Ag NC; the Ag NC absorbs light and generates optical near field in its vicinity, and then the Au film is efficiently excited by the near field (i.e., the nanoantenna effect[23–25]) and causes PICS. In both cases, the current would be increased by increasing the amount of Ag NCs.[34]

In order to obtain further information about the mechanisms of photocurrent enhancement, we prepared another type of electrode by drop-casting the Ag NCs onto the Au thin film coated directly on TiO_2. The photocurrent action spectrum of the obtained $ITO/TiO_2/Au/Ag$ NC electrode was similar to that of the $ITO/TiO_2/Ag$ NC/Au electrode (Fig. 2), and a broad peak was observed at around 535 nm. The photocurrent enhancement factors at the peak wavelength are 23 and 5 with reference to the $ITO/TiO_2/Ag$ NC and the $ITO/TiO_2/Au$ electrodes, respectively. These photocurrent enhancements can also be explained in terms of both of the two possible mechanisms, namely the PICS with accelerated electron transfer and PICS enhanced by the nanoantenna effect. However, it is more likely that the Au thin film is excited by the optical near field of the NC proximal mode (i.e., the nanoantenna effect) because the PVP may also block the electron transfer from Ag NCs to the Au film.

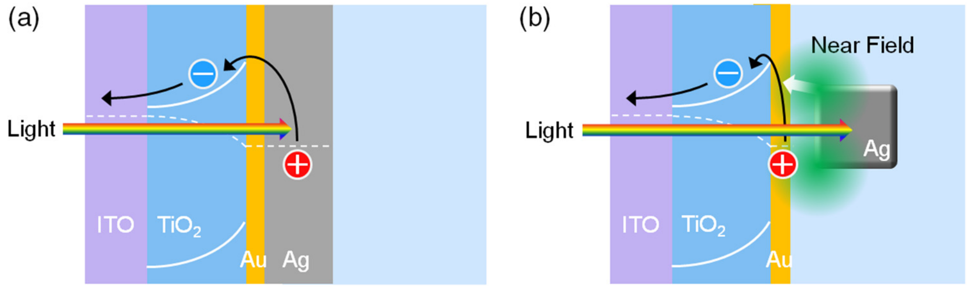

Fig. 4 Possible mechanisms of (a) the PICS with accelerated electron transfer and (b) PICS enhanced by the nanoantenna effect.

4 Conclusions

Photocurrent responses based on PICS from the ITO/TiO_2/Ag NC/Au and the ITO/TiO_2/Au/Ag NC electrodes are much higher than those from the ITO/TiO_2/Ag NC and ITO/TiO_2/Au electrodes. These enhancements are likely due to PICS with accelerated electron transfer or PICS enhanced by the nanoantenna effect. These results would provide an easier way to improve PICS efficiency of photovoltaics, photocatalysis, and other systems with commercially available or chemically synthesized plasmonic NPs with protecting layers.

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