Synthesis and Characterization of Dye-sensitized Solar Cell Using Photoanode of TiO$_2$ Nanoparticles/Ti-Mesh Electrode

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The photoanode of a dye-sensitized solar cell (DSC) utilizing Ti-mesh electrode is fabricated for high-efficiency, low-cost solar cell application. Ti-mesh electrode replaces transparent conducting layer (TCO). The TCO-less DSC is composed of a glass/dye sensitized TiO$_2$ layer/Ti-mesh electrode/electrolyte/metal counter electrode. The Ti-mesh electrode with high conductivity can collect electrons from the TiO$_2$ layer and allows the ionic diffusion of I$^-$/I$_3^-$ through the mesh hole. Thin Ti-mesh(~40 μm in thickness) electrode material is processed using the rapid prototype method. Both the photocurrent (6.02 mA/cm^2) and fill factor (0.303) are low, and these can be further improved by controlling the pore size and thickness of the mesh, and the contact between the TiO$_2$ particles and the Ti-mesh metal, respectively.

Keywords: dye-sensitized solar cell, photoanode, Ti-mesh, photocurrent, fill factor, rapid prototype

1. INTRODUCTION

Transparent conductive oxide (TCO) film is an important part in the synthesis of dye-sensitized solar cells (DSCs)[1,2] because of the low sheet resistance, sufficient light transparent ability, and high photoelectrical response as a porous photo-electrode material of DSCs. Among many TCO materials, the most commonly used for DSCs is fluorine-doped tin-oxide (FTO). The FTO film can be prepared by either physical vapor deposition or chemical vapor deposition methods. However, both of these processes are expensive and somewhat complicated for application to mass production. In addition, the FTO layer has its limitations in infrared ray (IR) transmission and thermal resistance as a transparent conductor.[3] The use of TCO glass for the two DSC electrodes can also result in a significant cost increase for the less effective DSC compared to an Si based solar cell.[4,5] Therefore, the replacement of TCO is required for the commercial production of DSCs. In this work, a new type of DSC photoanode replacing the TCO layer is developed to produce a highly efficient low-cost solar cell. The DSC structure using the new photoanode electrode is composed of a glass/dye-sensitized TiO$_2$ nanoparticle layer/Ti-mesh electrode/electrolyte/metal counter electrode/glass.

Typical DSCs use a layer of TiO$_2$ nanoparticles attached on a TCO as an electron collecting layer. 15 nm to 20 nm-sized TiO$_2$ nanoparticles are interconnected in three dimensions on TCO. The large number of dye molecules injected into the layer of TiO$_2$ nanoparticles becomes attached to the large surface area of nanoparticles, which enables efficient light harvesting. Use of TCO in a photoanode limits the competiveness of DSCs due to the reasons mentioned above. Thus, the typical photoanode layer structure of TCO/TiO$_2$ nanoparticles is less competitive. A completely different structure of photoanode is proposed in this report.

Ti-metal in the form of a mesh scaffold can replace TCO as an anode electrode, where the TiO$_2$ nanoparticles are attached to the Ti-mesh. However, to facilitate the Ti-mesh metal as an anode electrode, a modification of the photoanode structure is required since the Ti-metal is neither light transparent nor permeable to electrolytes. DSC using this hybrid structure, as schematically shown in Fig. 1, is discussed in further detail in the next section. The Ti-mesh electrode with high conductivity can easily collect electrons from the TiO$_2$ layer and effectively maintain the ionic diffusion of I$^-$/I$_3^-$ through the mesh holes. As the Ti-mesh electrode material facilitates TCO-less DSCs, a tissue type Ti-mesh with a 3-dimensional mesoporous structure is introduced.

The distance between the photoanode and the counter electrode is ~200 μm in DSC; thus the use of thick Ti-mesh may increase electrical resistivity, resulting in less efficient solar cell performance. However, it is not only very hard to produce very thin mesh-type Ti metal by typical metallurgical routes, but such material is also very scarce in the commercial market due to the high processing cost.

