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Review Paper

Surface-Plasmon Resonance for Photoluminescence and Solar-Cell Applications

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The surface plasmon of metal nanostructures influences surrounding semiconductors in various ways. In particular, a surface plasmon modifies recombination rates of excitons in a semiconductor, and intensifies photon flux in the vicinity of metal nanostructures. These phenomena have contributed to the improvement of photoluminescent properties both by enhancement of radiative recombination and by electromagnetic-field amplification, even though the degree of nonradiative energy dissipation is sensitively dependent on the metal-semiconductor distance. Strong light absorption induced by surface plasmons is also attractive for photovoltaic applications, so metal nanostructures can be incorporated into diverse solar-cell systems with a reduced solar-cell thickness.

Keywords: surface plasmon, photoluminescence, solar cell, nanoparticle

1. SURFACE-PLASMON RESONANCE

1.1 Introduction

Surface plasmons are the collective oscillation of electrons that propagate through a metal/dielectric interface. At the metal/dielectric interface, the electrons are excited by the electromagnetic field, and the interactions between surface electrons and electromagnetic field constitute the surface plasmon. The schematic illustration of a surface plasmon is shown in Fig. 1(a). The electric field from oscillating electrons at the metal surface decays exponentially in the dielectric medium (Fig. 1(b)). The dispersion relations of surface plasmons can be obtained by solving Maxwell's equations. In the case of a 2-D metal/dielectric interface, the dispersion relation becomes:[1]

$$k = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \tag{1-1}$$

where k, ω, and c are wavevector, angular frequency, and light velocity, respectively, and ε_d and ε_m are the frequency-dependent permittivity of dielectric materials and metal, respectively. As shown in Fig. 2 demonstrating the dispersion relations $\omega(k)$ vs. k, the momentum ($\hbar k$) of a surface plasmon is larger than that of the light-dispersion relation.[2] For this reason, the coupling of light and surface plasmon does not always happen. However, surface plasmons propagating along a grating or a rough surface can satisfy the momentum conservation with the incident photon, so that the surface plasmons become excited by light waves.[2]

Metal nanostructures strongly interact with photons which have similar energy with their plasmon-resonance energy. For example, an aluminum nanoparticle of 13 nm diameter has a surface-plasmon resonance energy of ~8.8 eV, and its absorption efficiency for light of energy 8.8 eV is 18,[3] which means that its cross section for absorption is 18 times greater than its geometrical cross section. Field lines of the Poynting vector illustrate the photon paths, as shown in Fig. 3. The strong convergence of field lines near the nano-

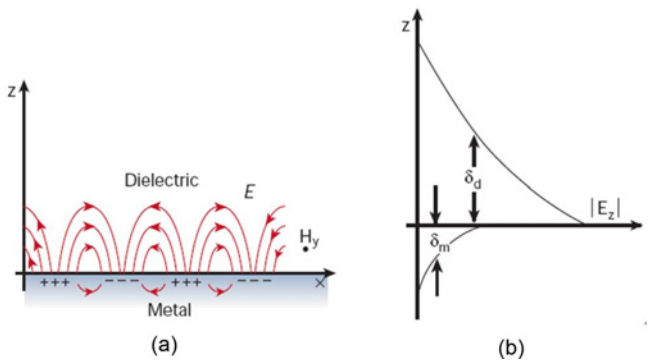

Fig. 1. (a) The charges and electromagnetic field of the surface plasmon propagating through a surface in the x direction are shown schematically. (b) The exponential dependence of the electric field (E_Z). Reprinted with permission from W. L. Barnes, A. Dereux, and T. W. Ebbesen.[1] Copyright 2003, Nature Publishing Group.

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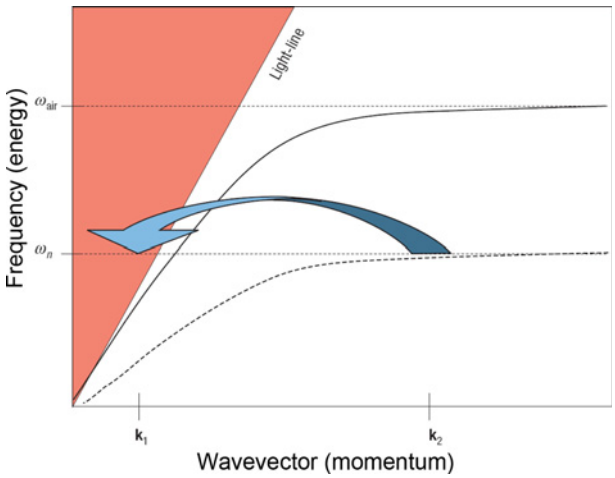

Fig. 2. Dispersion relation of the surface plasmon and the light line. Reprinted with permission from W. L. Barnes.[2] Copyright 2004, Nature Publishing Group.

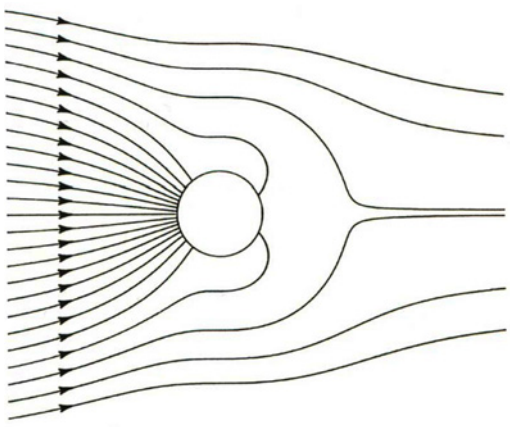

Fig. 3. Field lines of the total Poynting vector around an aluminum nanoparticle illuminated by 8.8 eV photon, which is the surface-plasmon resonance energy of an aluminum nanoparticle. From Ref. [3].

particle indicates that light passing near the metal deflects toward it, that is, light is strongly absorbed by the nanoparticle.

1.2 Surface-Plasmon Effect on the Luminescence Properties

In recent years, compound semiconductor nanoparticles have been widely researched as luminescent materials,[4-24] and various attempts have been conducted to enhance their luminescent properties by modification of the density of states in the excitation and emission modes.[25-36] The optical properties of semiconductors are affected by nearby metal nanostructures. Mostly, the surface plasmon enhances the luminescence properties in two ways: modification of radiative/nonradiative recombination rates, and localized-field enhancement. First, the radiative/nonradiative recombination rates of a semiconductor can be controlled by the nearby metal nanostructures. The schematic diagram of how the surface-plasmon coupling occurs is shown in Fig. 4.[37]

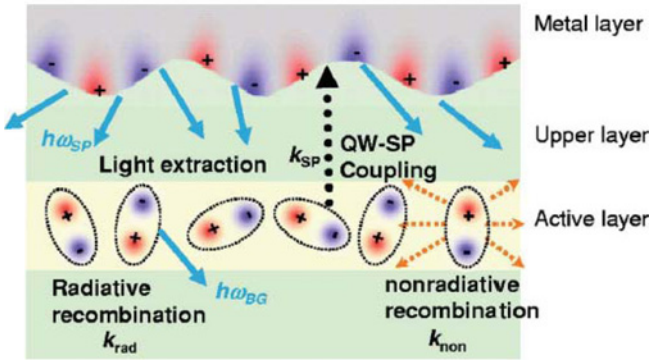

Fig. 4. Schematic diagram of the electron-hole recombination and quantum-well (QW) surface-plasmon coupling mechanisms. Reprinted with permission from K. Okamoto.[37] Copyright 2011, American Institute of Physics.

