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Self-ordering anodized nanotubes: Enhancing the performance by surface plasmon for dye-sensitized solar cell

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ABSTRACT

In the present work, electrochemical anodization has been used to prepare uniform TiO_2 nanotube array photoelectrode. The average internal diameter, tube length and wall thickness of the optimized morphology is ~180 nm, 14 µm and 10 nm, respectively. It was found that the tube diameter increases with the anodization voltage. Diffraction data reveals that the nanotubes consist solely of anatase phase. Back illuminated geometry of dye-sensitized solar cell (DSSC), with nanotubes grown at 60 V for 2 h, gave a cell performance of 4.5%. TiO_2 nanotubes are loaded with silver (Ag) nanoparticles synthesized by a hydrothermal route. The Ag particle size is controlled resulting in solar conversion efficiency to increase by 22%. The DSSC based on TiO_2 nanotube with Ag nanoparticles shows power conversion efficiency of 5.5%. Detailed characterization are performed, presented and discussed.

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1. Introduction

Ever since Desilvestro et al. [1] reported absorption of Rubased complex on TiO₂ electrode, a new road for solar energy conversion has been opened. Later on Grätzel and co-workers [2–4] extended this concept to make a DSSC. The reaction kinetics and thermodynamics of the solar cell play a crucial role in obtaining high conversion efficiency. The rate constant of the electron injection has to be faster than the de-excitation of the dye [5]. Also, the regeneration time for the dye has to be fast to avoid depletion effects [6]. DSSC made with nanoparticle morphology suffer from low electron transport time constants like electron diffusion coefficients, etc. [7,8]. The reason is that the transport of electron in these films is via trapping and de-trapping mechanism, leading to electron recombination via defects, surface states and grain boundaries. To overcome this problem research has now been focused on utilizing one-dimensional (1D) nanostructures for the DSSC.

1D nanostructures are expected to significantly improve electron transport due to directional electron mobility. Accelerated electron transport and lower recombination is expected, as electron motion is not limited by the random walk inside the semiconductor. Among the many 1D nanostructures, the nanotubes are especially researched. Electrochemical anodization technique of titanium metal is able to produce highly ordered

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arrays of nanotubes as a result of two competitive and continuous processes; one being oxide dissolution at the electrolyte/oxide interface, and the other being oxidation of metal at the oxide/ metal interface [9]. The advantage of this technique is that the size, length, and interval of the nanotubes can be controlled by changing the anodization conditions [10–12]. Zwilling et al. [10] first introduced the process of anodization of Ti and Ti alloys in chromic acid-HF mixture. Self-organized and vertically oriented TiO₂ nanotubes recently been applied in solar cells [13–16]. Studies done by Zhu et al. [17] demonstrated that for a pure TiO₂ nanotube system apart from tube length, the top morphology of the tubes also plays a crucial part, and an increase in solar conversion efficiency from 1.6% to 1.9% could be obtained. However, considering that the crystallographic features, diameter and length of the tubes can be tuned over a wide range [16,18-20], the structures currently used are far from being optimized for solar cell applications. Hence it is important to study the parameter response on a broader level, and even more important to extract the key factors controlling the conversion efficiency in TiO₂ nanotube based DSSC.

Apart from manipulating the semiconductor morphologies for enhancing the solar conversion efficiencies, other routes like adding scattering centers, using reflective surfaces, etc., have also being employed. Another promising concept is the use of localized surface plasmon. Ag is especially attractive due to its lower absorption and lower cost. Surface plasmon resonance when applied to solar cells increases the photocurrent response over a wide range of wavelengths [11]. Shinkai et al. [21,22] has examined the deposition of Ag and Pd nanoparticles on TiO_2 nanotubes. It is shown that resonant frequencies of the surface

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plasmon depend greatly on the particle's material, size, shape and spatial orientation [12,21,22]. The challenge in using surface plasmon resonance in solar cells relies on optimizing the geometric properties of the metallic nanoparticles to obtain a large electromagnetic field, along with having an optimum coverage that does not block off the incident light. Being a very new field especially in photovoltaic applications, the excitation of surface plasmon to increase the efficiency of DSSC is not well studied. Furthermore, plasmon enhancements for Ag nanoparticles have not been as thoroughly investigated as Au nanoparticles although Ag has four times the absorbance coefficient compared to Au [23].

