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Novel Application of Platinum Ink for Counter Electrode Preparation in Dye Sensitized Solar Cells

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Platinized counter electrode is common in most of the dye sensitized solar cell (DSSC) researches because of its high catalytic activity and corrosion stability against iodine in the electrolyte. Platinum (Pt) film coating on fluorine doped tin oxide (FTO) glass surface by using alcoholic solution of hexachloroplatinic acid (H_2PtCl_6), paste containing Pt precursors or sputtering are widely used techniques. This paper presents a novel application of Pt ink containing nanoparticles for making platinized counter electrode for DSSC. The characteristics of Pt films coated on FTO glass surface by different chemical methods were compared along with the performance parameters of the DSSCs made by using the films as counter electrodes. The samples coated with Pt inks were sintered at 300 ºC for 30 minutes whereas Pt-film and Pt-paste were sintered at 400 ºC for 30 minutes. The Pt ink diluted in *n*-hexane was found to a promising candidate for the preparation of platinized counter electrode. The ink may also be applicable for DSSC on flexible substrates after optimization its sintering temperature.

Key Words : Dye sensitized solar cell, Counter electrode, Nanoparticles, Platinum, Conversion efficiency

Introduction

In order to make dye sensitized solar cells (DSSC) a cost competitive source of power, a few studies of the electrocatalytic characteristics of the counter electrode have already been carried out.[1-9] The standard catalyst on the counter electrode found in most of the research publications on DSSC is platinum because of its high catalytic activity and high corrosion stability against iodine in the electrolyte.[10] As a precious metal, Pt is subject to price variations. A few nanometer thick layer of Pt is required to fabricate an efficient DSSC, which keeps the cell manufacturing costs low even if platinum is an expensive element. Platinum is also chemically stable in the electrolyte due to which no remarkable dissolution of Pt from the counter electrode has been noticed over the time. Conventional counter electrodes of DSSCs were prepared by methods such as electrochemical deposition, sputtering and thermal decomposition.[11] Conventional counter electrodes of DSSCs prepared by the methods such as electrochemical deposition and sputtering have the higher platinum loadings due to which they are not suitable for the low cost approach for the fabrication of DSSCs. Thermally deposited platinum (Pt) on fluorine doped tin oxide (FTO) glass surface is the most widely used counter electrode for DSSC. As a simple method, an alcoholic solution of hexachloroplatinic acid (H_2PtCl_6) is spread on the FTO glass surface followed by sintering at 400 ºC for 30 minutes that evaporates the solvent and ensures the Pt coating on the surface of the substrate by thermal decomposition of the acid. This process involves the reduction of metallic platinum as tightly adhered nanoscale clusters on the substrate surface. DSSCs with conversion efficiencies greater than 11% also employ Pt as a catalyst for the counter electrode.[12-14] However, the high temperature involved in the process of thermal decomposition makes this method unsuitable for flexible substrates. Since platinum is an expensive catalyst, other materials such as nanostructured and/or activated carbon and conducting polymers such as PEDOT or PANI (polyaniline) have been studied as its replacement.[10] Very thick layers of such materials are needed in order to reach high enough catalytic activity, which ultimately slows down the cell manufacturing process and hence increases the fabrication cost. Also such cells have conversion efficiency relatively low compared to a cell with a Pt counter electrode. Interest in nanoparticles of materials increased in recent years with the realization that unique properties may be obtained from otherwise ordinary materials. Colloidal metal particles are of interest because of their use as catalysts, photocatalysts, adsorbent and sensors and application also in optical, electronic and magnetic devices. Nanostructured materials promise unique properties with potential applications in a wide range of technologies including advanced ceramics, electronics, catalysis, sensors, *etc*. The catalytic reactivity depends on size and shape of nanoparticles and therefore synthesis of controlled shapes and size of colloidal platinum particles could be critical for these applications.[15] This paper reports the novel application of platinum ink for the counter electrode preparation in DSSC. Two types of platinum inks were synthesized at Advanced Nano Products Co. Ltd., South Korea and used for this study in conjunction with other materials too for the Pt film coating on FTO glass surface for DSSC fabrication. The first Pt ink (Pt ink-thick) was prepared with Pt nanoparticles in terpineol base having metal content of 4 wt % whereas the second type of ink (Pt ink-thin) was prepared by diluting the first ink sufficiently with *n*-hexane so that its viscosity got reduced and the resulting metal content of the ink went as low as 0.05 wt %. Counter electrode preparation by using such a platinum ink