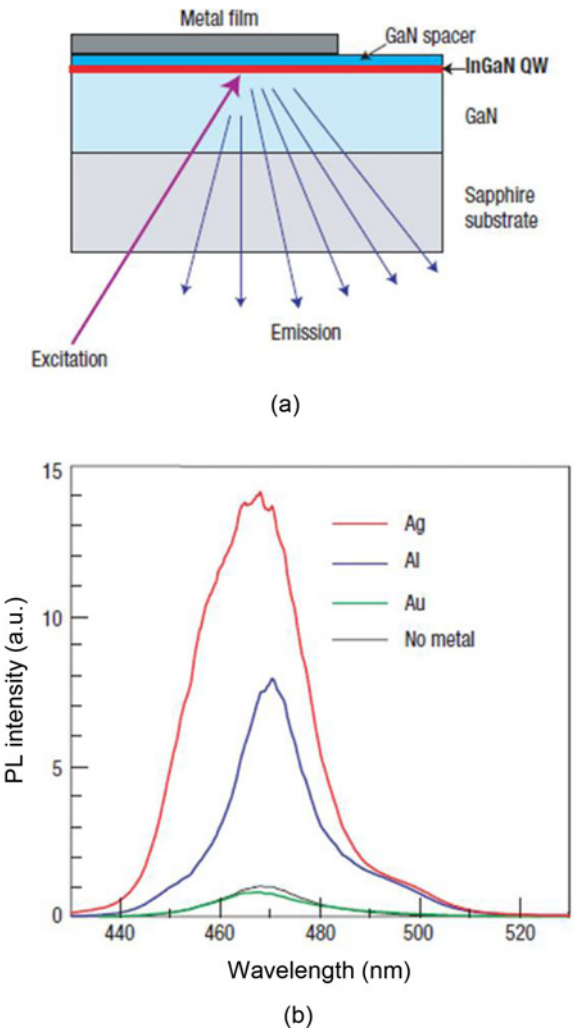

Fig. 5. (a) Sample structure and excitation/emission configuration of photoluminescence, and (b) photoluminescence spectra of InGaN/GaN quantum well (QW) coated with Ag, Al, Au, and no metal. The distance between the metal layer and QW was 10 nm. Reprinted with permission from A. Scherer.[38] Copyright 2004, Nature Publishing Group.

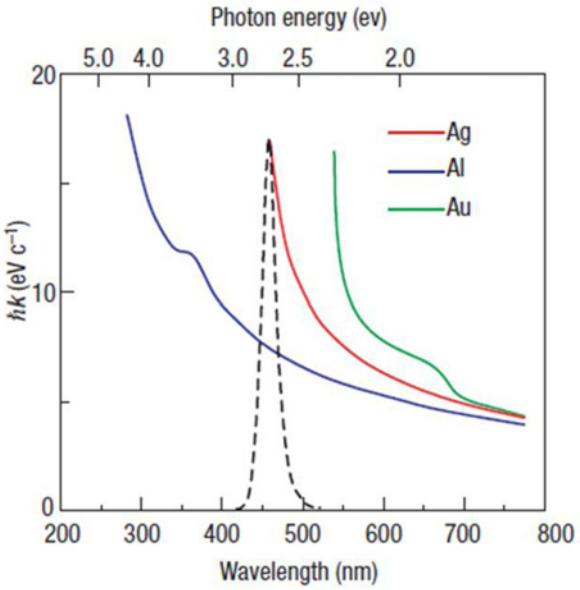

Fig. 6. Dispersion diagrams of surface plasmons generated on Ag/GaN, Al/GaN, and Au/GaN surfaces. Wavevector of the surface plasmon is denoted as *k*, and the dashed line is the photoluminescence spectrum of InGaN/GaN. Reprinted with permission from A. Scherer. [38] Copyright 2004, Nature Publishing Group.

When the semiconductor absorbs the incident light, excitons in the semiconductor interact with the surface plasmons of metal nanostructures.

Scherer's group examined the photoluminescence of an InGaN quantum well (QW) that was coated with various metal layers and ~10 nm GaN spacer.[38] With an appropriate selection of metal, the photoluminescence from the quantum well layer increased by one order of magnitude (Fig. 5). They correlated the increased luminescence with the dispersion relation for the surface plasmon of various metals (Fig. 6): the surface-plasmon energy of an Ag layer matches well with the InGaN emitter, thereby a large increase of luminescence intensity is observed. In the case of an Au layer, however, there is no surface-plasmon mode at the emission energy of the nearby semiconductor, so the photoluminescence intensity is not affected.

As for the localized-field enhancement, the enhanced field is induced by the localization of the electromagnetic field in the vicinity of metal nanostructures. The enhancement factor η (intensity ratio of the resultant to incident field) can be calculated assuming one isotropic metal sphere is placed in a homogeneous medium:[39]

$$\eta = \frac{\left|\vec{E}_2\right|^2}{\left|\vec{E}_0\right|^2} = \left(\left| 1 + 2\frac{a^3}{r^3}\frac{\varepsilon_{metal} - \varepsilon_{medium}}{\varepsilon_{metal} + 2\varepsilon_{medium}} \right|^2 \cos^2\theta + \left| -1 + \frac{a^3}{r^3}\frac{\varepsilon_{metal} - \varepsilon_{medium}}{\varepsilon_{metal} + 2\varepsilon_{medium}} \right|^2 \sin^2\theta \right) \quad (1\text{-}2)$$

where ε_{metal} and ε_{medium} are the dielectric constants of the metal nanoparticle and the surrounding medium, respectively, and *a* and *r* are the radius of the metal nanoparticle and the distance from the center of the metal nanoparticle, respectively. Figure 7 shows the field enhancement factor of an Au nanoparticle at the wavelength of 550 nm. Excitation of the localized surface plasmons in metal nanoparticles accelerates the creation of electron-hole pairs in the semiconductor.[40] As shown in Fig. 8, dye-adsorbed TiO_2 photoelectrode absorbs more light when silver nanoparticles are contained in the electrode, due to the localized-field enhancement.[41]

On the other hand, a surface plasmon near a semiconductor also affects the nonradiative recombination rate by energy dissipation. Once the distance of metal and semiconductor

