Plasmon-enhanced photocurrent in quasi-solid-state dye-sensitized solar cells by the inclusion of gold/silica core–shell nanoparticles in a TiO$_2$ photoanode

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Direct evidence of the effects of the localized surface plasmon resonance (LSPR) of gold nanoparticles (Au NPs) in TiO$_2$ photoanodes on the performance enhancement in quasi-solid-state dye-sensitized solar cells (DSCs) is reported by comparing gold/silica core–shell nanoparticles (Au@SiO$_2$ NPs) and hollow silica nanoparticles with the same shell size of the core–shell nanoparticles. The Au nanoparticles were shelled by a thin SiO$_2$ layer to produce the core–shell structure, and the SiO$_2$ hollow spheres were made by dissolving the Au cores of the gold/silica core–shell nanoparticles. Therefore, the size and morphology of the SiO$_2$ hollow spheres were the same as the Au@SiO$_2$ NPs. The energy conversion efficiency was improved nearly 36% upon incorporating the Au nanoparticles, mostly due to the increase in $J_{sc}$ while $V_{oc}$ and FF were unchanged. The improvement was mostly contributed by the LSPR of the Au@SiO$_2$ NPs, whereas the other parameters, such as the electron lifetime and electron diffusion coefficient, were nearly unchanged. Therefore, LSPR is an effective tool in improving the photocurrent and consequently the performance of DSCs.

Introduction

Dye-sensitized solar cells (DSCs) have currently received much attention due to several advantages, such as the low fabrication cost and high power conversion efficiency greater than 12% under 1 sun illumination condition.$^{1-3}$ The most widely studied DSC is comprised of an electrolyte sandwiched between two electrodes coated on a transparent conducting glass, such as fluorine-doped tin oxide (FTO) glass; a photoanode and counter electrode. The photoanode consists of a mesoporous semiconductor such as a TiO$_2$ layer with sensitizers, whereas a typical counter electrode is made of a reduction catalyst such as platinum coated onto FTO. Upon light illumination, dye sensitizers adsorbed to the surface of the mesoporous TiO$_2$ layer generate electrons, which are subsequently injected into the TiO$_2$ layer for electricity production. Therefore, light absorption by sensitizers on the photoanodes plays a major role in determining the overall energy conversion efficiency of DSCs. A large body of research has been conducted to enhance the light harvesting efficiency in TiO$_2$ photoanodes. In this context, the development of more efficient dye sensitizers, including organic dyes with a higher extinction coefficient$^{3-6}$ and energy-relay dyes,$^7$ and their effective utilization methods, such as cocktail dye$^{8,9}$ and selective dye adsorption$^{10-13}$ concepts, have prevailed. In addition, the introduction of a scattering layer and inverse opal nanostructures are also common.$^{12-14}$

The localized surface plasmon resonance (LSPR) phenomena of metal nanoparticles has also been investigated to enhance light harvesting efficiency.$^{15-17}$ The LSPR, which refers to the resonance between the electromagnetic field and free-electron oscillation, amplifies the electromagnetic field near the metal nanoparticles, resulting in plasmon enhanced light absorption of dye sensitizers in DSCs.$^{18-21}$ The Hupp group first reported plasmon enhanced light harvesting in DSCs using silver
nanoparticles on flat TiO₂ film, demonstrating considerable potential to increase the photocurrent. The photocurrent and power conversion efficiency of the DSC increased nearly 6–7-fold upon incorporating silver nanoparticles into a dye monolayer on the flat TiO₂ film (J_{sc} from 14.6 to 85.7 μA cm⁻², from 0.007 to 0.045%). Recently, enhanced charge carrier generation in solid-state DSCs was demonstrated by the LSPR effects of Au NPs coated on a mesoporous TiO₂ photoanode and a hexagonal array of Ag nanodome-structured counter electrode.