containing nanoparticles could be instrumental in materializing low cost approach for the fabrication of DSSCs on FTO glass surface as well on flexible substrates. A comparative study of the properties of different types of chemically prepared platinized counter electrodes for their application in DSSC has been reported in this article along with the performance parameters of the DSSCs thus fabricated.

Experimental

Platinum Nanoparticles and Ink. The platinum inks used for this study were the Commercial product of Advanced Nano Products Co. Ltd, South Korea. The solid content of the original ink was 40%, which was diluted to make 4% and further diluted in *n*-hexane to make it 0.05% to be used as Pt ink-thick and Pt ink-thin, respectively. The Pt nanoparticles in the ink were subjected to Transmission Electron Microscopy (TEM) to determine the size of the primary particles. Colloid containing the platinum nanoparticles was also studied under Particle Size Analyzer to determine the distribution of the size of the nanoparticles in the ink.

Preparation and Characterization of Counter Electrodes. The FTO glass pieces of dimensions 1.5 cm × 1.5 cm × 0.22 cm were first cleaned with DI water followed by cleaning with a mixture of ethanol and acetone in an ultrasonic bath and drying under dry air jet. The FTO coated surfaces of the samples were coated with alcoholic solution of H_2PtCl_6, Pt-paste, Pt ink-thin and Pt ink-thick by spin coating or doctor blading depending upon the suitability of the process. The samples coated with Pt inks of both types were sintered at 300 °C for 30 minutes whereas other samples were sintered at 400 °C for 30 minutes. All the samples were then subjected to sheet resistance measurement with four point probe, UV-Visible transmittance measurement with spectrophotometer and surface morphology observation with Scanning Electron Microscope (SEM). A clean piece of FTO glass was also subjected to each characterization along with Pt coated samples for comparative analysis. For the fabrication of DSSC using all the characterized types of FTO glass surfaces coated with Pt film as counter electrodes, two holes were drilled on the back side of each piece of FTO glass of dimensions 1.5 cm × 1.5 cm × 0.22 cm for the injection of electrolyte. After different types of Pt film coating on each of the perforated FTO glass surfaces, the samples were used as counter electrodes for DSSCs fabrication.

DSSC Fabrication and Characterization. The materials other than the TiO_2 paste and Plantinum inks used for this study were obtained from market as commercial products. FTO coated glass of sheet resistance ~10 Ω/sq and dimensions 30 cm × 30 cm × 0.22 cm was cut into smaller pieces of dimensions 1.5 cm × 1.5 cm × 0.22 cm to be used as substrates for both electrodes in DSSC. For the preparation of the nanoporous photoelectrodes, TiO_2 paste was cast on the FTO glass surfaces by doctor blading. The area for casting the paste on the FTO glass surface was defined by guider made by using 3 M Scotch tape of two layers. The TiO_2 films were then sintered in a muffle furnace at 500 °C for 30 minutes, which was followed by soaking of the films in N 719 dye for 24 h. The counter electrodes of FTO glass surface coated with Pt catalyst using different methods and the photoelectrodes of FTO glass surfaces coated with porous TiO_2 film were assembled into sandwich type cells and sealed with thermoplastics of thickness ~50 mm. A drop of electrolyte, Iodolyte AN-50 (Solaronix), was injected into the sealed space between two electrodes through a hole on the back of the counter electrode of each cell. Finally, the holes were sealed using pieces of thermoplastics (Surlyn, t = 50 μm) and cover glass to avoid loss electrolyte by evaporation. The DSSCs fabricated by following the processing sequence were characterized under Global solar spectrum of AM 1.5 to study the illuminated current density-voltage (J-V) characteristics and extract performance parameters of all the cells fabricated by using counter electrodes platinized with different techniques. A DSSC was also fabricated and characterized using bare FTO glass surface as counter electrode for comparison. The performance parameters of all the DSSCs fabricated in the same lot were used for comparative analysis.