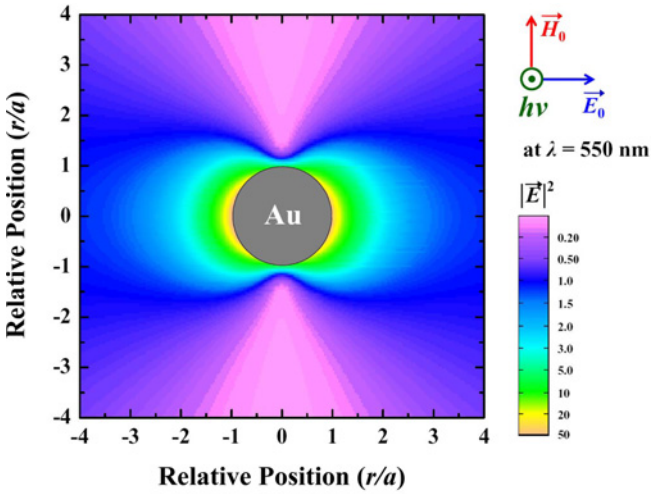

Fig. 7. Calculated field-enhancement factor of Au nanoparticle. The dielectric constants of metal and surrounding medium are −5.181 + 2.094 · *i* and 2.220 + 0 · *i*, respectively. From Ref. [40].

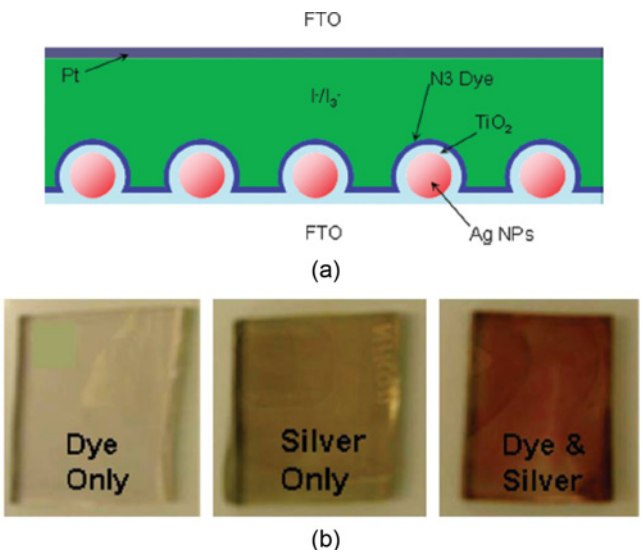

Fig. 8. (a) Configuration of solar cells containing silver nanoparticles and dye, and (b) photos of anodes showing the enhancement of light absorption by the introduction of Ag. From Ref. [41].

gets close enough, energy transfer between the semiconductor and metal occurs, so that the electron-hole pair recombines nonradiatively. Schematic illustrations of energy transfer from semiconductor to metal are shown in Fig. 9(a),[42] and this energy-transfer time lies approximately within the 0.1 - 1 ns range (Fig. 9(b)).[43-46] Therefore, the degree of nonradiative energy dissipation is strongly dependent on the metal-semiconductor distance. Due to this nonradiative effect, fluorescence intensity shows an optimum efficiency at an appropriate metal-semiconductor distance.[47-49] The effect from an isolated Au nanoparticle on the fluorescence rate of a single molecule emitter was calculated considering both the localized-field enhancement and the nonradiative energy-transfer loss (Fig. 10). The fluorescence

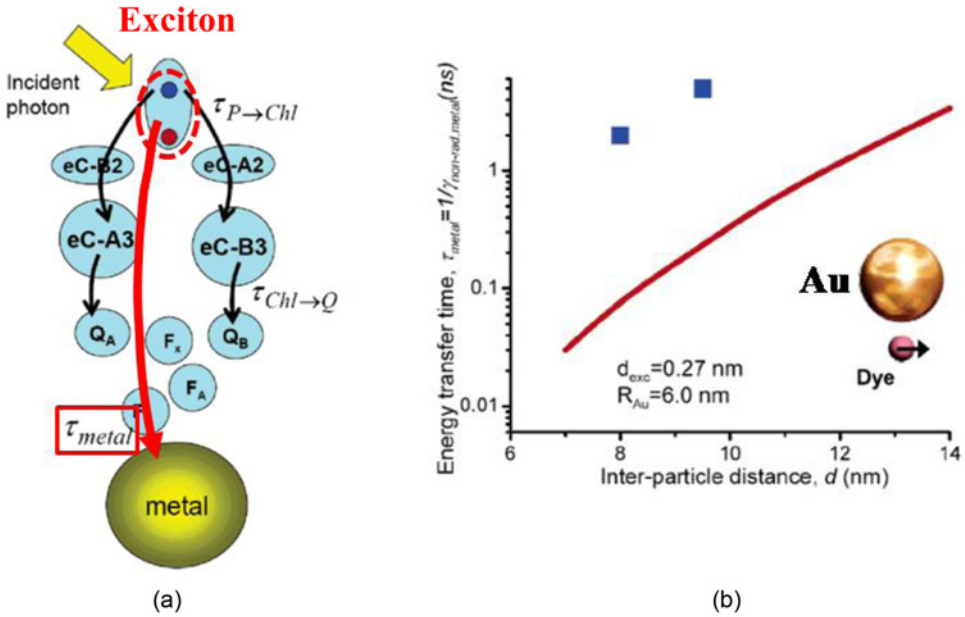

Fig. 9. (a) A schematic diagram of energy transfer (quenching) to metal. From Ref. [42]. (b) Energy-transfer time as a function of the distance between dye molecule and Au nanoparticle. The curves are obtained by numerical analysis, and the square symbols represent experimental data. From Ref. [43].

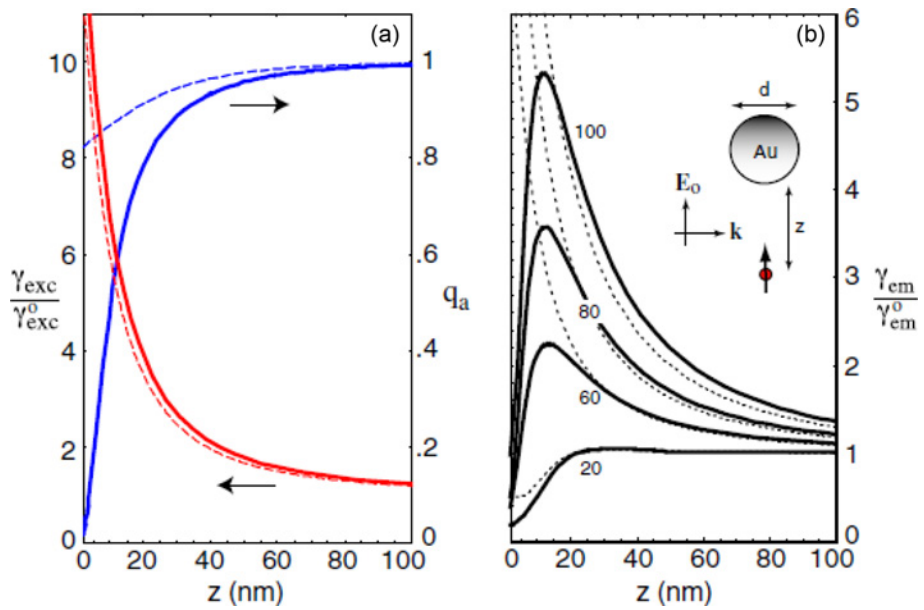

Fig. 10. Calculated quantum yield q_a, excitation rate γ_{exc}, and fluorescence rate γ_{em} as a function of molecule-particle separation. The γ_{exc} and γ_{em} are normalized by their corresponding free-space values ($z\rightarrow\infty$). The solid curves are the results of calculations whereas the dashed ones correspond to the dipole approximation which fails for short distance z. In (a) the particle diameter is d = 80 nm, and in (b) Au diameters are indicated in the figure. Excitation wavelength is λ = 650 nm, and $\varepsilon = -12.99 + 1.09 \cdot i$ (gold).[50] Copyright 2006 by the American Physical Society.