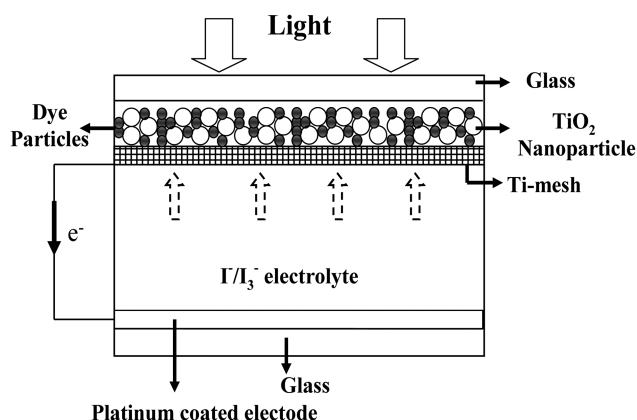Processing routes of very thin Ti-mesh are presented, in

Fig. 1. Schematic of DSC showing the photo-anode layers of TiO₂-nanparticles/Ti-mesh without using TCO film.

Fig. 2. Processing routes of thin Ti-mesh using Ti-powder/polymer composite by robotic deposition device.

which the three dimensional Ti-mesh scaffolds are fabricated by the direct exclusion of the Ti-powder/polymer composite paste using a robotic deposition device.[6] Processing and electrical characterization of the DSCs using this photoanode cell structure are also presented in this report.

2. PHOTOANODE OF DSC USING Ti-MESH/TiO₂-NANOPARTICLE LAYERS

A DSC is schematically shown in Fig. 1, in which the photoanode is the layers of TiO₂-nanoparticles/Ti-mesh. The electron collecting layer in the photoanode is TiO₂-nanoparticles (around 15 nm to 20 nm in diameter) attached with dye molecules. The collected electrons diffuse into the Ti-mesh metal and transport to the counter electrode. The electrons at the counter electrode are transferred to the I^-/I_3^- electrolyte, which subsequently transports the electrons to the dye molecules. Ti-mesh allows the charge-carrying electrolyte to flow to the dye molecules. Ti-mesh was fabricated using Ti powders mixed with polymer binders as described in the following section. A DSC structure in sequence is glass/TiO₂-nanoparticle/Ti-mesh/electrolyte/counter-electrode/glass, as shown in Fig. 1.

3. EXPERIMENTAL

Cellular Ti-mesh scaffolds were prepared using modified rapid prototype (RP) technique. Commercially pure Ti powder (CP-Ti, Sigma-Aldrich, USA) with particle size of about <45 μm was mixed with an organic polymeric binder to make the Ti/binder composite slurry, which was then placed into a syringe like injector. Using a modified RP machine, the flow of Ti/binder slurry comes through the syringe nozzle under pressure and is plotted on a stage as a fiber using a robotic deposition device. As-plotted Ti-mesh scaffolds are rapidly solidified by drying and the scaffold is finally fabri-
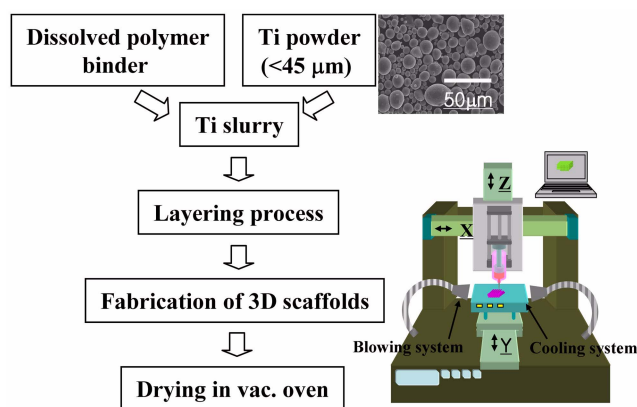
cated by layering a pattern of fibers. The porosities and pore size of the cellular scaffold were controlled by changing the space between fibers, the layer thickness, and the layering mode. As-fabricated Ti-mesh scaffold was then sintered at 1200°C in vacuum (5.0×10^{-6} torr). Figure 2 shows the processing routes of thin Ti-mesh, in which the three dimensional Ti-mesh scaffolds are fabricated by the direct exclusion of the Ti-powder/polymer composite paste using a robotic deposition device.

The rapid elimination of the solvent in the paste plays a key role in inducing the rapid solidification of the scaffold and subsequently in maintaining its 3D scaffold morphology, because the solvent remaining in the paste can induce the collapse of the 3D architecture. However, the chloroform in the polymer binder paste is not easily eliminated with ethanol medium and the collapse of the 3D structure occurs as a consequence. A heat-controlled blowing system as well as a chilled substrate was employed to solve this problem. Figure 3 shows the optical and scanning electron micrographs of the as-fabricated three dimensional Ti-mesh scaffold. Porosity of Ti-mesh can be controlled by wire diameter and the distance between wires. The thickness of as-fabricated Ti-mesh is ~400 μm, which is too thick to be used in DSC. Subsequent mechanical grinding and chemical etching of Ti-mesh in a solution of HF and HNO₃ reduces the thickness to ~40 μm.

