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Plasmonic effects of quantum size gold nanoparticles on dye-sensitized solar cell

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Abstract

Surface plasmonic resonance is the effect of electron oscillation in a structure stimulated by incident light. When noble materials such as Au or Ag are added into the titania structure of the sensitized solar cell, the plasmonic effect of such materials will result an improved performance of the device. Different size of plasmonic materials will produce a variety of result. Here we demonstrated the effect of extremely small size of Au nanoparticles on the performance of dye-sensitized solar cell (DSSC). In this work, Au nanoparticles with average diameter of 5 nm were mixed into commercial TiO_2 powders (average diameter 25 nm) for the fabrication of photoanode. Commercial N749 dye (black dye) was used as the sensitizer in a sandwich-type DSSC. The small size of Au nanoparticles is thought to be responsible for the plasmon resonance shift to higher energy. Inclusion of 5-nm Au nanoparticles in the titania has increased the efficiency by 50% compared to that without Au nanoparticles. The improvement was analyzed using data acquired from electrochemical impedance spectroscopy (EIS) measurements.

Keywords: Gold nanoparticles; Plasmonic; Dye-sensitized solar cell; Electrochemical impedance spectroscopy

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1. Introduction

As the global demand for energy consumption is increasing from year to year, it is crucial to ensure the continuity of the energy supply to avoid any massive energy disruption. Currently, majority of the energy supplies are from fossil fuel. The usual fossil fuel derived energy is very dependent on the supply of crude oil and coal, which are non-renewable. Fortunately, as the earth receives abundant sunlight throughout the year, it is wise to harvest such alternative resource for energy conversion and consumption. One of the direct ways of harnessing solar energy is through solar cell. The recent development of solar cell technologies has provided much hope in the renewable energy field. Some of the widely studied solar cell technologies are dye sensitized-solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSC) [1-5].

Since the introduction of DSSC in early 90's, it has created much interest in the past few years due to their ease of fabrication and low cost [1-4]. To date, the highest reported efficiency of DSSC is about 13% [6]. Recently, DSSC structure with high performing perovskite as sensitizer has emerged as a new breakthrough in the solar cells field where efficiency as high as 20% has been reported [7-9].

The main working mechanism of DSSC relies on the photon absorption by the sensitizers followed by the transfer of photogenerated electrons within the circuit. The absorption process can be enhanced with the inclusion of noble metal nanoparticles in the TiO_2 mesoporous structure. Noble materials such as Ag or Au nanoparticles are thought to enhance the photocurrents of DSSC as a result of localized surface plasmon resonance (LSPR) of the nanoparticles [10]. In general, surface plasmon resonance is the effect of electron oscillation in a structure stimulated by incident light. The effect of the LSPR on Ag or Au nanoparticles results in enhanced light absorption and scattering which ultimately enhances the performance of DSSC.

In this work, gold nanoparticles with average diameter of 5 nm were mixed into commercial TiO_2 powders (average diameter 25 nm) to produce a paste for the photoanode of DSSC. Au was selected due to its advantages as high conductor, and chemical and thermal stability [11]. Compared to Ag nanoparticles, Au nanoparticles are quite stable in iodide-based electrolyte. Commercial N749 dye (black dye) was then used as the sensitizer in a sandwich-type DSSC. Although there are few works reported on the plasmonic effect of gold nanoparticles in DSSC, such effect has not been reported on gold nanoparticles having quantum size of 5 nm or less [12]. Such small size is thought to result in plasmon resonance shift to higher energy [13].

2. Experimental

2.1. Sample preparation

Fluorine doped tin oxide (FTO) (sheet resistance 8 Ω square^{-1}, Solaronix) was used as a substrate for both photoanode and counter electrode. 0.38 M di-isopropoxytitanum bis(acetylacetonate) in ethanol was spin-coated at 3000 rpm for 10 s on the photoanode FTO. This was followed by sintering at 450°C for 30 min to form a compact layer.

TiO_2 paste was prepared from commercial TiO_2 powder (Degussa P25) by grinding 0.20 g powder with 2 ml of 1 M nitric acid, 0.10 g of polyethylene glycol and two drops of triton X-100. The paste was then spread on top of the compact layer by doctor blade method. The newly deposited layer on the FTO was sintered at 450°C for 30 min.