exhibits a maximum at a distance between metal and molecular emitter of ~10 nm, and these calculations correlate well with experimental results.[50] However, they did not consider the influence of the radiative recombination rate as a function of metal-semiconductor distance.

2. PHOTOLUMINESCENCE ENHANCEMENT IN SEMICONDUCTOR NANOPARTICLES BY SURFACE-PLASMON RESONANCE

2.1 Introduction

The important factors determining surface-plasmon resonance are the metal-semiconductor distance and energy matching between the surface plasmon and semiconductor emitter. The metal-semiconductor distance has an influence on the radiative and nonradiative energy-transfer rates. Energy matching is also important because the emission of semiconductor must be located close to the surface-plasmon energy for an effective surface-plasmon resonance. The density of surface-plasmon states can be also tuned for efficient energy matching.

2.2 Surface-Plasmon Resonance in Colloidal Mixtures of Semiconductor/Metal Nanoparticles

To investigate radiative/nonradiative recombination rates and quantum efficiency as a function of metal-semiconductor distance, the CdS and Au nanoparticles were investigated in colloidal mixtures with various molar fractions.[51] As shown in Fig. 11, photoluminescence intensities improved with increasing gold fraction, and a mole fraction of 10:1 resulted in the strongest emission peak. As expected, the luminescence intensity started to decrease at higher Au fractions, indicating the existence of an optimum resonance distance between metal and semiconductor.[52]

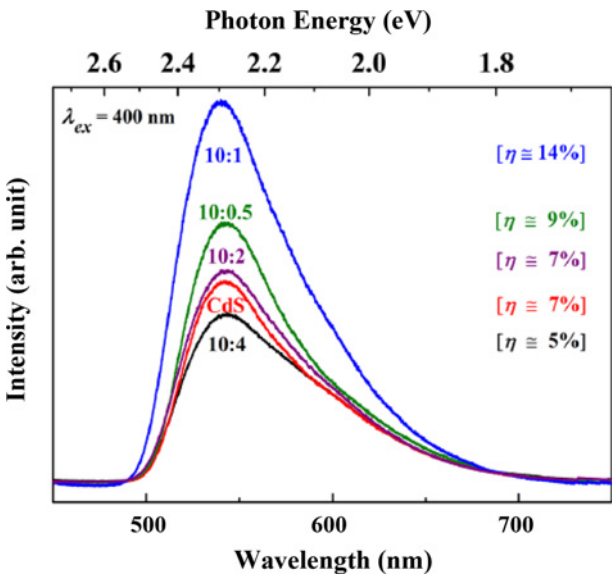

Fig. 11. Photoluminescence spectra of mixed CdS/Au nanoparticles with various CdS/Au mole fractions. Reprinted with permission from B. Park.[51] Copyright 2011, American Institute of Physics.

The radiative and nonradiative recombination rates can be easily determined considering the total recombination rate and quantum efficiency when the time-resolved photoluminescence shows single-exponential decay behavior. The quantum efficiency (η) is the ratio of the radiative recombination to the total recombination:

$$\eta = \frac{k_{rad}}{k_{rad} + k_{nonrad}} = k_{rad} \times \tau \qquad (2\text{-}1)$$

where k_{rad}, k_{nonrad}, and τ are the radiative, nonradiative recombination rates, and decay time respectively. Obvious correlations between the quantum efficiency and radiative/nonradiative recombination rate are shown in Fig. 12. The incorporated gold nanoparticles promote the radiative recombination indicating that surface-plasmon resonance accelerates the radiative recombination of electron-hole pair. However, when a metal is in close proximity to a semiconductor or other metal, destructive interference occurs, and consequently, a decrease in the luminescence efficiency is observed at higher Au fractions.[37]

Figure 13 shows the schematics of a possible mechanism of resonance between surface plasmon and exciton. If there are no Au nanoparticles around the CdS nanoparticles, nonradiative recombination is dominant with the quantum efficiency of ~10%. Radiative recombination of an electron-hole pair is dominant when Au nanoparticles are present at an appropriate distance (several tens of nanometers) from the CdS nanoparticles,[53] and the emission energy of the CdS nanoparticles matches well with the surface plasmon of Au nanoparticles. On the other hand, if the amount of Au becomes too high, the nonradiative energy transfer between CdS and Au occurs, and also destructive interferences of surface plasmons become dominant due to the metal-metal nanoparticle distance.

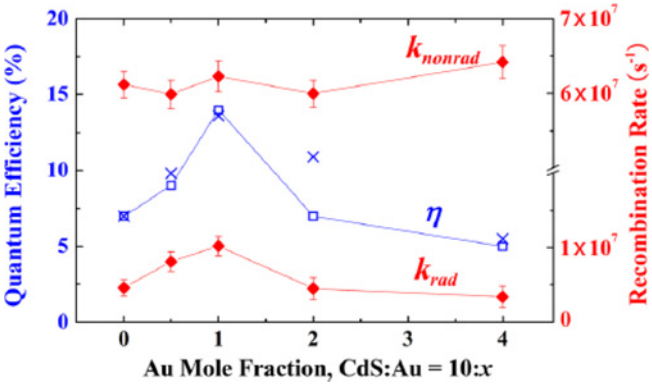

Fig. 12. Quantum efficiency, radiative recombination rate, and nonradiative recombination rate of the CdS/Au mixtures with various mole fractions. The estimated quantum efficiency is also shown (× symbol). Reprinted with permission from B. Park.[51] Copyright 2011, American Institute of Physics.