Direct effects of LSPR by metallic nanoparticles on the performance of DSCs may not be readily evaluated in common redox couples which dissolve metallic nanoparticles, such as gold, by the following reaction:

\[ 2Au + 1I^- + \Gamma \rightarrow 2[AuI]^- \]  

One way to avoid the dissolution problem of metallic nanoparticles is to create a shell with an inert material, such as SiO₂. In this study, Au@SiO₂ NPs were synthesized in a solution process and mixed with a TiO₂ paste to fabricate Au@SiO₂ NPs incorporated mesoporous TiO₂ photoanodes. In addition, we used polyethylene glycol (PEG) based electrolyte to achieve stability of the Au core, inhibiting interaction between the Au core of Au@SiO₂ NPs and I⁻/I₃⁻ ions in the electrolyte. However, the properties of the core–shell nanoparticle-incorporated photoanodes were affected by both the metal cores and shell. Thus, the effects of the shell material on the cell performance must be considered. Until recently, even though a number of studies have been presented to improve the cell performance by utilizing the LSPR effects with metal/TiO₂ or SiO₂ core–shell structures, the quantitative analyses of the LSPR by metal cores and other changes in the photoanodes by shells are still difficult to separately evaluate. This problem may be solved by comparing the results of the same photoanode structures with and without core metal: core–shell and hollow shell. The hollow shell structure can be prepared by dissolving the core metal of the core–shell sphere by the dissolution reaction with I⁻/I₃⁻, which readily diffuses through a shell layer, such as SiO₂. In this context, SiO₂ hollow spheres-incorporated TiO₂ photoanode was fabricated to quantify the effects of the LSPR clearly by the Au nanoparticles without disturbing the shell properties or structure. The TiO₂ photoanodes incorporating SiO₂ hollow spheres have the same morphology as the initial TiO₂ photoanodes incorporating Au@SiO₂ NPs, which is helpful for accurate comparison of photoanodes with and without LSPR. Through this novel approach, the LSPR effect in DSCs can be independently demonstrated with the effect of SiO₂ shells, such as the charge injection problem from dyes into the SiO₂ shell and the change of morphology and resistance.

### Experimental

#### Materials

All chemicals were used without further purification, and water was doubly ionized. The chemicals used for the synthesis of Au@SiO₂ NPs, hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O), hexadecyltrimethylammonium bromide (CH₃(CH₂)₁₅N(Br)(CH₃)₃), sodium citrate (HOC(COO)Na)·(CH₂COONa)₂·2H₂O), ascorbic acid (C₆H₇O₆), (3-mercaptopropyl)trimethoxysilane (HS(CH₂)₃Si(OCH₃)₃) and a sodium silicate solution (Na₂O(SiO₂)·x·H₂O) were purchased from Sigma-Aldrich. For the fabrication of the dye-sensitized solar cells, polyethylene glycol dimethylether (PEGDME, M₉₆: 500), 1-methyl-3-propylimidazoliumiodide (MPII), iodine (I₂) and fumed silica (~14 nm) were obtained from Sigma-Aldrich. TiO₂ paste (DSL 18NR-T) and sensitizer dye, cis-dithiooctanobis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719), were purchased from Dyesol.

#### Synthesis of gold nanoparticles

Au NPs were prepared using a seed-mediated method. First, 15 nm-diameter Au NP seeds were synthesized via citrate reduction. In a typical procedure, 10 ml of a 1 mM gold(III) chloride trihydrate aqueous solution was refluxed at boiling temperature under vigorous stirring, followed by the quick injection of 1 ml of a 39 mM sodium citrate solution. After 15 min, the heating was stopped, and the reaction contents were cool to room temperature. To make larger nanoparticles, a 2 ml seed particle solution was added to 100 ml of a 0.5 mM gold(III) chloride trihydrate aqueous solution containing 0.03 M CTAB and 1 mM ascorbic acid. The solution was reacted for 4 hours, and the product was collected using centrifugation (9000 rpm, at room temperature for 10 min).

#### Synthesis of gold/silica core–shell nanoparticles

Au@SiO₂ NPs were synthesized by a modified procedure previously reported by Obare et al. In this method, growth of silica was performed after surfactant substitution with a silane coupling group, (3-mercaptopropyl)trimethoxysilane (MPTMS). MPTMS in ethanol was added to the Au NPs solution. After three hours, an aqueous sodium silicate solution was added and reacted for three additional days. The contents were purified several times by precipitation using centrifugation and were redispersed in ethanol.

#### Paste preparation

As-prepared Au@SiO₂ NPs dispersed in ethanol were added and well mixed with the commercial titanium dioxide (TiO₂) paste with an average size of 20 nm (DSL 18NR-T, Dyesol). In order to achieve the same thickness of photoanodes after sintering, excess ethanol from the paste was evaporated using nitrogen to produce a homogenous concentration of paste materials.