For samples with the inclusion of Au nanoparticles, the TiO_2 paste was added with 5 nm Au nanoparticles in suspension (Sigma-Aldrich). The amount of Au nanoparticles added are described in Section 3. The mixture was then sonicated and stirred for about 20 minutes to ensure homoegenous distribution of the Au nanoparticles within the TiO_2 particles. All the as prepared photoanodes were soaked overnight in 0.2 mM black dye (N749, Solaronix) in ethanol and acetonitrile (1:1) solution.

Solar cell assembly was prepared by sandwiching the liquid electrolyte between the sensitized TiO_2 electrode and Pt counter electrode. Counter electrode was prepared by spin coating a Pt catalyst (Solaronix) on a FTO. The Pt-coated FTO was then sintered at 450°C for 30 min. The iodide-based liquid electrolyte used was prepared from 0.6 M 3-propyl-1-methylimidazolium iodide, 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-tert-butylpyridine in acetonitrile. A parafilm spacer was used to contain the liquid electrolyte within the cell assembly.

2.2. Characterization

Black dye-sensitized TiO$_2$ electrode was characterized with Terra benchtop X-ray diffractor (XRD). Surface morphology of the photoanode was analyzed with transmission electron microscopy (TEM, Jeol JEM-2100F). Solar cells performance was measured using Keithley 2400 electrometer under illumination from a xenon lamp at the intensity of 1000 W m^{-2}. The current-voltage (*I-V*) characteristics of the cells were analyzed and the efficiency data was calculated using Equation 1.

$$\eta = \frac{J_{sc} \times V_{OC} \times FF}{P} \tag{1}$$

where J_{SC} is the short-circuit photocurrent density, V_{OC} is the open-circuit voltage, FF is the fill factor and P is the intensity density of the incident light. Measurement on each cell was repeated three times to ensure the consistency of the data. Photocurrent density-voltage (*J-V*) curves and their distribution are analyzed.

Electrochemical impedance spectroscopy (EIS) study on the cells was performed using an Autolab potentiostat/galvanostat in the frequency range from 10^6 Hz to 0.01 Hz under dark condition. Cells were biased at 0.7 V with a 15 mV RMS voltage perturbation. The acquired Nyquist plots were analyzed with ZSimWin software for curve fitting and modelling of equivalent circuits.

3. Results and discussion

Black dye-sensitized TiO$_2$ electrodes were prepared by varying the amount of wt.% of Au nanoparticles in the pristine TiO$_2$ paste. Six samples were prepared with one being a control sample. The weight ratio of Au/TiO$_2$ prepared was 0.01, 0.03, 0.05, 0.07 and 0.10. The as prepared photoanodes were characterized with XRD and TEM. For TEM analysis, excess Au nanoparticles were added into the TiO$_2$ paste in order to show the presence of Au. The XRD results and TEM images are shown in Figure 1.

Based on the TEM images, Au nanoparticles were observed to have an average size of 5 nm. In Au/TiO$_2$ samples, it was observed that tiny Au nanoparticles were scattered randomly within the larger TiO$_2$ particles. The scattering location of Au nanoparticles have certain degrees of effect on the performance of DSSC [14]. As the distance of dye molecule to Au nanoparticle increased as in the case of low concentration of nanoparticles, the plasmonic effect is suppressed. Thus, an optimum amount of Au nanoparticles is desirable [15]. On the other hand, the XRD spectra show pronouced Au peaks at 2θ of 37.5 and 45 degrees in the sample of Au/TiO$_2$:0.01 and Au/TiO$_2$:0.03. This could signify an optimum performance due to LSPR. Overall, all the samples showed the presence of Au nanoparticles in the TiO$_2$ particles.