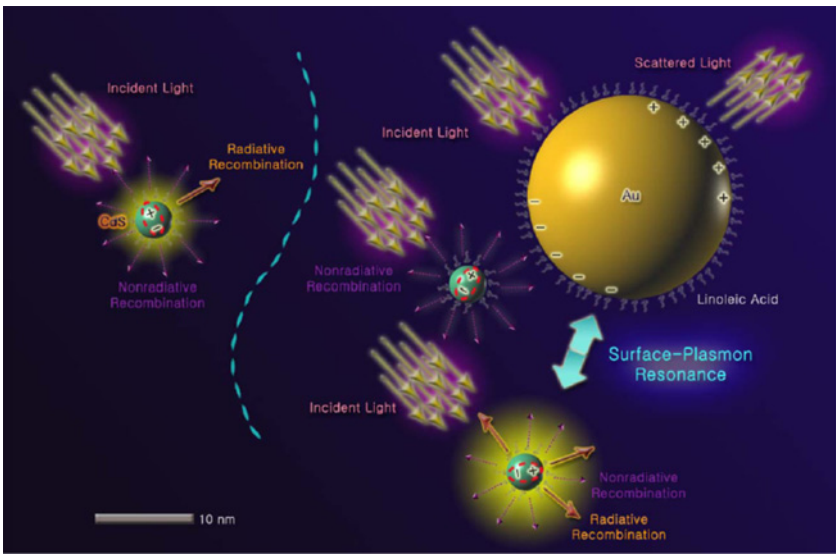

Fig. 13. Schematic figure of the proposed mechanism of photoluminescence enhancement by surface-plasmon resonance. Reprinted with permission from B. Park.[51] Copyright 2011, American Institute of Physics.

2.3 Enhanced Photoluminescence of Semiconductor Nanoparticles on Metal/Insulator Nanocomposite Film

The photoluminescence of CdS nanoparticles was also measured on Au/SiO_2 nanocomposite film deposited by sputtering.[54] Co-sputtering of metal and insulator leads to the formation of a nanocomposite film composed of metal nanoclusters and surrounding insulator matrix.[55-60] As shown in Fig. 14, the photoluminescence intensities were enhanced with the incorporation of Au/SiO_2 nanocomposite films. Since there have been few reports considering back reflection from the metal layer, it was necessary to separate only the surface-plasmon effect in the photoluminescence enhancement, not from the reflecting light making prolonged optical-path lengths.

Absorption spectra in Fig. 15 show that the plasmon peaks of the Au/SiO_2 film shift from ~500 nm to ~560 nm with increasing Au fraction. The 75% Au film shows a surface-plasmon peak at the wavelength of ~540 nm which matches

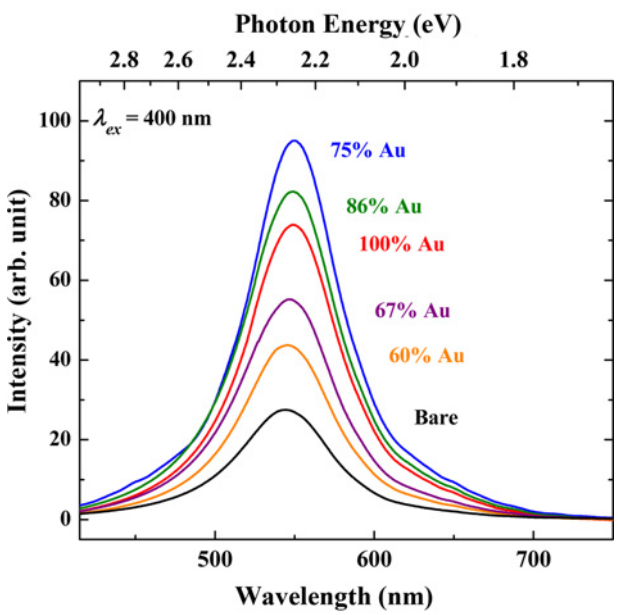

Fig. 14. Photoluminescence spectra of CdS nanoparticles with different Au fractions. Reprinted with permission from B. Park.[54] Copyright 2012, Elsevier.

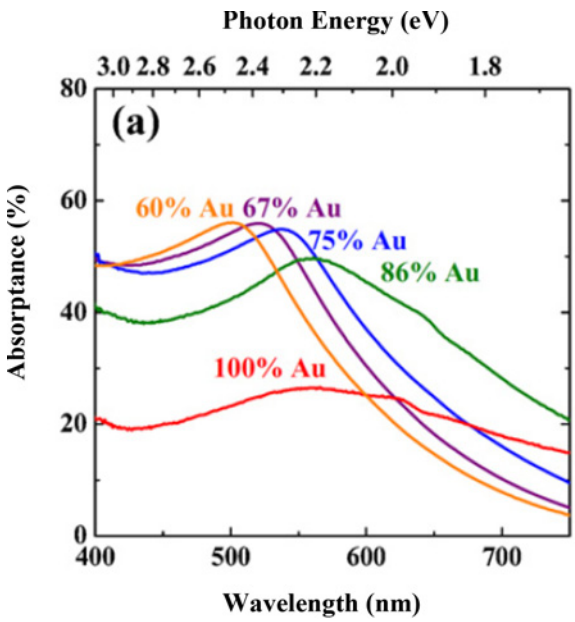

Fig. 15. Absorptance of Au/SiO_2 nanocomposites with various volume fractions of Au. Reprinted with permission from B. Park.[54] Copyright 2012, Elsevier.

well with the optimum photoluminescence (Fig. 14). The schematics of photoluminescence enhancement by the Au/SiO_2 surface-plasmon resonance is shown in Fig. 16.

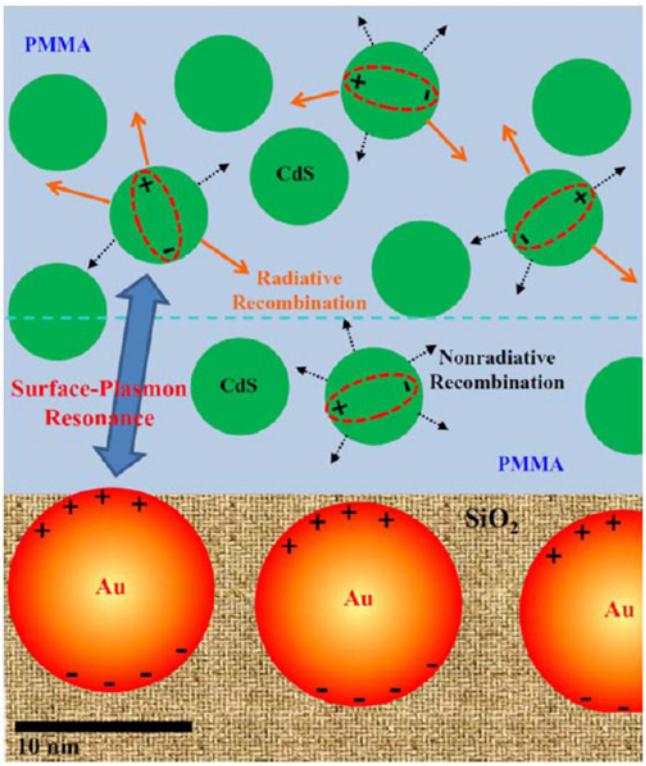

Fig. 16. Schematic figure of the proposed mechanism of photoluminescence enhancement by surface-plasmon resonance from Au/SiO_2 nanocomposites. Reprinted with permission from B. Park.[54] Copyright 2012, Elsevier.