Here we fabricate vertically oriented TiO₂ nanotube arrays on Ti foil with controllable diameter and length. Ethylene glycol (EG) based electrolyte is chosen for anodization due to its good performance [24,25], ease of preparation and availability of materials. The nanotubes are investigated for their potential application in liquid DSSC, where variation in the diameter of the nanotube arrays has been demonstrated to critically influence the solar conversion efficiency. Silver (Ag) nanoparticles are used with TiO₂ nanotubes to scatter the light and generate localized surface plasmonic effect. The DSSC performance is remarkably enhanced in the presence of Ag nanoparticles.

2. Experimental

2.1. Anodization of Ti foil

The electrochemical electrolyte was prepared by adding 0.25 wt% of ammonium fluoride (NH₄F, Merck 99.0%) and 1 vol% of distilled water into ethylene glycol ($C_2H_6O_2$, EG, Sigma Aldrich 99.0%). The mixture was used for anodization after aging for 24 h. Ti foil (2 mm thick, Aldrich 99.8%) was sonicated with isopropyl alcohol, methanol, and ethanol and finally dried under nitrogen stream to serve as anode. The cathode was prepared by sputtering 300 nm thick platinum layer on a glass slide. Both anode and cathode were separated by approximately 3 cm in a beaker and supported by retort stand, and attached to a programmable DC power supply. Applying varying voltages for 2 h with 10 V intervals grew the nanotubes.

2.2. Synthesis of silver (Ag) nanoparticles

1 mL of 38.8 mM tri-sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, Sigma Aldrich 99.0%) was added into 49 mL of boiling aqueous solution containing 9 mg of silver nitrate (AgNO₃, Sigma Aldrich 99.9%) under vigorous stirring. The mixture was heated until color's change is evident (pale yellow). Then it was removed from the heating element and stirred until cooled to room temperature. The as-prepared silver colloid was centrifuged at 8500 rpm for 10 min to remove larger nanoparticles. Half of the collected silver nanoparticles were dried in Memmert oven to obtain SEM images and the other half were suspended in distilled water to be implemented in DSSC. Concentration of sodium citrate was varied between 20–80 mM to study its effect on the silver nanoparticles size. Other parameters such as reaction temperature and reaction time were also varied.

2.3. DSSC assembly

The photoanode with nanotubes was annealed at 450 °C for 30 min at a ramp rate of 5 °C min⁻¹ in nitrogen ambience in Carbolite CWF1200 burn-off furnace. The suspension of Ag nanoparticles was spin coated on the nanotube film at 1500 rpm for 40 s. Adsorption of the dye to the photoanode is achieved by immersion in an ethanolic solution containing 0.3 mM Ru-dye,

(cis-dithiocyanate-N,N'-bis(4-carboxylate-4 tetrabutyl ammoniumcarboxylate-2,2'-bipyridine) ruthenium(II) (known as N719, Solaronix), for 24 h at room temperature. This results in the conformal adsorption of the dye monolayer to the film surface. The films were subsequently rinsed with ethanol and dried. To prepare the counter electrode, a hole was drilled in the FTO glass by sand blasting. The perforated sheet was washed with ethanol and DI water. Then 20 nm thick Pt layer is sputtered on the FTO. The dye-covered electrode and Pt-counter electrode were assembled into a sandwich type cell. A drop of the electrolyte, solution containing 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in acetonitrile, was put on the hole in the back of the counter electrode. The electrolyte was introduced into the cell via vacuum backfilling. Finally, the hole was sealed with a hot-melt gasket made of the ionomer Surlyn (Dupont).