#### Device fabrication

For the formation of an electron blocking layer between the FTO substrate and oxidized species in the electrolyte, 0.1 M of Ti(IV) bis(ethyl acetocetato)diisopropoxide in a 1-butanol solution was spin-coated on FTO glass (TEC 8, Pilkington) followed by sintering at 500 °C. TiO₂ photoanodes were fabricated on the blocking layer with TiO₂ paste using a doctor blade method followed by sintering at 500 °C for 15 min. Subsequently, TiO₂ nanostructure-coated FTO substrates were dipped into 40 mM...
TiCl_4 in H_2O solution at 70 °C for 30 min and sintered at 500 °C for 15 min.

TiO_2 photoanodes were dipped into the 0.3 mM N719 dye (cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(n) bis-tetrabutylammonium, Dyesol) in an acetonitrile and tert-butanol solution (1:1 v/v) at 30 °C for 18 hours and then rinsed with acetonitrile and dried using a stream of nitrogen. A Pt counter electrode was prepared by thermal decomposition of 0.01 M H_2PtCl_6 in an isopropyl alcohol solution on the FTO substrate followed by sintering at 500 °C for 30 min. After loading the dyes onto the TiO_2 electrodes, Surlyn (25 μm, Solaronix) was attached to the TiO_2 photoanode as a spacer. The polymer electrolyte was spread on the spacer gap, and the Pt counter electrode was placed on top.

The electrolyte consists of poly(ethylene glycol dimethyl ether) (PEGDME) (M_w: 500, Sigma-Aldrich), 1-methyl-3-propylimidazolium iodide (MPII, Sigma-Aldrich), iodine (I_2, Sigma-Aldrich), and fumed silica nanoparticles (14 nm, Sigma-Aldrich). The composition of [–O–][MPII][I_2] was 10:1:0.1, and the silica NPs were 9 wt% of the total polymer electrolyte.\(^{31}\)

**Solar cell characterization**

The thickness of TiO_2 films was characterized with a surface profiler (alpha-step IQ, Tencor) and field emission scanning electron microscopy (JSM-6701F, JEOL). Absorption properties of photoanodes were measured by UV-Vis spectrophotometry (V-670, Jasco) with an integrating sphere. Transmission electron spectroscopy (TEM) of various sizes of Au@SiO_2 NPs by varying the Au core size were characterized. The electron lifetime in the photoanodes were characterized by electron transient spectroscopy (IMPS) under short-circuit conditions and intensity-modulated photovoltage spectroscopy (IMVS) under open-circuit conditions as a function of light intensity using a controlled intensity modulated photo spectroscopy (CIMPS) system (Zahner) and a white light source (Zahner). The detailed measurement conditions are described elsewhere.\(^{32}\)

**Results and discussion**

Fig. 1a–c show TEM images of three, differently sized Au NPs shelled with thin SiO_2 (Au@SiO_2 NPs). The average diameter of Au NPs obtained by varying the concentration of the Au precursor was (a) 30, (b) 50, and (c) 160 nm. Subsequently, their surfaces were modified with 3-mercaptopropyl trimethoxysilane (MPTMS), and the thickness of the SiO_2 shells were controlled to approximately 11 nm by adding an aqueous sodium silicate solution.

Even though the Au NPs were protected by the SiO_2 shell, the Au cores were dissolved by contact with I^-/I_3^- ions penetrating the thin silica shell in a few hours. Therefore, the SiO_2 shell was treated with TiCl_4 to block the penetration of I^-/I_3^- ions and consequently improve the stability of the Au core nanoparticles against dissolution. In addition, a poly(ethylene glycol) dimethylether (PEGDME, M_w: 500)-based polymer electrolyte, instead of typical acetonitrile-based liquid electrolytes, was used for quasi-solid-state DSCs in order to retard the possible penetration of the I^-/I_3^- ions through the SiO_2 shell. Based on our experimental results, a SiO_2 shell thinner than 8 nm hardly protected the Au core from the electrolyte contact, even though high M_w PEGDME was applied as a viscous solvent for quasi-solid electrolytes. Experimental data suggests that 10 nm was the minimum thickness of the SiO_2 shell necessary to protect the Au core from the dissolution.