2.4 Density of Surface-Plasmon States and Luminescence Enhancement

To study the effect of the density of surface-plasmon states on luminescence, CdS nanoparticles with various Au-film thicknesses were investigated.[61] As shown in Fig. 17(a), the photoluminescence efficiency was enhanced by increasing the Au layer thickness, and showed a tendency toward saturation after 100 nm. Furthermore, the luminescence efficiency was further increased by annealing the Au layer (Fig. 17(b)), probably due to the enhanced roughness produced by the thermal treatment.

The surface-plasmon relation can be obtained using Maxwell's equations in a three-layer system (the inset of Fig. 17). The surface-plasmon dispersion relation at the Au/PMMA interface for various Au film thicknesses are derived from a dispersion equation, and can be shown as

$$\frac{\gamma_2\varepsilon_3}{\gamma_3\varepsilon_2}+\frac{(\varepsilon_1\gamma_2+\varepsilon_2\gamma_1)+(\varepsilon_1\gamma_2-\varepsilon_2\gamma_1)\exp(-2\gamma_2 t)}{(\varepsilon_1\gamma_2+\varepsilon_2\gamma_1)+(\varepsilon_1\gamma_2-\varepsilon_2\gamma_1)\exp(-2\gamma_2 t)}=0 \qquad (2\text{-}2)$$

where ε_i and γ_i ($\gamma_i^2=k^2-k_0^2\varepsilon_i$) are the dielectric constant and decay constant for material i, respectively (i = 1 for glass, 2 for Au, and 3 for PMMA), and t is the thickness of the Au film. Figure 18 shows the derived dispersion relation of the metal/dielectric/semiconductor system. By differentiating $E(k)$ with respect to k, the density of surface-plasmon states can be easily obtained as

$$\rho(\hbar\omega)=\frac{2\pi kL^2dk}{(2\pi)^2d(\hbar\omega)L^2}\frac{1}{}=\frac{d(k^2)}{4\pi d(\hbar\omega)}. \qquad (2\text{-}3)$$

The density of surface-plasmon states as a function of photon energy (inset of Fig. 18) increased with the increased Au film thickness, which can be correlated with the

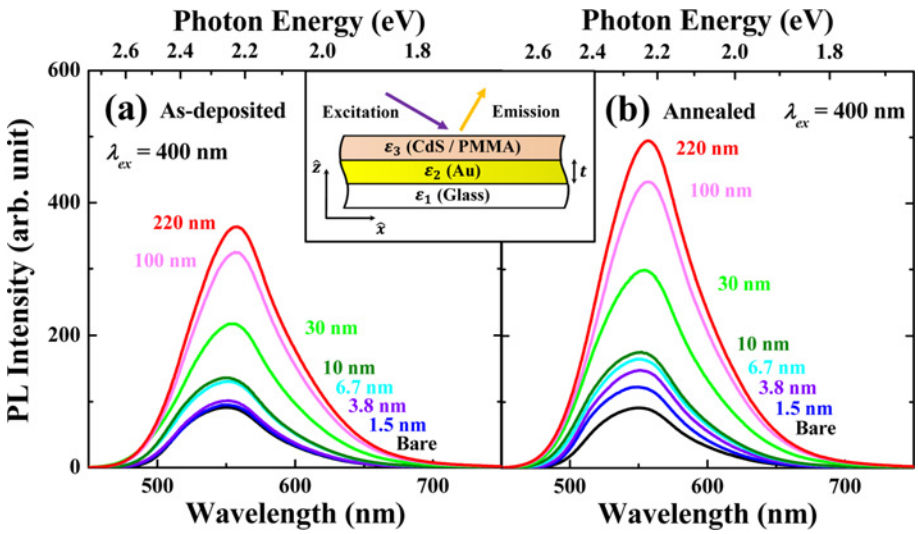

Fig. 17. Photoluminescence spectra of CdS nanoparticles with different thicknesses of Au film: (a) as-deposited and (b) annealed at 400°C for 30 min. The inset shows a schematic figure of a sample geometry and photoluminescence configuration. Reprinted with permission from B. Park.[61] Copyright 2012, Elsevier.

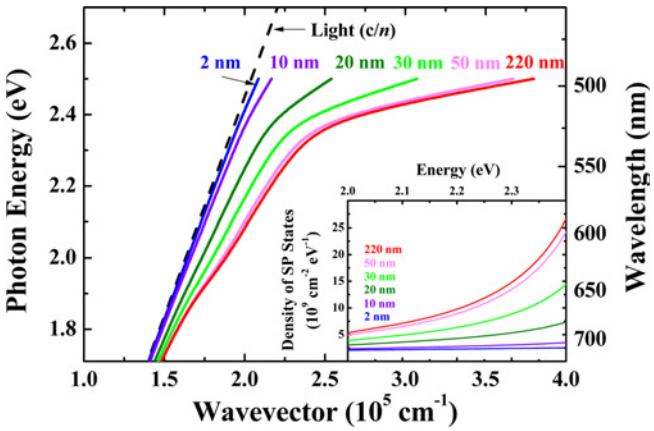

Fig. 18. Dispersion relation of surface plasmon at a planar Au/PMMA interface of a three-layer system for various Au film thicknesses. The light line in PMMA (index of refraction $n \cong 1.61$) is shown as a dashed line. The inset shows the calculated density of surface-plasmon (SP) states as a function of photon energy for different Au thicknesses. Reprinted with permission from B. Park.[61] Copyright 2012, Elsevier.

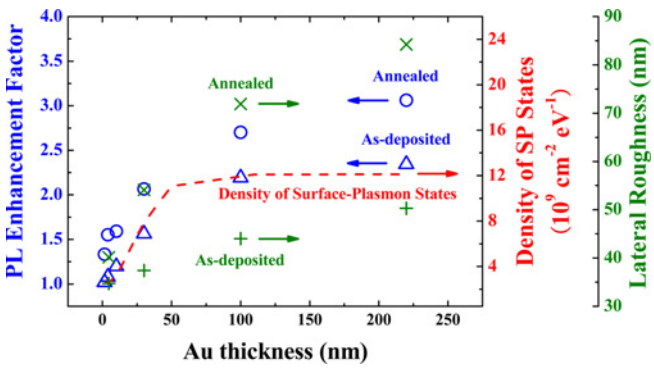

Fig. 19. The calculated PL enhancement factor and lateral roughness as a function of nominal thickness of Au film with and without annealing. The density of surface-plasmon (SP) states at 2.25 eV is shown as a dashed line. Reprinted with permission from B. Park.[61] Copyright 2012, Elsevier.

photoluminescence enhancement. Furthermore, by annealing the metal film to form a rough surface morphology, the CdS emission was further enhanced by the improved excitation and coupling of the surface-plasmon modes, as summarized in Fig. 19.

