International Nano Letters (2019) 9:83–87
https://doi.org/10.1007/s40089-018-0258-y

SHORT COMMUNICATION

Silver nanowire-based transparent electrode as FTO replacement for dye-sensitized solar cell

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Received: 12 July 2018 / Accepted: 3 December 2018 / Published online: 14 December 2018

Abstract

In this paper, we present a novel usage of silver nanowire-based transparent electrode instead of fluorine-doped tin oxide for a ZnO–TiO_2 core–shell dye-sensitized solar cell. The Ag nanowire-based transparent electrode was fabricated with a simple coating method at room temperature and atmospheric pressure. This method potentially helps to reduce the production cost of dye-sensitized solar cell significantly by eliminating vacuum deposition processes for transparent electrodes and also enables the usage of various flexible substrates as a glass alternative. The Ag nanowire-based electrode is characterized using scanning electron microscope, four-point probe, and UV–Vis methods. With the short-circuit current density, I_{sc}, of 4.3×10^{-4} A/cm^2 and the open-circuit voltage, V_{oc}, of 0.63 V, the performance of the dye-sensitized solar cell shows promising preliminary data for a low-temperature ZnO–TiO_2 DSSC.

Keywords Silver nanowire · Transparent electrode · Core–shell nanoparticles · Dye-sensitized solar cell

Introduction

The first transparent electrode was introduced in 1907 by Karl Badeker [1]. A thin film of cadmium metal was sputter deposited on a substrate before oxidizing it with a heat treatment process to create what we now call a transparent conductive oxide (TCO). Since then, a few other types of TCO have been reported such as SnO_2 in 1947 [2] and indium tin oxide in 1954 [3]. Due to their excellent optical properties in addition to the electrical properties, TCO has been a very crucial element of many modern devices used in a wide range of important applications which include deicing plane windows [2], light-emitting diodes [5], solar cells [6], etc. However, all of the TCO materials mentioned above are to be processed under a vacuum environment, which is a costly process and feasible for relatively small-size substrates fitting within the vacuum chamber. Thus, the production cost and time of solar cells has not been significantly reduced, although many former efforts have been made to find improvements in advanced production protocols [7–9].

Among various solar-energy-harvesting methods, dye-sensitized solar cells (DSSCs) are a newer generation that possesses several advantages such as relatively low production cost, use of wider visible spectrum absorption materials, and simplification of the manufacturing process [10]. Recently, DSSC has been fabricated on various types of flexible substrates with different low-temperature fabrication methods [11, 12]. However, much research remains to be done before DSSC can replace current solid-state p–n junction solar cells. One of its major drawbacks includes the need of high-temperature process for TiO_2 and ZnO nanostructures, which require the usage of fluorine-doped tin oxide (FTO) transparent electrodes formed under vacuum, precluding it from manufacturing using a mass productive continuous roll-to-roll method. The fabrication processes of FTO are inherently complicated and typically require high-temperature and vacuum processes [13, 14]. It limits the production capacity and simply increases the production cost. Thus, we have been making efforts to find an alternative transparent electrode produced with a simple and scalable fabrication process to make DSSC available for low-cost

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industrial production methods. We have learned about a recently introduced silver nanowire electrode [4] and studied its feasibility for DSSC.

In this paper, we present a silver nanowire-based transparent electrode for dye-sensitized solar cell to replace the typical fluorine-doped tin oxide electrode. Without the need of high-temperature and high-vacuum processes, fabrication process for the silver nanowire-based electrode (SNE) is simply performed by spreading Ag nanowire-contained ink on a transparent substrate. Moreover, the simplicity of the SNE fabrication also makes it possible to use alternative flexible substrates instead of glass substrates in the future. The SNE helps to simplify the overall production process and to reduce the fabrication cost of DSSC. It may advance other DSSC-related technologies and envision alternative options for the current expensive Si-based commercial solar cells.