DSSCs were fabricated and their *J-V* curves behavior were investigated. Figure 2(a) shows the *J-V* curves of all the Au/TiO$_2$ samples while Figure 2(b) shows the efficiency range obtained from three measurements. The best individual results are also tabulated in Table 1. The normal DSSC, i.e. cell without the inclusion of Au nanoparticles, achieves an efficiency of 2.09%. Its photocurrent density, J_{SC} and open circuit voltage, V_{OC} are 3.89 mA cm^{-2} and 0.745 V respectively. The measured *J-V* curve of the control sample has a fill factor, FF value of 72%. With the inclusion of Au nanoparticles in TiO$_2$ paste, the cell performance improved substantially. DSSC with Au/TiO$_2$:0.01 shows an improved efficiency of 2.97% while the best performance was obtained in the cell with Au/TiO$_2$:0.03. The best measured efficiency for such cell is 3.12%, a near 50% improvement compared with that without Au nanoparticles. The improved efficiency was largely attributed to the increased J_{SC} although there's a slight decrease in V_{OC}. This enhanced J_{SC} is a result of plasmonic effect of the 5 nm Au nanoparticles.

However, further increase of Au/TiO$_2$ ratio does not improve the cell performance. DSSCs with Au/TiO$_2$ ratio of 0.05, 0.07 and 0.10 have efficiency of 2.97%, 2.65% and 2.86%, respectively. Therefore, cell with Au/TiO$_2$:0.03 is the optimum composition in order to get the maximum plasmonic effect of the Au nanoparticles. The slight decrease of the performance with higher Au/TiO$_2$ ratio could be due to the increase recombination within the cell. Such phenomenon can be verified with EIS results.

EIS was performed in order to investigate the kinetic processes within the DSSC. An EIS spectrum for a DSSC consists of three semicircles in the Nyquist plot [16]. The three semicircles denote the responses in high-frequency,

intermediate-frequency and low-frequency regions when the solar cell is biased at its V_{OC}. Nyquist plot in the high-frequency region is attributed to the charge transfer between the electrolyte and counter electrode interface while the plot at intermediate-frequency signifies the electron transport in the dye-sensitized TiO_2 layer and the recombination process at the dye-sensitized layer and the electrolyte interface. Finally, the low-frequency arc is related to the diffusion process in the electrolyte. In some cases, the low-frequency arc will merge with the intermediate-frequency arc as a result of low-performing cell.
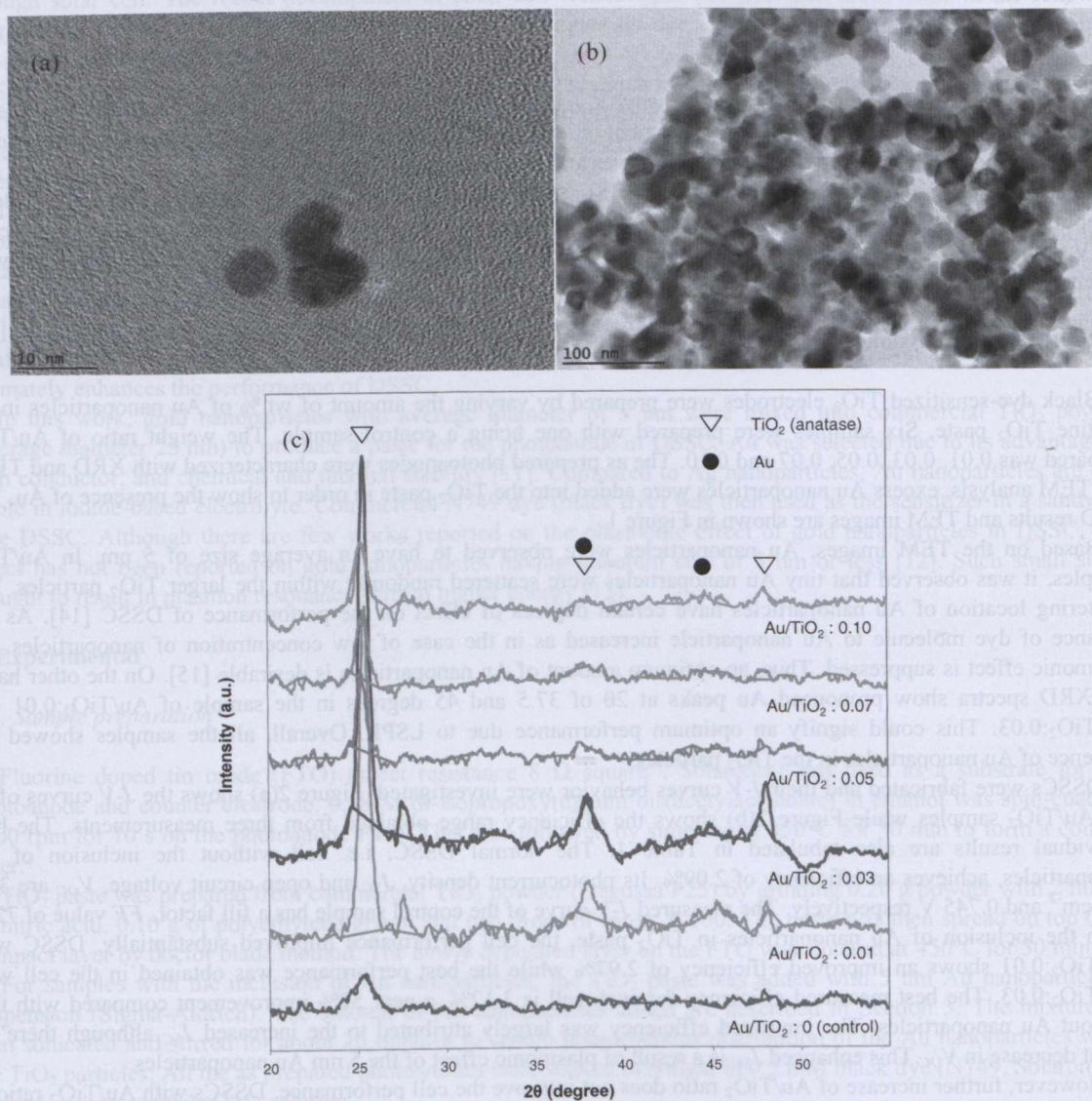