3. ENHANCED LIGHT ABSORPTION OF DYE MOLECULES BY LOCALIZED PLASMON RESONANCE IN SOLAR CELL

3.1 Introduction

The localized-field enhancement by the nearby metal nanoparticles can be effectively utilized for light harvesting in various solar cells.[62-74] By a localized surface plasmon, the electromagnetic field near metal nanoparticles can be amplified, and therefore more photons are absorbed with the same semiconductor-absorber thickness.[75] While there are many reports regarding nanostructured metals for the purpose of absorbing more light in solar cells by surface plasmon, the enhanced light absorption can also be achieved by light scattering from the submicron-sized metal particles.[76-80] Therefore, the separation of the field-enhancement effect from the light scattering (optical-path lengths) is necessary both for better understanding of the surface plasmon itself and for the practical application to solar-cell design. The nanoporous photoelectrode of a sensitized solar cell[81-98] is a suitable system to incorporate metal nanostructures and thereby to study plasmonic effects on the photovoltaic properties.

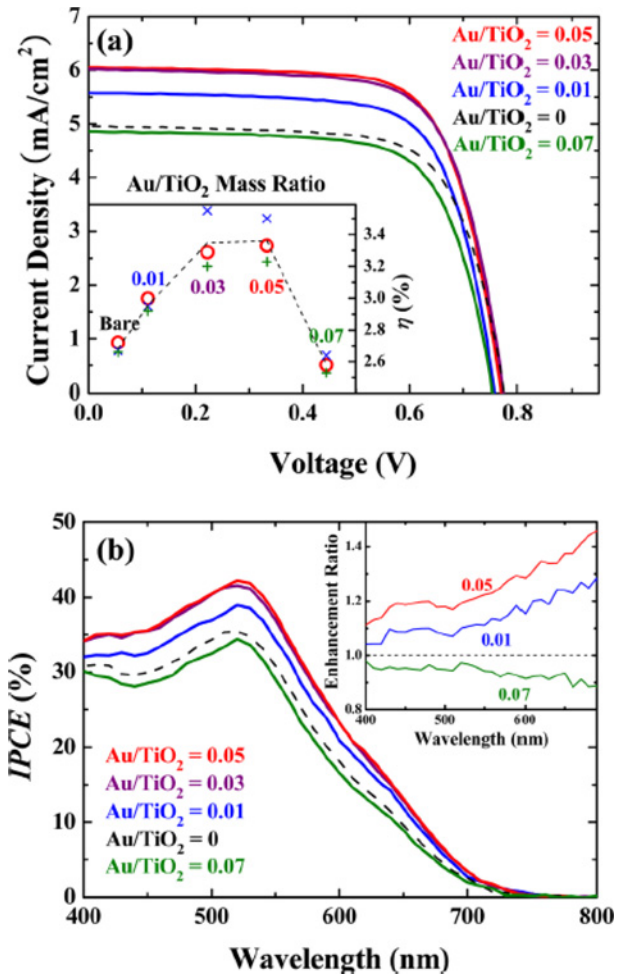

Fig. 20. (a) Photocurrent density-voltage characteristics of DSSCs at various Au/TiO_2 mass ratios. The inset shows the power-conversion efficiency of DSSCs with respect to the Au/TiO_2 mass ratio. (b) Incident photon-to-current conversion efficiency (*IPCE*) spectra of DSSCs at various Au/TiO_2 mass ratios. The *IPCE*-enhancement ratios are also shown compared with the bare DSSC ($Au/TiO_2 = 0$) in the inset. Reprinted with permission from B. Park.[99] Copyright 2011, American Institute of Physics.

3.2 The Effects of 100 nm-Diameter Au Nanoparticles in Sensitized Solar Cell

The effect of incorporating gold-nanoparticles in a dye-sensitized solar cell (DSSC) was investigated.[99] Approximately 100 nm-diameter Au nanoparticles were mixed with TiO_2-nanoparticulate photoelectrode, and then dye molecules were chemisorbed onto the TiO_2 nanoparticle surface. Figure 20 shows the current density-voltage (*J-V*) curves and the incident photon-to-current conversion efficiency (*IPCE*) spectra of solar cells as a function of Au/TiO_2 mass ratios. The enhanced power-conversion efficiency (η) of solar cells is attributed to the increased current density, which comes from the increased light absorption of the dye molecules, and is consistent with the *IPCE* data.

The extinction and diffused reflectance of the Au/TiO_2 film were measured to separate the scattering effect from the field-enhancement effect of the Au nanoparticles, since extinction represents a degree of both absorption and reflection. The definition of extinction is as follows:

$$\text{extinction} = -\log (I / I_0) = -\log T \quad (3\text{-}1)$$

$$A + R + T = 1 \quad (3\text{-}2)$$

where A, R, and T are absorptance, diffused reflectance, and transmittance, respectively.

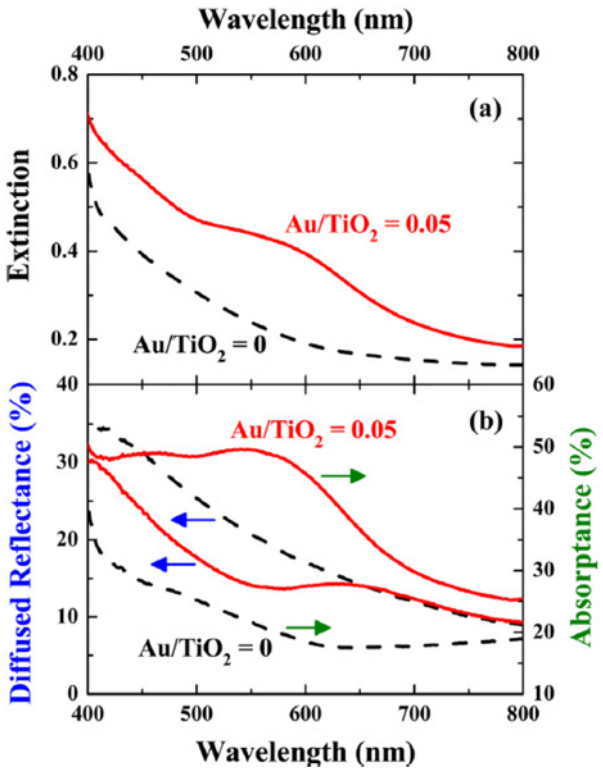

Fig. 21. (a) Extinction of Au/TiO_2 film (solid-red line) and TiO_2 film dashed-black line) before dye adsorption. (b) Diffused reflectance (blue arrows) and absorptance (green arrows) of films before dye adsorption. Reprinted with permission from B. Park.[99] Copyright 2011, American Institute of Physics.