The localized surface plasmon resonance (LSMR) effects of Au@SiO_2 NPs by varying the Au core size were characterized using UV-vis spectroscopy, as shown in Fig. 1d. The absorption peak appears at 537, 547, and 565 nm for Au@SiO_2 NPs with the size of the Au core/SiO_2 shell 30/12, 50/11, and 160/10 nm, respectively. This shift in the absorption band is attributed to the change in the oscillation frequency of LSPR caused by varying the average diameter of the Au NPs. The absorption band of LSPR shifts to a longer wavelength by increasing the size of Au NPs as a result of the decrease in the oscillation frequency. The coupling between the LSPR of the Au NPs and the absorption of dyes is one of the key factors for the enhanced performance of DSCs using Au NPs. In this case, the absorption peak difference or coupling wavelength mismatch of Au NPs (160 nm) with respect to the N719 dyes was ~40 nm, as shown in Fig. 1d.
incorporated photoanode with cross-sectional scanning electron microscopy (SEM) image of Au@SiO$_2$ NP-incorporated photoanode with ~20 nm diameter TiO$_2$ nanoparticles (white arrows indicate Au@SiO$_2$ NPs).

in Fig. 1(d). Additionally, when larger Au NPs were incorporated into the TiO$_2$ photoanodes, Mie scattering which is a long range effect should occur and it can be mixed with the effect of LSPR. Alternatively, as the size of the Au NPs increases, the field enhancement is more widely developed, leading to increased light harvesting of the dyes. Therefore, 50/11 nm Au@SiO$_2$ NPs were chosen for the fabrication of photoanodes to investigate the effects of LSPR in DSCs considering their coupling wavelength mismatch, the change in surface area, and the near-field enhancement effects.

Fig. 2a shows the schematic illustration of a Au@SiO$_2$ NP-incorporated TiO$_2$ photoanode. The LSPR of Au@SiO$_2$ NPs in TiO$_2$ photoanodes was observed by the reddish photoanode (inset photograph) and by the UV-vis spectrum, as shown in Fig. 2b. Fig. 2c shows Au@SiO$_2$ NPs in the photoanodes surrounded by TiO$_2$ NPs using scanning electron microscopy (SEM). Noticeably, the shapes of the Au@SiO$_2$ NPs were unchanged after sintering at 500 °C.