2.4. Analysis techniques

The morphology of synthesized TiO₂ films is examined with a JEOL-2100 high-resolution transmission electron microscope (HRTEM) with an accelerating voltage of 200 kV and with a JEOL FEG JSM 6700F field-emission scanning electron microscope (FESEM) operating at 10 kV. Film thickness is determined with Ambios Technology XP 200 profilometer. Structural characterization of the synthesized morphology is obtained by means of X-ray diffraction (XRD) on Philips X-ray diffractometer with CuK α radiation. The photocurrent–voltage of the samples are measured with a solar simulator (Newport 91160A) equipped with an AM filter and a 150 W Xe lamp as the light source. The solar cells are tested at 25 °C with source meter (Keithley 2420) using Newport IV test station software. The light intensity corresponding to AM 1.5 (100 mW cm⁻²) is calibrated using a standard silicon solar cell (Oriel, SRC-1000-TC).

3. Results and discussion

Fig. 1 shows the morphology of the nanotubes obtained at different anodization voltages for 2 h. Below 20 V no growth of nanotubes is observed. When anodization is carried out at 20 V, nanotubes of \sim 30 nm diameter are formed, but the growth is not uniform (Fig. 1a). The nanotubes are not fully formed and broken tops can be observed. Also the tube length is seen to vary across the sample indicating that the anodization is not uniform throughout the foil. Fig. 1b and c shows the FESEM image of the TiO₂ nanotube array grown at 30 and 40 V, respectively. It can be seen that the diameter of nanotubes increases as the anodization voltage increases. Fig. 1d shows the top view of the nanotubes grown by anodization at 60 V for 2 h. The TiO₂ nanotubes in the array have similar length ($\sim 14 \,\mu m$), internal diameter $(\sim 180 \text{ nm})$ and wall thickness $(\sim 10 \text{ nm})$. The tubes are uniform and compact as revealed by the tilted view of FESEM (Fig. 1e). Such a compact packing of the arrays can reduce the contact between Ti foil and electrolyte, which is considered vital to suppress the dark current in the DSSC [26]. The TiO₂ nanotubes grow vertical to the Ti foil, featuring highly parallel 1D nanostructure. The inset shows that the exterior walls are relatively smooth and continuous. Fig. 1f is the TEM image of bunch of closely packed nanotubes annealed at 450 °C for 30 min. The dark areas may result from either varying crystalline density or due to overlap of nanotubes. The broken edges of the nanotubes arise during the sample preparation for TEM. The parameters of the nanotubes are summarized in Table 1.

Despite the substantial changes in the nanotube diameter, it is noteworthy that the overall nanotube architecture is retained

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Fig. 1. SEM images of TiO₂ nanotubes grown for 2 h at different voltages: (a) 20, (b) 30, (c) 40 and (d) 60 V. (e) Tilted SEM view and (f) TEM image of nanotubes grown at 60 V for 2 h. Inset shows the high magnification SEM and TEM image of the TiO₂ nanotubes. *D* and *L* on the SEM images indicate diameter and length of the nanotubes.

 Table 1

 Photovoltaic characteristic of TiO2 nanotubes grown at different anodization voltages.

Anodization voltage (V)	Tube diameter (nm)	Tube length (μm)	DSSC efficiency (%)	Fill factor (%)	J _{sc} (mA cm ⁻²)	V _{oc} (V)
20	30.0	2.0	0.2	64.4	0.6	0.50
30	40.0	3.0	1.0	53.8	3.0	0.62
40	60.0	3.7	2.3	58.0	7.0	0.58
60	180.0	14.0	4.5	68.2	10.6	0.62

over the entire anodization voltage range. Fig. 2a displays the trend of nanotube growth with the anodization voltage. Nanotube diameters seem to obey power law dependence from 30 to 60 V. TiO_2 nanotubes are well aligned and no change is the alignment is observed when the applied voltage is varied. Also the nanotubes produced using higher anodization voltages are much straighter and have rough surface. This may be ascribed to the slower chemical dissolution rate of the anodic reaction, which leads to formation of straight-line tubes in stable sites. The lower anodization voltages produce nanotubes by fast chemical dissolution process, which leads to smother tube surface because there is