Results and Discussion

Size of synthesized platinum nanoparticles was measured with TEM as shown in Figure 1. The micrograph clearly shows that the size of primary particles of Pt ranges from ~3 to 5 nm. For every practical purpose it is difficult to make size of primary particles effective because the particles of such a small scale have tendency of aggregation. The effective size distribution of the Pt nanoparticles available in the Pt ink was determined by taking colloidal solution of Pt nanoparticles in a particle size analyzer as shown in Figure 2. It shows that the size of the nanoparticles in the colloid is distributed in the range of ~6 to 15 nm. The average size of the nanoparticles was calculated to be 9.6 nm in the colloidal solution. Smaller the particle size larger becomes the effective surface area of the nanoparticles and such larger surface area of the particles enhances the catalytic action of the Pt in the counter electrode of DSSC. Since the mesoporous photoelectrode contains TiO_2 nanoparticles of size ~20 nm, the

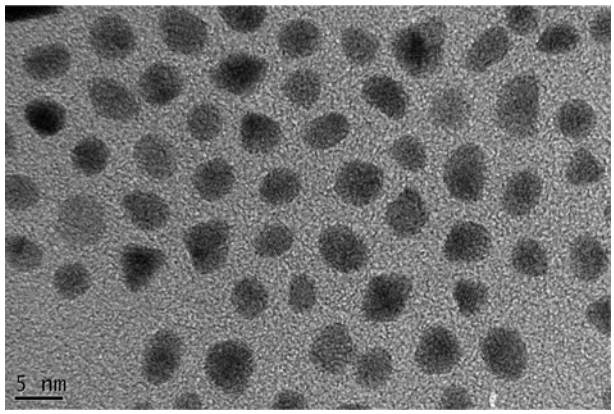

Figure 1. TEM micrograph of the Platinum nanoparticles used for the preparation of the Pt ink.

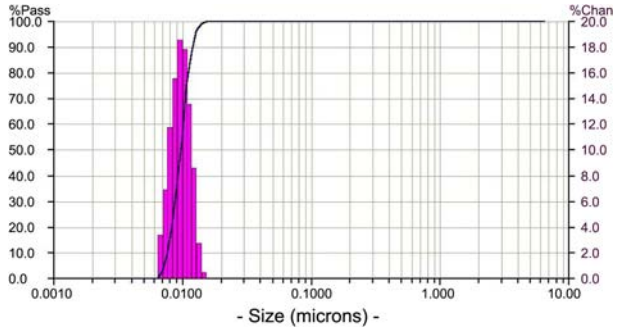

Figure 2. Distribution of size of the nanoparticles in the Pt ink as observed through particle size analyzer.

