The effects of 100 nm-diameter Au nanoparticles on dye-sensitized solar cells

Changwoo Nahm,1 Hongsik Choi,1 Jongmin Kim,1 Dae-Ryong Jung,1 Chohui Kim,1 Joonhee Moon,1 Byungjoo Lee,2 and Byungwoo Park1(a)

1WCU Hybrid Materials Program, Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Korea
2Samsung Electronics Co. Ltd., Gyeonggi-Do 446-712, Korea

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Gold nanoparticles of ~100 nm in diameter were incorporated into TiO2 nanoparticles for dye-sensitized solar cells (DSSCs). At the optimum Au/TiO2 mass ratio of 0.05, the power-conversion efficiency of the DSSC improved to 3.3% from a value of 2.7% without Au, and this improvement was mainly attributed to the photovoltaic current. The Au nanoparticles embedded in the nanoparticulate-TiO2 film strongly absorbed light due to the localized surface-plasmon resonance, and thereby promoted light absorption of the dye. In the DSSCs, the 100 nm-diameter Au nanoparticles generate field enhancement by surface-plasmon resonance rather than prolonged optical paths by light scattering. © 2011 American Institute of Physics. [doi:10.1063/1.3671087]

The optical properties of metal nanoparticles are clearly different from bulk materials due to resonance in the collective motion of free electrons oscillating within a small sphere, and this collective electron oscillation induced by electromagnetic wave is called surface-plasmon resonance. As the plasmonic resonance induces a dipole on the metal nanoparticle, the electric field is enhanced around the metal nanoparticle, and the optical extinction, such as scattering and absorption, is intensified. In particular, it is explained that the electric-field enhancement is the origin of the fluorescence enhancement induced by metal nanostructures and the surface enhanced Raman scattering (SERS). The plasmonic resonance of gold and silver nanoparticles has been intensively studied because they strongly interact with visible light, and it has been applied on a wide scale with chemical sensing, Raman spectroscopy, photoluminescence enhancement, etc.

In a solar cell system, it is important that the active layer of the solar cell absorbs as many photons as possible to produce more carrier electrons. In other words, the same photo-current may be produced with a reduced film thickness, and additional enhancement is also expected in thinner solar cells owing to the suppressed carrier recombination and therefore decreased internal resistance. Metal nanoparticles can contribute to the effective light absorption of solar cells, both by local field enhancement through the localized surface-plasmon resonance and by light scattering leading to prolonged optical-path lengths.

The enhanced photovoltaic properties from the incorporation of metal nanoparticles have been studied for various systems. More recently, metal nanoparticles were also introduced to the electrodes of dye-sensitized solar cells (DSSCs), and the solar-cell properties were improved by the plasmon-enhanced absorption of the dyes. However, the size of the metal nanoparticles used in the previous studies for DSSCs was limited to 10–30 nm, and the effects of larger metal nanoparticles on DSSCs have not been investigated yet.

Many researchers demonstrated that the size of the metal nanoparticles is a key factor for determining the plasmonic phenomena, and especially, light scattering occurs more dominantly than light absorption as the size of the metal nanoparticles increases. Nevertheless, in this article, we report that the Au nanoparticles with 100 nm diameters can improve the photovoltaic efficiency of DSSCs mainly by the localized surface-plasmon resonance, not by light scattering.

Gold nanoparticles were synthesized by reduction of Au ions in aqueous solution, and it is confirmed that the diameter of synthesized nanoparticles was approximately 100 nm (Fig. S1, see Ref. 19). Concentrated Au colloid and commercial TiO2 nanopowders (P25: Degussa, average diameter of 25 nm) were mixed to make a paste for the photoelectrode of DSSCs. Commercial N719 dye (Solaronix) was used as sensitizer, and sandwich-type DSSCs were fabricated. The experimental methods are thoroughly described in supplementary material (see Ref. 19).

Commercial TiO2 nanopowders, instead of TiO2 pastes from Solaronix or Dyesol, were used for mixing with ~100 nm Au nanoparticles and for better reproducibility of experiments. In addition, thinner TiO2 films (4 µm) than the typical thicknesses of DSSCs (~10 µm) were employed to clarify the effects caused by metal nanoparticles. These factors led to the lower power-conversion efficiency of 2.7% for the bare DSSC, compared with typical DSSCs exhibiting over 5%.