The photocurrent–voltage characteristics of DSCs with TiO$_2$ photoanodes incorporating Au@SiO$_2$ NPs are represented in Fig. 3. The film thickness of photoanodes with and without Au@SiO$_2$ NPs was adjusted to 2 μm to more clearly characterize the effects of LSPR, which is thinner than a conventional TiO$_2$ layer (Fig. S1†). In order to optimize the incorporation of Au@SiO$_2$ NPs for DSC performance, the concentration of Au@SiO$_2$ NPs in the TiO$_2$ paste was varied from 0.25 to 1.5 wt%. The short circuit current density ($J_{sc}$) was increased upon the incorporation of Au@SiO$_2$ NPs, while the open-circuit voltage ($V_{oc}$) and fill factor (FF) remained nearly unchanged. The $J_{sc}$ and power conversion efficiency (PCE) of DSCs with the addition of 1.0 wt% of Au@SiO$_2$ NPs into the TiO$_2$ layer were increased to 5.67 mA cm$^{-2}$ and 2.66%, respectively, with respect to the same thickness reference TiO$_2$ photoanode without Au@SiO$_2$ NPs (4.35 mA cm$^{-2}$, 1.94%). However, at concentrations greater than 1.0 wt% Au@SiO$_2$ NPs, the $J_{sc}$ (5.44 mA cm$^{-2}$) and PCE (2.53%) were slightly decreased, as shown in Fig. 3b and Table 1. The inclusion of Au@SiO$_2$ NPs in the photoanode may have possible side effects. First, the Au@SiO$_2$ NPs could inhibit the light absorption of dyes in the photoanodes while the Au@SiO$_2$ NPs in the photoanodes absorb the incident light as well as dyes but without converting photons to charges. On that account, the light harvesting efficiency may slightly decrease when the concentration of Au@SiO$_2$ NPs in the photoanode becomes higher than the critical point. Secondly, Au@SiO$_2$ NPs with a size of ~70 nm decrease the total amount of dye loading in the photoanodes due to the smaller surface area relative to 20 nm TiO$_2$ NPs. Finally, it is difficult to inject electrons from the excited dyes into the insulator SiO$_2$ shell. These side effects of the inclusion of Au@SiO$_2$ NPs may result in a decrease in photocurrent and consequently the photovoltaic performance of DSCs to a small extent. However, the overall energy conversion efficiency increased from 1.94 to 2.66%, which was nearly 30% improvement, suggesting that the positive effects of LSPR are significant. Therefore, the performance was further characterized in the following sections. In order to evaluate the quantitative effects of LSPR from Au cores excluding the SiO$_2$ shell effects, the Au@SiO$_2$ NP-incorporated photoanodes with and without the Au cores were compared. Experimentally, TiO$_2$ photoanodes incorporating SiO$_2$ hollow spheres with the same size of Au@SiO$_2$ NP shell but without the Au core were
introduced by dipping Au@SiO₂ NP-incorporated photoanodes in an I⁻/I₃⁻ liquid electrolyte for a few hours, which has the same morphology and thickness of the photoanode with Au@SiO₂ NPs. As expected, the SiO₂ hollow sphere was formed without a change in morphology due to the exclusive dissolution reaction eqn (1) of Au with I⁻/I₃⁻ ions, which was easily demonstrated by the disappearance of the reddish color and characterized by scanning electron microscopy, as shown by the inset photographs of Fig. 4 and S2(a).† Fig. 5a shows the decreased light absorption of N719 dyes upon incorporating the SiO₂ hollow spheres rather than Au@SiO₂ NPs, indicating the effects of the presence of Au cores. The amount of dyes adsorbed on the TiO₂ surface were characterized and this result shows that the dyes loaded in SiO₂ hollow sphere incorporated photoanodes are nearly the same as the amount in the Au@SiO₂ NPs incorporated photoanode (Fig. S2(c)†). The only difference between these photoanodes was the Au cores, suggesting that the enhanced light absorption is primarily attributed to the LSPR effects of the Au core. In order to confirm the LSPR effect more distinctly, we characterized absorption spectrum of the photoanodes additionally with N749 dyes (green dye) which absorb longer wavelength of light (>600 nm) compare to Au NPs (~530 nm), as shown in Fig. 5a. Through the distinguished peaks of LSPR and light absorption of N749 dyes, the effect of LSPR on the enhanced light absorption of dyes was clearly verified. Moreover, almost the same reflectance of Au@SiO₂ NPs and SiO₂ hollow spheres incorporated photoanodes were characterized by UV-vis spectroscopy with an integrating sphere and both photoanodes show only ~2% off-specular reflection by scattered light (Fig. S3†). This provides convincing evidence that absorption enhancement was mainly induced by LSPR which is near-field effect and not Mie scattering which is far-field effect.

Fig. 5b shows the photocurrent–voltage (J–V) characteristics of DSCs that are consistent with the results obtained from the difference in the light absorption, as shown in Fig. 5a. DSCs based on the TiO₂ photoanode incorporating Au@SiO₂ NPs exhibited ~28% greater J_{sc} and PCE than those with the hollow SiO₂ spheres. The increase of J_{sc} agrees well with the incident photon-to-current efficiency (IPCE) results, and the difference obtained by subtracting IPCE values increased at the same wavelength as the absorption band of LSPR (Fig. 5c). Moreover, the photoanode incorporating SiO₂ hollow spheres shows similar J_{sc} of 4.4 mA cm⁻² and PCE of 1.97% with respect to the reference TiO₂ photoanode, as summarized in Table 1. For the photoanodes incorporating SiO₂ hollow spheres, only the Au cores were removed from the Au@SiO₂ NPs photoanode, while

![Image](image1.png)

**Table 1** J–V characteristics of the DSCs with TiO₂ photoanodes employing Au@SiO₂ NPs and SiO₂ hollow spheres

| Type of TiO₂ photoanode | Concentration of Au@SiO₂ NPs (wt%) | J_{sc} (mA cm⁻²) | FF (%) | Efficiency (%) |
|-------------------------|------------------------------------|-----------------|--------|---------------|
| Reference (only TiO₂)   | —                                  | 0.664           | 4.35   | 67.0          | 1.94          |
| TiO₂ w/Au@SiO₂ NPs     | 0.25                               | 0.657           | 4.73   | 67.8          | 2.12          |
|                         | 1.0                                | 0.684           | 5.67   | 68.6          | 2.66          |
|                         | 1.5                                | 0.676           | 5.44   | 68.7          | 2.53          |
| w/SiO₂ hollow spheres  | 1.0                                | 0.665           | 4.4    | 67.7          | 1.97          |