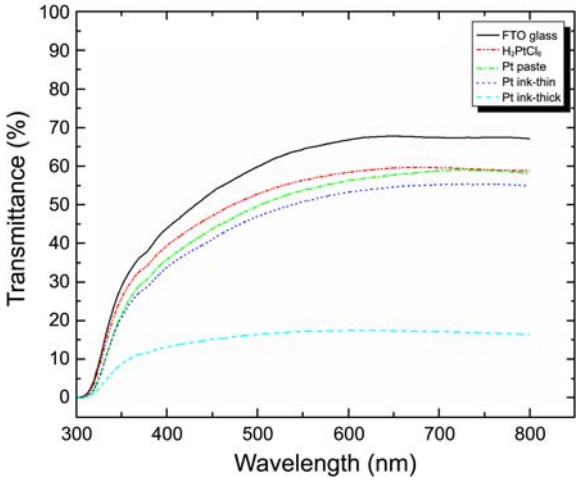

Figure 3. Comparison of the UV-Vis Transmittance of FTO glass surfaces with and without Pt films coated by using different methods.

porosity of the Pt film containing nanoparticles of size ~10 nm could be a good choice. Counter electrode of a well-operating DSSC should have good electrical conductivity for transferring electrons, excellent catalytic activity for triiodide reduction, and poor light transmission characteristics to improve light harvesting efficiency. However, electrical conductivity and the catalytic activity of the counter electrodes are the two factors that mostly influence the performances of the DSSCs composed of the counter electrodes of porous Pt films.

Figure 3 shows the comparison of Transmittances of the FTO glass surfaces with and without Pt coating of different types. There is a significant difference in the transmittance of the bare FTO glass surface and that with Pt film made out of Pt ink-thick. The film of Pt ink-thick on FTO glass has average transmittance of 14.66% in the wavelength range of 300-800 nm due to which it can be the most suitable to trap the light that would have otherwise been transmitted through the counter electrode. Similarly, the Pt films made with H_2PtCl_6 solution, Pt-paste and Pt ink-thin on FTO glass surfaces show the average transmittance of 48.56%, 46.31% and 43.74%, respectively in the same range of wavelength. Out of the three films, the Pt film made with Pt ink-thin has an advantage of blocking light in a more effective way. SEM micrographs with surface morphologies of a bare FTO glass

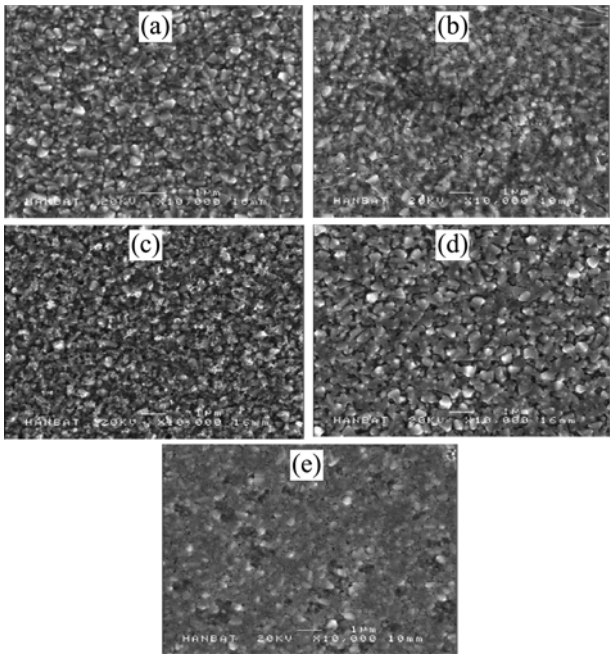

Figure 4. Comparison of the morphology of the FTO glass surfaces with and without different types of Pt films through SEM micrographs.

and the counter electrodes with Pt films of different types can be seen in Figure 4. The bare FTO glass with scale-like rough structure on its surface due to the fluorine-doped tin oxide (SnO_2:F) layer coated on the glass sheet is shown in the Figure 4(a) whereas the Figure 4(b) shows the micrograph of the FTO glass surface coated with the Pt film by using alcoholic solution of H_2PtCl_6. It clearly shows that the FTO glass surface is not uniformly covered with Pt film. The film seems to be thicker with no porosity in some places on FTO glass surface whereas some areas have a very thin or no Pt film at all. Similarly, Figure 4(c) shows the surface morphology of the counter electrode platinized with Pt-paste. The uniformly distributed clusters of platinum particles seem to have poor interconnection as a result of which it may be good enough for catalytic action of platinum at the counter electrode but not suitable in terms for electrical conductivity. Figures 4(d) and (e) show the surface morphologies of the platinized counter electrodes prepared by using Pt ink-thin and Pt ink-thick, respectively. The platinum film, as seen in Figure 4(d) has uniformly distributed pores and good interconnection between the platinum nanoparticles. This film can have a proper balance between catalytic effect of platinum at the counter electrode and good electrical conductivity for the transfer of charge.