Fig. 1. (a) TEM image of Au nanoparticles; (b) TEM image of TiO_2 particles with Au nanoparticles; (c) XRD spectra of the Au/TiO_2 photoanodes with various amount of Au.
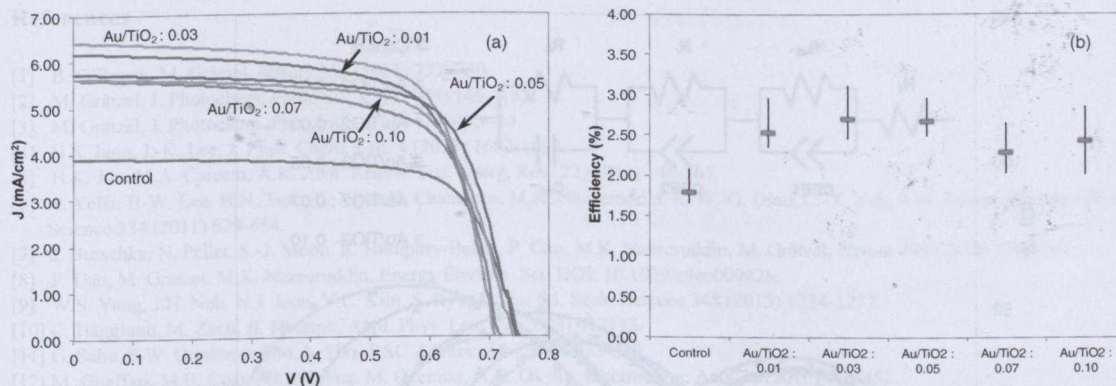
Fig. 2. (a) *J-V* curves of Au/TiO₂ DSSCs; (b) Efficiency range of Au/TiO₂ DSSCs.

Table 1. *J-V* curves and EIS results for Au/TiO₂ DSSCs.