insufficient time for the nanotubes to grow on stable sites of Ti foil. Fig. 2b plots the curve of current-density, with respect to time in the initial anodization state. The steady state growth of nanotubes starts from stage "A", as marked in figure. Considerable current fluctuations could arise from the suppressed heat transfer around the electrodes in ethylene glycol solution. As seen from the graph the anodization starts off with a relatively high current-density. This is because there is no barrier layer present to inhibit the current flow. However, the current decreases sharply due to formation of the oxide layer. The initial oxide layer persists only for few seconds at the beginning and thereafter the formation of oxide bundle occurs. Thus, the drop in the current is both due to the formation of compact oxide layer and the formation of oxide bundles on the surface, after which the bundles begin to disperse in the electrolyte. As anodization proceeds, the conductivity of the electrolyte increases causing the applied anodization potential to shift away from the electrolyte towards the oxide layer. With a larger electric field across the oxide layer, the oxide starts to form more rapidly, thus causing the current-density to rise to a maximum value, which is represented by the peak around 500 s. The current then begins to drop to a rate of oxide formation, which is determined by rate of field-assisted oxide growth, field-assisted dissolution and

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Fig. 2. (a) Graph showing variation of TiO₂ nanotube diameter and length with anodization voltage, (b) current-density graph of anodization process and (c) XRD spectrum of TiO₂ nanotubes at 60 V, 2 h.



Fig. 3. J-V curve for the DSSC made with TiO₂ nanotubes grown at different anodization voltages.

chemical etching. The as-prepared TiO₂ nanotube arrays are amorphous after anodization. As the TiO₂ nanotubes have been heat-treated they possess polycrystalline nature. This is confirmed by XRD analysis (Fig. 2c). The presence of peak at 25.45° in XRD pattern indicates that the calcined nanotubes are composed of pure anatase phase (JCPDS file no. 21-1272). Good crystallinity is required for smooth electron flow in the nanotubes for an efficient DSSC. Annealing TiO₂ nanotubes at 450 °C does not lead to single crystalline material but forms very large grains. These grain sizes are considerably larger than that observed for Grätzel nanoparticles [27] and therefore higher electron mobility can be expected for nanotubes.

Fig. 3 shows the *J*–*V* results and for the DSSC assembled with the different photoanodes. Detailed photovoltaic performance parameters are presented in Table 1. It can be observed that as the tube diameter increases the conversion efficiency of the DSSC

increases. As discussed earlier with low anodization voltage the nanotube growth is not uniform, which leads to low solar conversion efficiency. With application of higher voltages (50-60 V) the nanotubes are longer, bigger in diameter and more uniform. The longer and larger diameter nanotubes help in better dye wetting and also may lead to higher surface area, which eventually leads to higher solar conversion efficiency. Also longer TiO₂ nanotubes are better able to scatter light, which may also contribute towards better performance of these tubes in DSSC. The length of the nanotubes can be tuned from 2 to $14 \,\mu\text{m}$ by simply increasing the anodization voltage from 20 to 60 V, which is accompanied with increase in internal diameter (30-180 nm). The fill factor (FF), however, decreases first and then gradually rises with the anodization voltage. The initial decrease in FF may be due to a thicker barrier layer that forms at higher voltages, thus increasing the series resistance of the DSSC. The V_{oc} is slightly lower for 20 and 40 V nanotubes. The lower V_{oc} may be ascribed to the higher series resistance and higher number of recombination centers present for the tubes. Consistent with reported literature the internal quantum efficiency of the DSSC increases with the increase in tube length [28–30]. With increase in the tube length with anodization voltage, the tube thickness also increases. This in turn increases the surface area and helps to absorb more dye on the TiO₂ nanotubes, leading to better light harvesting. The nanotubes grown at 60 V for 2 h shows the best solar conversion efficiency and are used to incorporate Ag nanoparticles.