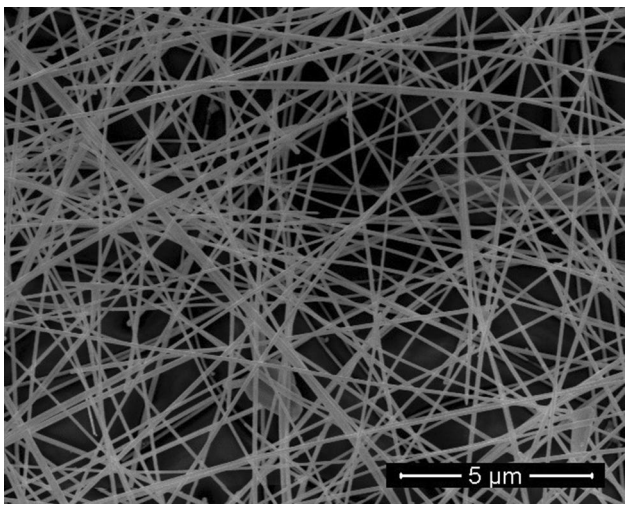

Fig. 1 SEM image of the silver nanowire network as a conductive electrode

Materials and methods

The silver nanowire-based transparent electrode is fabricated from the silver nanowire ink (SNI) which contains nanowires, approximately 115 nm in diameter, and in the range between 20 and 50 nm in length. The concentration of the Ag nanowires in isopropanol is 0.5%. To fabricate an SNE, SNI was dropped on a glass substrate. The ink was spread out and formed a uniform layer. After the samples were slowly dried in air to avoid aggregation, they were gently pressed under a rolling cylindrical glass rod to enhance the film's conductance by reducing the junction resistance between the nanowires. Patterning of the SNE was made with a lift-off process to form a clean, straight line. Figure 1 shows a scanning electron microscope (SEM) image of the silver nanowire network as a conductive electrode.

Figure 2 shows the structure of our ZnO–TiO_2 core–shell nanoparticles' dye-sensitized solar cell with the silver nanowire-based transparent electrode. The fabrication process started with preparation of the Ag nanowire-based transparent electrode as described on a glass substrate. Next, a thin layer of ZnO sol–gel was coated over the Ag nanowire-based electrode. The precursor solution was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in the 2-methoxyethanol solution. The concentration of zinc acetate dihydrate was 0.75 M. Monoethanolamine (MEA) was added to the solution with the molar ratio of 1.0 with zinc acetate dihydrate. Here, MEA serves as the stabilizer for the precursor. The solution was stir-mixed on a hot plate for 2 h at 60 °C. After the mixing process, we confirmed that the solution was clear and homogeneous. Subsequently, the

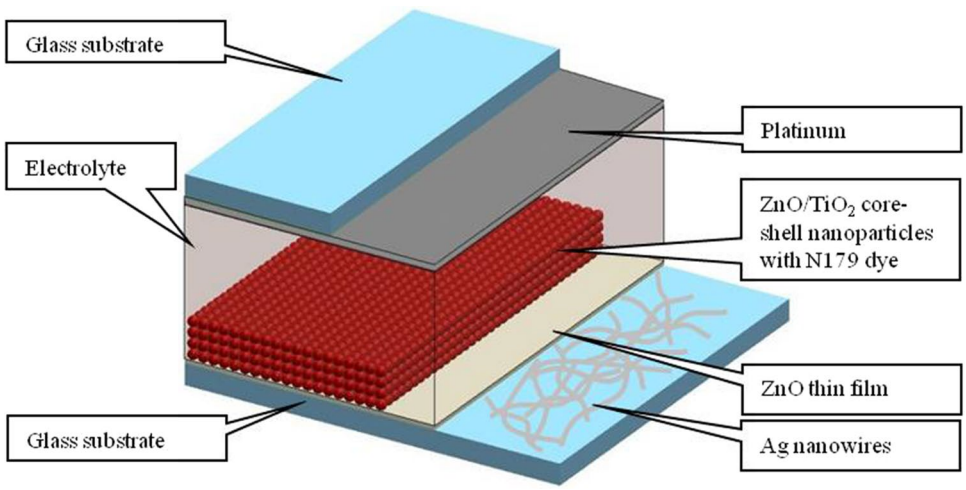

Fig. 2 Structure of the ZnO–TiO_2 core–shell nanoparticle DSSC

samples were dried at 250 °C for 10 min to vaporize solvents and other organic materials.

ZnO nanoparticles were coated on the thin ZnO layer. Zinc oxide nanoparticles (Alfa Aesar) are ranged from 40 to 100 nm in diameter. The ZnO nanoparticles were mixed with 0.1 M acetic acid solution in ethanol and spread-coated using the blade-coating technique. The nanoparticle-coated samples were baked on a hot plate at 250 °C for 30 min. This step also helps to enhance the bonding strength of the ZnO nanoparticles on the substrate.