Also the transmittance of the film, as shown in Figure 3, indicates its superiority over the Pt films prepared by using Pt-paste and H_2PtCl_6 solution. The morphology of the platinized FTO glass surface as shown in Figure 4(e) is good in terms of uniformity and adhesion of the film with the substrate and hence can have high electrical conductivity because it exhibits excellent interconnection between the clusters of Pt particles. However, the film does not show

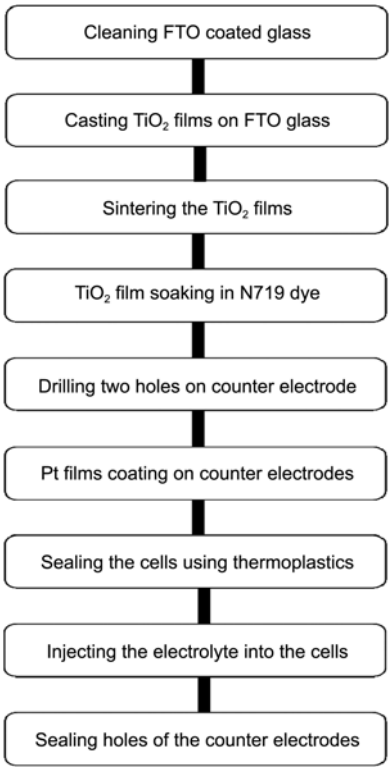

Figure 5. Processing sequence of Dye Sensitized Solar Cells using counter electrode of FTO glass surfaces coated with Pt films prepared by using Pt inks as well as other materials.

required level of porosity due to which the effective surface area of the film available for the transfer of charge to electrolyte becomes smaller. The rate-determining step of the counter electrode is the oxidation of iodide at the Pt surface due to which low surface area of the Pt clusters in the thick film results in poor catalytic effect of the film. This ultimately increases charge transfer resistance of the film. The variation of the sheet resistance (R_{sheet}) of counter electrodes with and without Pt films of different types is clearly depicted in Table 1. The R_{sheet} of counter electrode decreases as Pt film thickness increases. The R_{sheet} values of counter electrodes from Pt ink-thin, Pt paste, and Pt film are within experimental error range. However the R_{sheet} value of counter electrodes from Pt ink-thick is the smallest. Also, the R_{sheet} of the counter electrode decreases with the improvement in interconnection between the clusters of Pt nanoparticles in the film. The effect of Pt film thickness on the performance of DSSC has been studied elsewhere.[7] The electrical onductivities of different platinized FTO glass surfaces, as shown in Table 1, clearly follow the trend of interconnection of the clusters of Pt particles in the film as manifested by the micrographs of Figure 4. Better the interconnection between the clusters of Pt particles in the Pt film higher will be its electrical conductivity. Figure 5 shows the processing sequence followed for the fabrication of DSSCs using all types of platinized counter electrodes. This study was meant for novel application of Pt ink for the counter electrode preparation for DSSC by comparing the results with other conventional methods of plantinizing counter electrodes. Therefore, no additional steps were introduced in the processing sequence for high efficiency approach. The J-V characteristics curve along with the performance parameters of a representative DSSC fabricated by using counter electrode platinized with Pt ink-thin is shown in Figure 6. High fill factor of the cell indicates the effective role of Pt film as the counter electrode of the DSSC. Comparative analysis of performance parameters of all the DSSCs fabricated by using different types of platinized counter electrodes are presented in Figure 7. However, performance parameters of the DSSC fabricated by using bare FTO glass did not show comparable values due to lack of catalytic activity of the bare FTO glass for triiodide reduction, which is attributed to the very large charge transfer resistance at the interface of an FTO glass and the electrolyte. It can be seen that all the performance parameters of the DSSC fabricated by using the counter electrode platinized with Pt ink-thin are superior to that of other cells. The values of open circuit voltage (V_{oc}) and fill factor (FF) of the DSSC are as high as ~694 mV and ~70%, respectively. As the charge-transfer resistance influences the fill factor of the DSSC, the platinized counter electrode must have least charge transfer resistance among all the DSSCs fabricated. By optimizing the Dye coated porous film of TiO_2 nanoparticles with the application of the additional layers such as Blocking and Scattering layers, an appreciable enhancement in the values of the short-circuit current density (J_{sc}) as well as conversion efficiency (CE) of the DSSC can be achieved with this counter electrode.