Samples	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	Efficiency (%)	R_r (Ω)	CPE2-T (mS.s^n)	CPE2-P (0<n<1)	τ (m s)
Control	3.89	0.745	0.72	2.09	28.66	6.88	0.51	42.19
Au/TiO₂ : 0.01	6.19	0.705	0.68	2.97	32.82	9.23	0.47	78.10
Au/TiO₂ : 0.03	6.42	0.705	0.69	3.12	53.63	6.62	0.47	110.11
Au/TiO₂ : 0.05	5.74	0.740	0.70	2.97	35.56	7.57	0.51	77.50
Au/TiO₂ : 0.07	5.62	0.715	0.66	2.65	32.28	7.16	0.51	55.89
Au/TiO₂ : 0.10	5.63	0.735	0.69	2.86	35.95	6.07	0.55	64.14

The impedance data of the DSSC samples are tabulated in Table 1 while their Nyquist plots are shown in Figure 3. All the cells were measured at 0.7 V potential bias under dark. The equivalent circuit of the plots is shown in the inset of Figure 3. The circuit in a conductive state is represented by a combination of a series resistance (subscript s) and three time constants. The time constants are arranged in such a way so that the first time constant represents the first arc, and so on. Impedance at photoanode/electrolyte interface is denoted by subscript r while impedance at counter electrode/electrolyte interface is denoted by subscript CE. The symbol R and CPE represent the resistance and constant phase element, respectively.
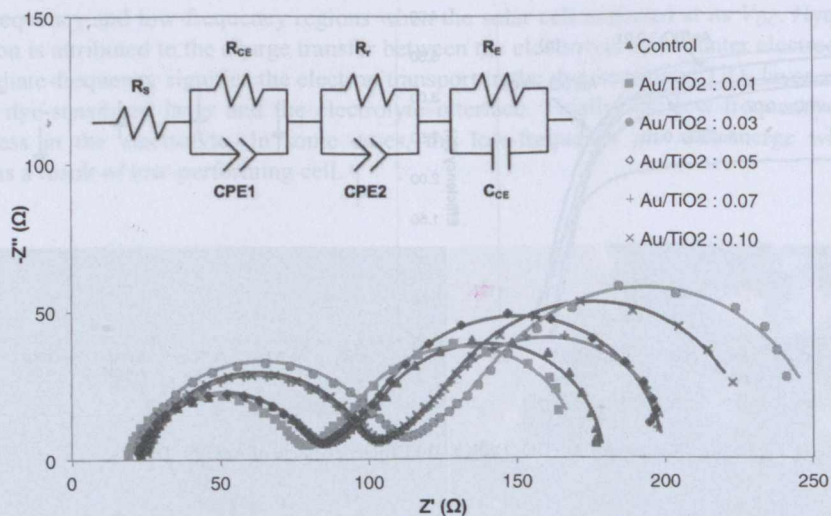
Fig. 3. Nyquist plots of Au/TiO₂ DSSC with the equivalent circuit.

In the Nyquist plots obtained, the second arc which corresponds to the electron transport and recombination process within photoanode interface was analyzed. It was observed that the recombination resistance for the control DSSC has the lowest value among the samples. In the cell with Au/TiO₂:0.01, its true capacitance increased. The same observation was obtained on the remaining cell with the inclusion of Au nanoparticles. Electron lifetime, τ which measures the electron recombination activity was calculated by incorporating the true chemical capacitance value. Higher τ value indicates delay of electron recombination at the photoanode/electrolyte interface. The best three cells with Au/TiO₂ = 0.01, 0.03, 0.05 have higher τ values as expected.On the other hand, the slightly lower performance of cells with Au/TiO₂:0.07 and Au/TiO₂:0.10 was attributed to the shorter electron lifetime. This shows that electron recombination still plays an important role when designing a high-performing DSSC.

It is also noted that our DSSC performance is slightly lower compared to that having larger Au nanoparticles within the TiO₂ particles [17]. In that work, Au nanoparticles of ~100 nm in diameter were doped into DSSCs and the cells had an improved efficiency of 3.3%. Such results may point to a better performance when Au nanoparticles size is larger than 5 nm. However, further research is needed in order to confirm this hypothesis.

4. Conclusions

Au nanoparticles with the average size of 5 nm were included in the TiO₂ paste to form the photoanodes of DSSC. Cell efficiency was improved with the inclusion of the Au nanoparticles. The efficiency was enhanced by about 50% compared to that without Au nanoparticles. The enhanced performance was largely attributed to the plasmonic effect of the Au nanoparticles. However, electron recombination at the photoanode/electrolyte interface remains a challenge as this process suppresses the performance of the DSSC.

Acknowledgements

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