Figure 1 shows the current-density-voltage (J–V) characteristics and the incident photon-to-current conversion efficiency (IPCE) spectra. The power-conversion efficiency (η) of the DSSCs exhibits a maximum at the Au/TiO2 mass ratio of ~0.05 and rapidly decreases at 0.07. The enhanced solar cell properties are attributed to the increased current density, while the open-circuit voltage (Voc) and fill factor of the DSSCs are not notably changed by the addition of Au nanoparticles. In addition, the IPCE-enhancement ratio in the...
Au/TiO₂-DSSCs is more noticeable at longer wavelengths (inset of Fig. 1(b)). To investigate the optical role of the Au nanoparticles, extinction and diffused reflectance of Au/TiO₂ films without dye were obtained. By measurements with an integrated sphere, scattered transmission and scattered reflection of films were detected, and as a result, absorption at the films was precisely calculated. Extinction is defined by the ratio of the transmitted-light intensity ($I$) to the incident-light intensity ($I_0$), representing the degree of both absorption and reflection:

$$\text{extinction} = -\log(I/I_0) = -\log T,$$

$$A + R + T = 1,$$

where $A$, $R$, and $T$ are absorptance, diffused reflectance, and transmittance, respectively. In this study, scattering and absorption by Au can be qualitatively separated by measuring diffused reflectance, because the Au nanoparticles in the optically quasi-isotropic matrix, consisting of the randomly distributed TiO₂ nanoparticles, scatter light also isotropically.² The backward-scattered light proceeds to the integrated sphere and contributes to the diffused reflectance.²¹ In Fig. 2(a), the Au/TiO₂ film (mass ratio 0.05) exhibits higher extinction than the TiO₂ film, but shows a lower reflectance and consequently higher absorptance at the wavelength of the surface-plasmon resonance of Au (Fig. 2(b)). These results indicate that the stronger extinction of Au/TiO₂ is attributed to absorption rather than scattering. Thus, the excessive addition of Au nanoparticles would be detrimental to absorption at the photoactive materials,²² and experimentally, photocurrent and power-conversion efficiency of DSSC drop when the Au/TiO₂ mass ratio was 0.07 (Fig. 1).

A 100 nm-diameter Au nanoparticle exhibits scattering efficiency of ~40% around the resonance frequency, and this value is much lower compared with a Ag nanoparticle of the same size showing over 80% in visible range (Fig. S2, see Ref. 19). Despite the relatively large size of Au nanoparticles, the higher imaginary part of dielectric function of Au gives rise to the dominant absorption-nature from surface-plasmon resonance, and thereby induces strong absorption of Au/TiO₂ film in this experiment.

The optical properties of the dye-adsorbed films were also measured. The Au/TiO₂ film exhibits stronger extinction (Fig. 3(a)) but similar reflectance spectra (Fig. 3(b)) compared with the bare TiO₂ film, over the whole wavelength region. The resultant absorptance data in Fig. 3(b) indicate that the dye-adsorbed Au/TiO₂ film absorbs much more photons than the dye-adsorbed bare TiO₂ film, particularly at the longer wavelengths. In addition, absorptance spectra are consistent with the IPCE-enhancement ratios, showing gradual rise as the wavelength increases (inset of Fig. 1(b)). Correlation between absorptance and IPCE indicates that the performance improvement of the Au/TiO₂-DSSCs is attributed

![FIG. 1. (Color online) (a) Photocurrent density-voltage (J-V) characteristics of DSSCs at various Au/TiO₂ mass ratios. The inset shows the power-conversion efficiency (η) of DSSCs with respect to the Au/TiO₂ mass ratio. (b) Incident photon-to-current conversion efficiency (IPCE) spectra of DSSCs at various Au/TiO₂ mass ratios. The IPCE-enhancement ratios are also shown compared with the bare DSSC (Au/TiO₂ = 0) in the inset.](image)

![FIG. 2. (Color online) (a) Extinction of Au/TiO₂ film (solid-red line) and TiO₂ film (dashed black line) before dye adsorption. (b) Diffused reflectance (left blue arrows) and absorptance (right green arrows) of films before dye adsorption.](image)
In Bode plots, peak frequencies related to the electrode in DSSCs can be analyzed by electrical impedance spectroscopy. The enhancement of light absorption and thereby improvement in electron transport and recombination reactions of DSSCs between Au/TiO2 and bare TiO2 electrodes (Fig. S3, see Ref. 19) indicates that the Au nanoparticles in DSSCs do not make critical changes in electron transport and recombination reactions.