*The thickness of TiO₂ photoanodes are adjusted with 2 μm; measured under 1 sun condition (AM 1.5, 100 mW cm⁻²) with 0.25 cm² active area.
the surface area and morphology of the TiO$_2$ photoanode were unchanged. Thus, the small change of the photovoltaic performance between the reference and SiO$_2$ hollow sphere photoanodes suggested that the effects of changes in surface area and morphology upon incorporating Au@SiO$_2$ NPs on the cell performance were nearly negligible. The performance enhancement upon incorporating Au@SiO$_2$ NPs into a photoanode is mostly due to the LSPR effects of the Au nanoparticles.

Electrochemical impedance spectroscopy (EIS) was performed in dark conditions with a bias potential of $-0.54$ V (Fig. 6) to characterize the cell performance, and the performance parameters were obtained by fitting with the general transmission model of DSCs.$^{33}$ In Fig. 6a, the Nyquist plots show two semicircles. The first semicircle at high frequency was attributed to the charge transfer resistance at the Pt counter electrode–polymer electrolyte interface ($R_{\text{Pt}}$), and the second semicircle at mid-frequency was associated with the electron recombination resistance ($R_{\text{rec}}$) and capacitance ($C$) at the TiO$_2$–polymer electrolyte interface. For Bode plots, the characteristic frequency peak in the mid-frequencies was unchanged (Fig. 6b), indicating nearly the same electron lifetimes for the two samples. The values are listed in the inset table of Fig. 6b.

The roles of the Au@SiO$_2$ NPs in the electron lifetime and the electron diffusion coefficient in the TiO$_2$ photoanodes were also evaluated with incident-modulated photovoltage spectroscopy (IMVS) and incident-modulated photocurrent spectroscopy (IMPS) as a function of the light intensity given in Fig. 7a. In accordance with the EIS measurements, the electron lifetime upon the inclusion of the Au@SiO$_2$ NPs was unchanged compared to that of the photoanode with the hollow SiO$_2$ spheres. Furthermore, the electron diffusion coefficient was also unchanged, and thus the diffusion lengths ($L_n$, $L_m = (D_n \tau_n)^{1/2}$) derived from these values were almost same between the photoanodes containing Au@SiO$_2$ NPs with and without the
Au core nanoparticles. In addition, the transient photocurrent and the diffusion coefficients of electrolyte \([D_{\text{i}1}^+]\) were measured, as shown in Fig. 7b and c. Nearly the same values of Au@SiO\(_2\) NPs \((2.36 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1})\) and hollow SiO\(_2\) spheres \((2.38 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1})\) incorporated photoanodes were evaluated. These results reveal that despite the enhanced light absorption of photoanodes by LSPR, the Au NPs had no influence on the electrochemical properties in the photoanodes and electrolyte due to the presence of the insulating layer inhibiting interaction between Au cores and electrolyte.

Conclusions

Au@SiO\(_2\) NPs incorporated into a conventional mesoporous TiO\(_2\) photoanode resulted in a significant increase in the energy conversion efficiency (up to 36% from 1.94 to 2.66%) with a 2 \(\mu\)m-thick photoanode under 1 sun illumination condition) in quasi-solid state DSCs, mostly due to the enhanced photocurrent density from 4.35 to 5.67 mA cm\(^{-2}\) by the LSPR effects of the Au NPs. In addition, the LSPR effects were directly observed by comparing results between the Au@SiO\(_2\) NPs- and SiO\(_2\) hollow spheres-incorporated TiO\(_2\) photoanodes, where the hollow spheres were obtained by dissolving the Au core with I\(^{-}\) / I\(_2\) ions and had same morphologies as Au@SiO\(_2\) NPs. The influences from LSPR of the Au core in optical, electrochemical, and photovoltaic properties of the photoanodes were characterized by UV-vis spectroscopy and EIS measurements separate from the effect of SiO\(_2\) shell and morphology change. From this, we demonstrated that the incorporation of the Au@SiO\(_2\) NPs enhanced the light harvesting efficiency of dye molecules without changing the electron lifetime and diffusion coefficient of the TiO\(_2\) photoanodes and were very effective in improving the power conversion efficiency of DSCs.

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