The TiO_2 shell was coated over the ZnO nanoparticles by dipping in a 0.01 M titanium isopropoxide (TTIP) solution in ethanol for 30 min. The next step was rinsing with ethanol and drying it on a hot plate at 250 °C for 30 min. Then, the samples were sensitized in a 0.15 mM solution of N179 ruthenium dye ((*cis*-di-(thiocyanato)bis(2,2′-bipryidyl)-4-4′-dicarboxylate) ruthenium-(II) from Solaronix) in ethanol (Sigma Aldrich) for 24 h. The sensitized solution was covered from light to prevent aggregation and degradation of the dye. The counter electrode was prepared by sputtering Pt onto a substrate. Before the sputtering process was initiated, the substrate was cleaned with acetone, methanol, and DI water to remove environmental impurities and organic contaminants. Finally, the samples were assembled, filled with iodide/tri-iodide electrolyte (Iodolyte AN50; Solaronix), and were ready for testing.

Results and discussion

We first characterized the electrical and optical properties of the SNEs. Values of the sheet resistance of the two SNEs were compared to that of a reference FTO electrode using a four-point probe system, as summarized in Table 1. The mean sheet resistance value of FTO is 88.28 Ω/sq; while the sheet resistance values of the FTO electrode are quite uniform, those of the SNE show relatively less consistency due to non-uniform aggregation of Ag nanowires on the substrate. The mean values for each of the two SNEs are 147.62 Ω/sq and 150.96 Ω/sq, respectively. Although the conductivity of the SNE can be increased by increasing the concentration of Ag nanowires, it will reduce the transparency of the electrode.

Table 1 Four-point probe measurement of Ag nanowire-based electrodes and FTO electrode

	SNE #1 (Ω/sq)	SNE #2 (Ω/sq)	FTO (Ω/sq)
Measurement 1	106.2	130.2	97.6
Measurement 2	75.6	103.4	85.5
Measurement 3	258.5	183.8	98.8
Measurement 4	69.9	268.1	78.9
Measurement 5	227.9	69.3	80.6

To study the optical transmittance of the SNE, we used a UV–Vis spectrometer with a blank glass substrate as the reference. The UV–Vis spectra of seven different films are shown in Fig. 3. The transmittance of the SNE in the visible spectrum from 400 to 700 nm was quite uniform. The difference in transmittance between the samples is about 10%. In addition, uniformity analysis of the SNE on one sample was also carried out. The transmittance spectra at different positions on one sample are presented in Fig. 4. The results show relatively uniform data across the sample. The results from the UV–Vis spectrum show that the SNE has comparable transparency with commercial FTO film which has about 80% transmittance in visible range.

After studying the electrode, we continue to study the properties of the ZnO film coated using the sol–gel method using the XRD. The film was coated five times to make it thicker on a glass substrate. Borosilicate glass was used in this experiment, because it has high thermal stability at an elevated temperature. Figure 5 shows X-ray diffraction

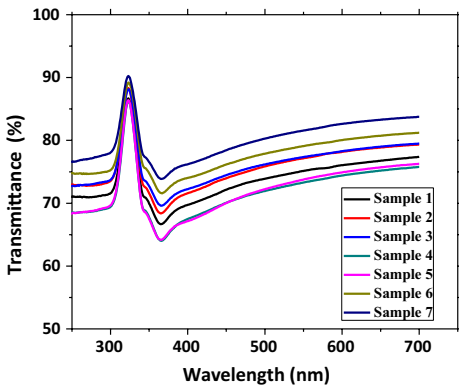

Fig. 3 UV–Vis spectra of different SNEs on glass

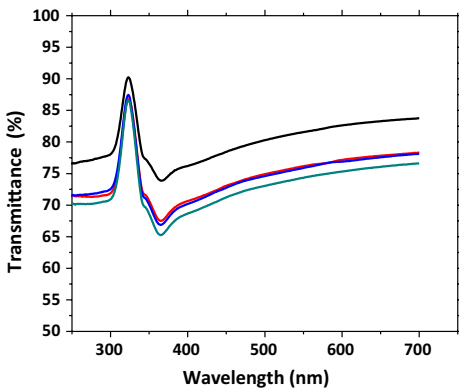

Fig. 4 UV–Vis spectra of Ag nanowire-based electrodes on glass substrate at four different positions