In metal nanoparticles, collective electron oscillations known as surface plasmons can be excited by light. When light is impinged on the localized surface plasmon on the metal nanoparticle surface, the irradiated light is scattered and absorbed on the surface. This results in an evanescent wave with a strong electromagnetic field to be generated on the metal nanoparticle surface. This wave remains localized on the surface at a distance less than the diameter of the metal nanoparticle. Localized surface plasmon enhances the optical phenomenon such as Raman scattering and light absorption, and the level of enhancement strongly depends on the material and the surface states [31]. Stuart and Hall [32] did pioneering work in enhancing efficiency of light sensitive devices by plasmon. When the particle is under the action of an electromagnetic (EM) field, its electron start to oscillate, transforming energy from the incident EM wave into another form of energy. The electrons can also be accelerated, and then they radiate energy in a scattering process. Mainly two mechanisms are proposed to explain the photocurrent enhancement by metal particles in solar cells: light scattering and nearfield concentration of light. The contribution of each mechanism and resonance frequency of the oscillations is determined by the dielectric properties, shape and size of the metal nanoparticles. The research done here is to obtain spherical silver nanoparticles with different dimensions. The SEM images of the synthesized Ag nanoparticles are shown in Fig. 4. Concentration of tri-sodium citrate is varied to obtain nanoparticles of different sizes. Citrate acts as stabilizing agent after silver nanoparticles are formed [33]. For 20 mM tri-sodium citrate the average diameter of 105 nm is obtained with almost spherical nanoparticles (Fig. 4a). The diameter increases to 115 nm for 40 mM tri-sodium citrate (Fig. 4b). For higher concentration of tri-sodium citrate, the diameter of nanoparticles tends to decrease. For 60 and 80 mM concentrations the nanoparticle diameter is \sim 87 and 85 nm, respectively (Fig. 4c and d). For 80 mM the nanoparticles are elongated in shape and agglomeration is observed. The variation of diameter with the concentration of sodium citrate is plotted in graph 4e. The reaction time of the synthesis process for Ag nanoparticles is also varied (Fig. 4f). The time is varied from 0.5 to 2 h keeping the temperature and tri-sodium citrate concentration fixed at 90 °C and 40 mM, respectively. The Ag nanoparticles are relatively larger for reaction time of 0.5 and 2 h. it is to be noted that when size of the metal particle becomes large (> 50 nm), the radiation effects becomes more and more important [34]. The displacement of the electronic cloud is no longer homogenous even for spherical particles. Thus high multipolar charge distributions are induced [34].

UV-vis absorbance is measured for synthesized Ag nanoparticles (Fig. 5a). Ag nanoparticles exhibit intense absorption peaks due to the surface Plasmon excitation [35]. The absorption band in visible region (400-550) is typical for Ag nanoparticles. It can be observed that as the particle size increases (for 40 and 80 mM samples) the absorption peak shifts towards the red wavelength [36]. Larger particles exhibit more scattering and re-radiation, leading to radiative damping correction. The overall effect is broadened plasmon resonance [37]. For larger particles the accelerated electrons produce an additional polarization field that depends on the ratio between the size of the particles and the wavelength of the incident light [37]. This secondary radiation causes electrons to lose energy and they experience a damping effect, which makes the surface plasmon resonance wider, as observed for the Ag nanoparticles. The peak for 80 mM sample is much broader than others. This broadening could be attributed to the clusters of nanoparticles (Fig. 4d).

Fig. 5b and Table 2 illustrates the relation between the size of Ag nanoaprticles and their DSSC performance. The measurements



Fig. 4. SEM images of Ag nanoparticles grown at different sodium citrate concentrations: (a) 20, (b) 40, (c) 60 and (d) 80 mM. *D* signifies the diameter range of the nanoparticles. Size variation of Ag nanoparticles with (e) concentration of sodium citrate and (f) reaction time.

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Fig. 5. (a) Normalized UV–vis absorbance spectra of Ag nanoparticles synthesized using different concentrations of sodium citrate. (b) *J–V* curve for DSSC decorated with different concentrations of Ag nanoparticles. Inset shows the energy levels of DSSC components.

Table 2

Photovoltaic characteristic of $\rm TiO_2$ nanotubes grown at 60 V for 2 h and loaded with different Ag nanoparticles.