As shown in Fig. 21, the Au/TiO_2 film (without dye adsorption) exhibits higher extinction compared to the bare TiO_2 film with lower reflectance. This indicates that the higher total extinction at the wavelength of the surface-plas-

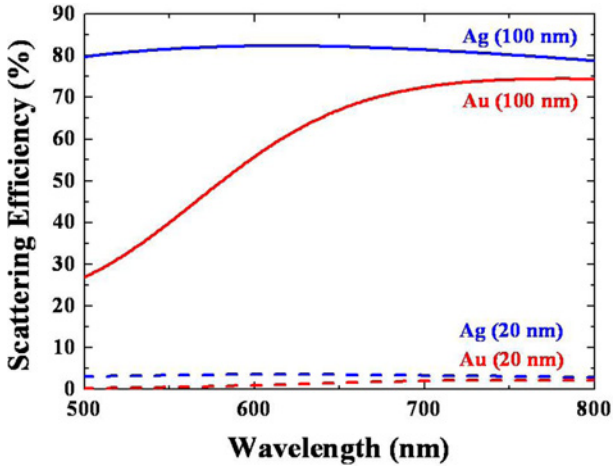

Fig. 22. Calculated scattering efficiency of Au and Ag nanoparticles. Dielectric function of medium (ε_d) was assumed as $2 + 0 \cdot i$. Reprinted with permission from B. Park.[99] Copyright 2011, American Institute of Physics.

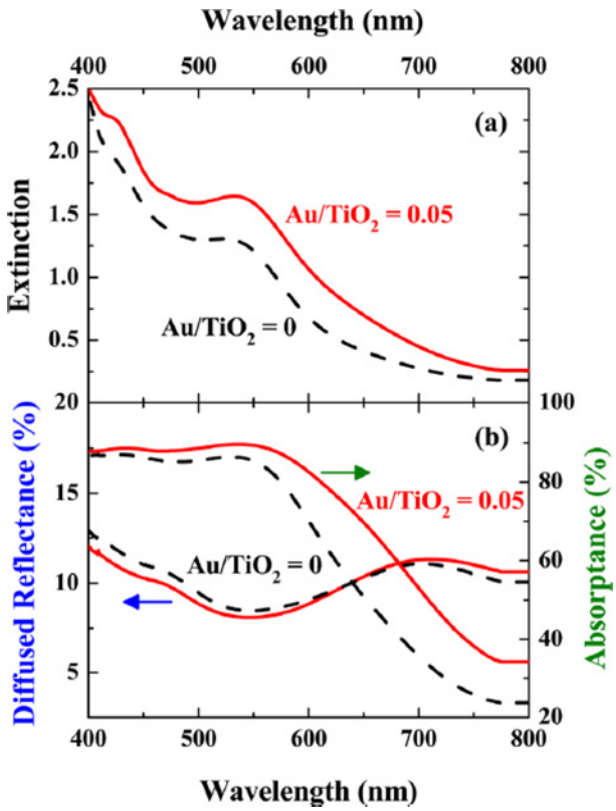

Fig. 23. (a) Extinction of Au/TiO_2 film (solid-red line) and TiO_2 film dashed-black line) after dye adsorption. (b) Diffused reflectance (blue arrows) and absorptance (green arrows) of films after dye adsorption. Reprinted with permission from B. Park.[99] Copyright 2011, American Institute of Physics.

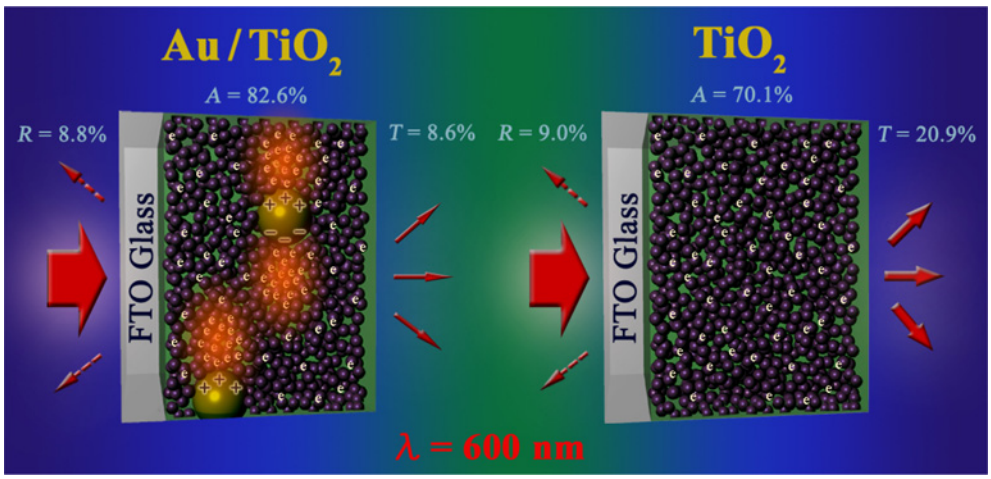

Fig. 24. Schematic figure representing the enhancement of Au/TiO_2-DSSC. Field enhancement near the Au nanoparticles is depicted as orange-color regions. Reprinted with permission from B. Park.[99] Copyright 2011, American Institute of Physics.

mon resonance is attributed to the absorption, and confirms that the scattering effect is negligible. This is consistent with the calculated scattering efficiency of Ag and Au nanoparticles (Fig. 22). Unlike Ag, the Au nanoparticles exhibit a dominant absorption-nature as opposed to scattering at the wavelength of surface-plasmon resonance, which confirms the strong absorption by field enhancement in the case of Au/TiO_2 film.

Optical properties were also measured with the dye-attached Au/TiO_2 photoelectrode. As shown in Fig. 23, the dye-absorbed Au/TiO_2 film exhibits stronger extinction with similar reflectance spectra. The resultant absorptance data considering the extinction and the reflectance shows that the incorporation of Au nanoparticles into the TiO_2 electrode helps to absorb more light with the same dye amount by local-field enhancement.

The surface-plasmon resonance of an Au nanoparticle can also induce quenching processes by the energy transfer between dye and metal nanoparticle. However, the time constant for electron transfer from the dye to the TiO_2 electrode (~1 ps)[100-104] is much shorter than that for quenching by metal nanoparticle (~100 ps).[43-46] Therefore, the quenching effect is believed to be negligible in DSSC. Figure 24 shows a schematic illustration of the effect of a surface plasmon for enhanced power-conversion efficiency in a solar cell. When the metal nanoparticle is located close to the dye molecules in the solar cell structure, more light can be trapped by the dye absorber due to the localized-field enhancement from Au nanoparticles, and thereby more photoelectrons can be collected in the electrode.

4. FUTURE WORK

Further studies are required to investigate the surface-plasmon effects on photoluminescence, such as the theoretical approaches to the radiative recombination rates considering the electrodynamic interactions between semiconductor and metal nanoparticle, and the nonradiative recombination rates based on the energy-transfer rate between single exciton and surface-plasmon band as a function of metal-semiconductor distance. The additional complex plasmon influences by multiple metal nanoparticles should also be investigated. Moreover, the quantitative relation between the density of surface-plasmon states and metal nanostructures needs to be identified. For the more practical applications of surface plasmons in luminescence and solar-cell structures, a theory for the effect of absorber-metal distance and the size/shape/concentration effects of metal nanostructures needs to be understood, for optimum efficiency in both applications.

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