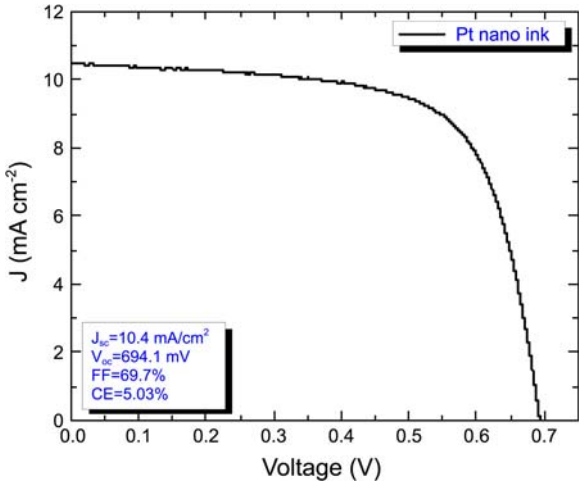

Figure 6. Current density-Voltage characteristics and performance parameters of a representative DSSC fabricated by using the counter electrode having catalytic layer of platinum deposited by using thin ink containing Pt nanoparticles.

Despite all the encouraging characteristics of the film of thick Pt-ink, all the performance parameters of the DSSC made by using the film as counter electrode are inferior to that of the DSSCs with counter electrodes platinized by using Pt ink-thin as well as Pt-paste. This is mainly attributed to its poor catalytic activity due to low porosity in the film. Porosity declines with the in the size of the Pt particles aggregates in the film. Therefore, there is no advantage of using Pt ink-thick for DSSC fabrication as it could be

Table 1. Comparison of sheet resistance of the FTO glass surface coated with Pt by different methods

S.N.	Type of Pt Coating on FTO Glass	R_{sheet} (Ω/sq)
1	Pt ink-thick	6.15
2	Pt ink-thin	8.08
3	Pt paste	8.16
4	H_2PtCl_6	8.44
5	Without coating	10.05

costlier than Pt ink-thin. In the case of the DSSC fabricated by using counter electrode platinized with alcoholic solution of H_2PtCl_6, non uniformity of the film is the major cause for the lowest V_{oc} of ~626 mV. Higher transmittance and sheet resistance could be the cause for its poor J_{sc} as well. In some cases, it may be observed that the DSSC having counter electrode platinized with H_2PtCl_6 solution shows better performance parameters than what has been observed in these studies, especially when uniform porous films of Pt is formed on FTO glass surface. However, reproducibility of such uniform films could be very difficult. For the selection of proper method to platinize counter electrode, several factors such as catalytic action, electrical conductivity, optical transmittance, Pt metal loading per unit area, reproducibility and sintering conditions are taken into consideration. The counter electrode made by using Pt ink-thick has all other good qualities except porosity of the film due to which it has very poor catalytic activity whereas the counter electrode made of Pt ink-thin has a proper balance of all the properties. It is superior to rest of the two films in terms of electrical conductivity, surface uniformity and porosity, interconnection of Pt particles, optical transmittance and cost competitiveness. The diluted ink used for the counter electrode preparation of this cell contained only 0.05% of Pt nanoparticles by weight due to which the net Pt loading in the counter electrode was only 2.6 μg/cm^2. The film made with Pt ink-thin requires lower temperature sintering than the temperature required for the films made with H_2PtCl_6 and