Sodium citrate concentration (mM)	Ag nanoparticle diameter (nm)	DSSC efficiency (%)	Fill factor (%)	J _{sc} (mA cm ⁻²)	V _{oc} (V)
0	_	4.5	68.2	10.6	0.62
20	90-100	3.6	64.2	8.6	0.65
40	100-120	4.5	68.3	10.5	0.62
60	70-80	5.5	68.8	11.6	0.69
80	90-140	3.1	64.2	7.2	0.65

are made under AM 1.5 simulated sunlight. Particles grown using 40 mM tri-sodium citrate concentration (diameter ~115 nm) show low J_{sc} . This may be because the particle size is big to show any surface plasmonic effect. Ag nanoparticles with 20 mM concentration (~105 nm) also show low J_{sc} , as the particles are agglomeration. 60 mM Ag nanoparticles when used for DSSC showed the best efficiency due to better dispersion and surface Plasmon effect. The DSSC efficiency decreased again as the concentration of sodium citrate is increased to 80 mM, due to formation of some rod like structures along with nanoparticles. These rods may lower the effective surface of the Ag nanoparticles leading to lower dye absorption and lesser scattering effect. The DSSC using 60 mM Ag nanoparticles appears to have the largest improvements in J-V characteristics compared to the other cells. This can be explained by the higher coverage of Ag nanoparticles

on the DSSC surface, resulting in higher plasmon resonance effect that enhances the electric field around the particles, increasing the effective molecular absorbance of the dye. The V_{oc} , in general, shows a negative shift as the Ag nanoparticles decreases in size. For small Ag nanoparticles, the V_{oc} adopts more negative potential; whereas bigger Ag particles take up more positive potentials. The magnitude of V_{oc} generally decreases with increasing Ag nanoparticle size, except for 80 mM nanoparticles. The larger photovoltage (\sim 0.69 V) for DSSC with 60 mM Ag nanoparticles suggest more negative Fermi-levels in the photoanode film. This is consistent with the results obtained by Kamat [38], whose previous studies showed that noble metal or metal ion doped semiconductor nanocomposites exhibit negative shifts in their Fermi levels compared to the pure semiconductor. By shifting the Fermi level closer to the conduction band, the semiconductor film facilitates charge rectification and improves the conversion efficiency. It is to be noted that the performance of DSSC without Ag nanoparticles and with 40 mM is almost the same. This may point out to the fact that large nanoparticles (> 100 nm) may not show any surface plasmon resonance and their effect is same as putting no nanoparticles at all. DSSC made with only TiO₂ nanotube photoanode yields a solar conversion efficiency of \sim 4.5% with I_{sc} of $\sim 10.6 \text{ mA cm}^{-2}$. When 60 mM Ag nanoparticles are added on top of TiO₂ nanotubes, the J_{sc} increases to 11.6 mA cm⁻² leading to conversion efficiency of 5.5%.

Surface plasmonic effect plays a major role in enhancing the solar power conversion efficiency of the DSSC. It can be safely said that the absorption coefficient of the DSSC increases by localized surface plasmon of Ag nanoparticles, which in turn increases the number of photoelectrons generated. The scattering of light and the evanescent wave with a strong electromagnetic field are considered localized surface plasmon effects in DSSC. When exposed to light, the surface of each Ag nanoparticle produces a strong local magnetic field due to large absorption coefficient of the Ag surface plasmon. The large size of Ag nanoparticles (> 50 nm) may also lead to scattering of light, which may increase the absorption of sunlight by the DSSC. Enhanced scattering will increase the I_{sc} due to increase in optical path lengths, thus leading to higher efficiency.

4. Conclusion

Optimization of TiO₂ nanotubes is carried out by varying the electrochemical anodization conditions voltage. It is found that the performance of the solar cell strongly depends on the morphology and structure of the nanotubes. DSSC with an overall conversion efficiency of 4.5% are obtained for nanotubes of 180 nm internal diameter and 14 μ m length. Further increase in cell performance is achieved using surface plasmon resonance effect by Ag nanoparticles. Spherical Ag nanoparticles with 87 nm diameter show the highest solar conversion efficiency of 5.5%. This significant improvement in efficiency is attributed to the enhanced plasmonic effect and scattering mechanism in the cell.

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