The field-enhancement effect in the vicinity of metal nanoparticles is a strong candidate for explaining the enhancement of light absorption induced by the Au nanoparticles.

The Au/TiO2 solar cells without dye were fabricated to examine direct photocarrier generation from Au nanoparticles. However, there are no remarkable differences between Au/TiO2 and bare TiO2 electrodes (Fig. S3, see Ref. 19), and their photocurrent density and efficiency are low enough (~0.2 mA/cm2 and ~0.05%, respectively). These results confirm that the direct photocarrier generation from Au is not the origin of the enhancement in the Au/TiO2-DSSCs.

Electrochemical reactions taking place at the interfaces of DSSCs can be analyzed by electrical impedance spectroscopy. In Bode plots, peak frequencies related to the electron lifetime in the TiO2 films are similar between the two DSSCs (Fig. S4(b), see Ref. 19), and this result indicates that the Au nanoparticles in DSSCs do not make critical changes in electron transport and recombination reactions.

The field-enhancement effect in the vicinity of metal nanoparticles is a strong candidate for explaining the enhancement of light absorption and thereby improvement of the photovoltaic performances. The electric field of incident light is strongly amplified by the oscillating surface charges in metal nanoparticles, and light absorption increases proportionally to the square of the electric-field amplitude. In this research, Au nanoparticles in DSSCs were obtained. In the case of the DSSCs, it is widely accepted that the time constant for charge separation at the dye-TiO2 interface (τseparation) is sub-picosecond. Consequently, it is expected that the quenching reaction would be negligible, since τseparation ≪ τmetal, thus the field-enhancement effect dominantly influences the performance of DSSCs. A possible mechanism of the surface-plasmon resonance in the Au/TiO2-DSSCs is schemed in Fig. 4.

In summary, we incorporated 100 nm-diameter Au nanoparticles into the photoelectrode of DSSCs, and the power-conversion efficiency of DSSCs increased by ~20%. The 100 nm Au nanoparticles and Au/TiO2 films exhibited unique light extinction caused by the localized surface-plasmon resonance, and this extinction in the DSSCs gave rise to effective light absorption by the field-enhancement effect rather than by prolonged optical-path lengths from scattering.

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**IPCE** in the entire wavelength (inset of Fig. 1(b)). Previous researches of metal-induced DSSC have reported similar tendency that the photocurrent enhancement is observed along the whole wavelength region.13,16 Metal nanoparticles also generate quenching processes, such as charge transfer and energy transfer to metals, which hamper the carrier generation at the active material. For higher enhancement by metal nanoparticles, quenching processes should be suppressed, or more specifically, the rate of electron-hole separation (1/τseparation) should be much faster than the rate of the quenching reaction by the metal (1/τmetal). Although τmetal is dramatically changed by the distance from the metal, the wavelength of incident light, and the dielectric function of materials, values over 100 ps were obtained. In the case of the DSSCs, it is widely accepted that the time constant for charge separation at the dye-TiO2 interface (τseparation) is sub-picosecond. Consequently, it is expected that the quenching reaction would be negligible, since τseparation ≪ τmetal, thus the field-enhancement effect dominantly influences the performance of DSSCs. A possible mechanism of the surface-plasmon resonance in the Au/TiO2-DSSCs is schemed in Fig. 4.

**FIG. 3.** (Color online) (a) Extinction of Au/TiO2 film (solid-red line) and TiO2 film (dashed black line) after dye adsorption. (b) Diffused reflectance (left blue arrows) and absorptance (right green arrows) of films after dye adsorption.

**FIG. 4.** (Color online) Schematic figure representing the enhancement of Au/TiO2-DSSC. Field enhancement near the Au nanoparticles is depicted as light grey (orange-color online) regions.
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Experimental Methods

**Synthesis of Au Nanoparticles**: Gold nanoparticles were synthesized by the reduction of gold chloride trihydrate (HAuCl₄·3H₂O; Aldrich) [1]. As a 0.5 mM aqueous solution of gold chloride trihydrate was stirred, ascorbic acid solution was added as a reducing agent. The resulting Au nanoparticle solution was concentrated by repeated centrifugation, and the contents of Au were varied (7 mg, 21 mg, 35 mg, and 49 mg) while the volume of the concentrated Au solution was fixed at 4.9 mL.