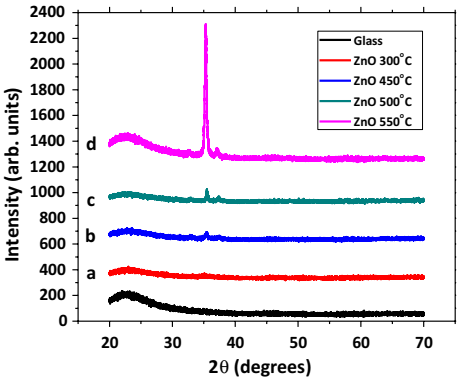

Fig. 5 XRD pattern of ZnO sol–gel spin coating on glass at different heat treatment temperatures: preheat at **a** 300 °C, and postheat at **b** 450 °C, **c** 500 °C, and **d** 550 °C

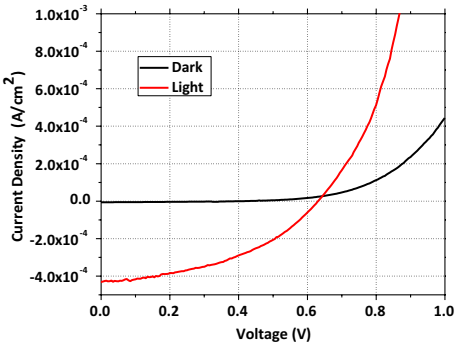

Fig. 6 *I–V* curve of the ZnO–TiO_2 core–shell nanoparticles solar cell with a silver nanowire-based transparent electrode

spectra of sol–gel-coated ZnO film treated under different temperatures. The very bottom curve shows the XRD spectrum with no peak of bare borosilicate glass. As shown in the second curve from the bottom, a very small peak occurred at 35.2°, corresponding to the (002) plane of ZnO after the spin coating and drying process at 300 °C. At a temperature of 300 °C or lower, the sol–gel ZnO layer is still mostly amorphous and has not formed a crystalline structure. The 35.2° peak grew as the postheat treatment temperature increased from 450 to 500 °C or 550 °C. A small peak at 37.1°, which appears on the 450 °C curve (curve b), corresponds to the (101) plane. It also grows as the treatment temperature increases. The 550 °C curve (curve d) shows a small peak at 32.6°, which corresponds to the (100) plane of ZnO. The peak of 550 °C at 35.2° is a strong peak and dominates the other two peaks.

The XRD patterns suggest that the ZnO film prepared by the sol–gel-coating process at an enough high temperature produces a polycrystalline wurtzite structure with primarily c-axis orientation. Although the quality of the ZnO film improves at a higher annealing temperature, we try to limit the baking temperature lower than 250 °C for the potential use of various alternative flexible substrate materials. Although the crystalline quality of the sol–gel ZnO layer would not be best, it is good enough to electrically isolate the SNE from the electrolyte. Thus, by treating the ZnO layer at a low temperature, we can enable the usage of alternative substrates which has lower melting point such as polymer. The fabrication process will be considerably simplified with possible role-to-role process.

Fabricated dye-sensitized solar cells were tested with an *I–V* measurement setup controlled by a Labview-based program and a solar simulator with a 100 mW output. The open-circuit voltage V_{oc} was 0.63 V. The short-circuit current density J_{sc} was 4.3×10^{-4} A/cm^2. The maximum power density was calculated to be 0.12 mW/cm^2 from the current density versus voltage (*J–V*) plot in Fig. 6. The fill factor was also calculated as follows:

$$\mathrm{FF} = \frac{1.2 \times 10^{-4}}{0.63 \times 4.3 \times 10^{-4}} \times 100\% = 44\%.$$

Although the efficiency of 0.12% is not as high as that of other reported ZnO-based DSSCs using an FTO electrode, our results are very intriguing for a device processed at a low temperature. The efficiency of the device can be enhanced by optimizing the device parameters such as the SNE, the size of the core ZnO nanoparticles, and the thickness of the TiO_2 shell layer. The fill factor could be further improved by decreasing the series resistance of the testing setup. The use of the Ag nanowire-based transparent electrode eliminates the need for a vacuum environment to fabricate transparent conducting electrodes. Together with low-temperature methods, it may enable the roll-to-roll process for mass production of DSSC at significantly reduced production cost.

Conclusion

The silver nanowire-based transparent electrode for a ZnO–TiO_2 core–shell nanoparticle dye-sensitized solar cell has been successfully demonstrated.

Silver nanowire-based transparent electrodes can potentially be used to replace FTO electrodes for DSSCs. The major advantage of Ag nanowire-based electrodes is that devices can be easily fabricated using simple techniques at low temperature without the requirement of a vacuum system for thin-film deposition. In the future, optimizing each individual parameter of the device may significantly improve the efficiency and fill factor of the devices.

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