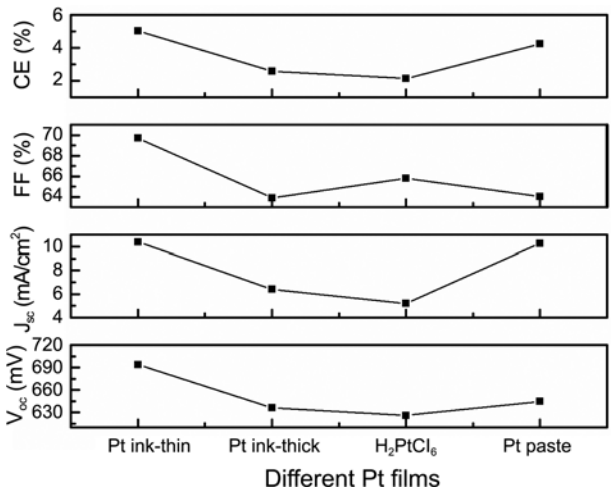

Figure 7. Comparison of the performance parameters of the DSSCs fabricated by using Pt films of different types to act as catalytic layers in counter electrodes.

Pt-paste. It further reduces processing time and thermal budget. Moreover, further optimization of the sintering temperature of the film made with the Pt ink-thin can make it applicable even for flexible substrates, which is impossible for the Pt films developed by thermal deposition at 400 °C. The self alignment of the Pt nanoparticles of the ink after it is applied on substrate ensures the reproducibility of uniform film. It can be concluded that the counter electrode prepared by using Pt ink-thin containing nanoparticles is a promising candidate for its application in DSSC on FTO glass substrate. The need of low temperature sintering of the Pt film made with the ink also opens a new possibility of its application in DSSC on flexible substrates.

Conclusion

Despite the high cost of platinum metal, platinized counter electrode is commonly used in DSSC because of its high catalytic activity and high corrosion stability against iodine in the electrolyte. Electrochemical deposition, sputtering and thermal decomposition are the conventional techniques used for the deposition of Pt films, however the processes such as electrochemical deposition and sputtering have the higher platinum loadings due to which they are not suitable for the low cost approach for the fabrication of DSSCs. The high temperature involved in the process of thermal decomposition makes this method unsuitable for flexible substrates. A novel application of platinum ink containing nanoparticles was carried out for the preparation of counter electrode in DSSC. The sufficiently diluted Pt-ink in *n*-hexane was found to form a film on FTO glass surface after sintering at 300 °C with Pt loading as low as 2.6 μg/cm^2 and sheet resistance ~8.08 Ω/sq along with moderate optical transmittance. A comparative study of four different types of chemically prepared Pt films on FTO glass surfaces showed that the FTO glass surface coated with thin Pt ink is a better candidate, which was supported by the comparison of the DSSCs fabricated using the similar films as counter electrodes. The DSSC fabricated by using counter electrode platinized with thin Pt-ink showed V_{oc}, J_{sc}, FF, CE of ~694 mV, 10.4 mA/cm^2, ~70% and ~5%, respectively. The counter electrode prepared by using thin Pt ink containing nanoparticles was found to be a promising candidate for its application in DSSC on FTO glass substrate. The requirement of relatively lower sintering temperature to form a suitable Pt film using the ink opens a new possibility of its application in DSSC on flexible substrates.

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