**Preparation of Au/TiO₂ Mixture Pastes**: Commercial TiO₂ nanopowders (P25: Degussa, average diameter of 25 nm) were used as the electrode material of DSSCs. Acid-treated TiO₂ powders [2,3] (0.7 g) were added to the concentrated Au solution (4.9 mL), and both polyethylene glycol (0.14 g, Fluka, average MW 20,000) and polyethylene oxide (0.14 g, Alfa Aesar, average MW 100,000) were added to the Au/TiO₂ mixture solution for the viscous paste [4,5]. Mixture pastes of various Au/TiO₂ mass ratios (0, 0.01, 0.03, 0.05, and 0.07) were prepared simultaneously, and these mixtures were stirred for a day to yield the homogeneous paste.

**Fabrication of Dye-Sensitized Solar Cells (DSSCs)**: For fabricating the nanoparticulate-TiO₂ films that were 4 μm thick, the resulting pastes were coated on a fluorine-doped tin oxide substrate (FTO, TEC 8: Pilkington) by a simple doctor-blade method [5,6]. A strip of Scotch Magic Tape (3M) was punched to make a mold for doctor blade and to fix the active area of DSSCs as 0.28 cm². After annealing at 500°C for 30 min, the paste-coated electrodes were immersed in 0.3 mM anhydrous ethanol solution of N719 dye (RuL₂(NCS)₂·2TBA, \(L = 2,2\'\text{-bipyridyl-4,4\'\text{-dicarboxylic acid}, TBA = tetrabutylammonium; Solaronix}\) for 12 h at room temperature. The dye-adsorbed electrode and Pt thin film for the counter electrode were
**Experimental Methods (continued)**

sealed with thermoplastic foil (Dupont, nominal thickness 60 μm), and an iodide-based redox electrolyte (AN-50: Solaronix) was injected into the gap between the two electrodes.

**Characterization:** Field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi) was used to investigate the size and morphology of Au nanoparticles. For the sample preparation of FE-SEM, an FTO glass was soaked in the as-synthesized Au colloid for 3 h. Optical properties were measured by an UV-Vis spectrophotometer (Lambda 35: Perkin-Elmer). For the extinction and diffused reflectance measurements of films, an integrated sphere was equipped to the spectrophotometer [7]. Photocurrent-voltage curves and electrochemical impedance spectra were obtained using a solar simulator (PEC-L11: Peccell) and potentiostat (CHI 608C: CH Instruments) under simulated solar illumination (AM 1.5 at 100 mW/cm²). Incident photon-to-current conversion efficiency (IPCE) spectra were obtained by using an IPCE measurement system (K3100: Mcscience).
Fig. S1. (Color) UV-Vis extinction spectrum of the colloidal Au nanoparticles. The inset shows the FE-SEM image of Au nanoparticles on FTO grains. Both the extinction peak and the FE-SEM image confirm that the diameter of synthesized nanoparticles is approximately 100 nm.
Surface-plasmon resonance of metal nanoparticles enhances the optical process: scattering and absorption. The relative strengths of these processes are expressed as cross sections, and the corresponding cross sections for scattering and absorption, $C_{sca}$ and $C_{abs}$, can be calculated using the dielectric function of metal ($\varepsilon_m$) and medium material ($\varepsilon_d$):

$$C_{sca} = \left(\frac{1}{6\pi}\right) \left(\frac{2\pi}{\lambda}\right)^4 \cdot 9V^2 \left|\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right|^2$$

and

$$C_{abs} = \frac{2\pi}{\lambda} \cdot 3V \cdot \text{Im} \left[\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right],$$

where $\lambda$ and $V$ are the wavelength of the incident light and the volume of the metal nanoparticle, respectively [8]. Scattering efficiency by plasmonic resonance is defined as $C_{sca} / (C_{sca} + C_{abs})$. For the calculation of scattering efficiency, the dielectric function of Au and Ag were adopted from polynomial fitting to the measured data [9], and the dielectric function of medium ($\varepsilon_d$) was assumed as $2 + 0\cdot i$. 

Fig. S2. (Color) Calculated scattering efficiency of Au and Ag nanoparticles, with a diameter of 100 nm.
Fig. S3. (Color) Photocurrent density-voltage ($J$-$V$) characteristics of DSSCs without dye.
Fig. S4. (Color) Electrochemical impedance spectra measured at open-circuit voltage: (a) Nyquist plots and (b) Bode plots. In Nyquist plots, two semicircles in the frequency regions of $10^3 - 10^5$ and $1 - 10^3$ Hz correspond to impedances related to the Pt/electrolyte interface ($Z_1$) and TiO$_2$/dye/electrolyte interface ($Z_2$), respectively.
References