Commercial TiO₂ paste (D-paste, Solaronix Inc.) was coated in a thickness of 10 mm on a glass by screen printing. Ti-mesh was then attached to the layer of TiO₂ paste, which was subsequently annealed at a maximum temperature of 450°C for 60 min. TiO₂-nanoparticles on Ti-mesh were immersed for eight hours in N3 dye (Solaronix, Switzerland) solution. Counter electrode was prepared by coating a solution of H₂PtCl·6H₂O and 2-propanol dyhydnate (v/v = 1:1) followed by drying at 450°C for 30 min. Electrode spacing was ensured by the use of Surlynfilm spacers, of 60 μm in thickness. The electrolyte used in the solar cell contained 0.5

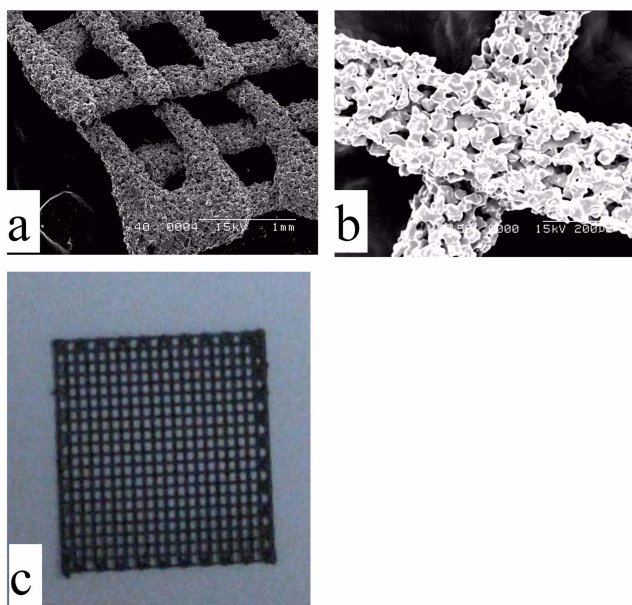**Fig. 4.** As-fabricated DSC using glass/TiO_2-nanoparticle /Ti-mesh/ electrolyte/counter-electrode/glass structure.

Fig. 3. As-fabricated three dimensional Ti-mesh (1.5×1.5 cm^2) scaffolds with ~50% porosity. (a) and (b) Scanning electron micrographs. (c) Optical micrographs.

mM iodide, 0.005M LiI, 0.0058M 4-tert-butylpyridine, and 5 ml acetonitrile. The electrolyte was introduced into the clamped electrode by capillary action. The resulting solar cell geometry is shown in Figs. 1 and 4.

4. RESULTS AND DISCUSSION

DSC using no TCO layer was fabricated with a hybrid structure of TiO_2-nanoparticle/Ti-mesh as a photoanode. TiO_2-nanoparticle arrays on Ti-mesh are the electron collecting layer, in which dye molecules are attached to the nanoparticles. Ti-mesh as an anode, made of Ti wires with ~40 μm in diameter, has ~50% porosity, as shown in Fig. 3. The porosity in the Ti-mesh allows the charge-carrying I^-/I_3^- electrolyte to flow to the dye molecules. Figure 4 shows the as-fabricated DSC using a glass/TiO_2-nanoparticle/Ti-mesh/ electrolyte/counter-electrode/glass structures.

The photocurrent (I) and the photovoltage (V) of the cell were measured with an active area of 0.2 cm^2 Ti-mesh using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator. *I-V* characteristics of the devices are shown in Fig. 5. Overall photoconversion efficiency is very low ($< 1.27\%$). This can be attributed to two major factors. The first is the photocurrent magnitude, 6.02 mA/cm^2, under 1.5AM illumination. The relatively large size of mesh pores may significantly affect the photocurrent. The electrons are injected from the dye molecules into the TiO_2 nanoparticles by photo energy. Then, the electrons diffuse through the networks of TiO_2 particles; however, if the electron lifetime is not long enough to avoid hole capture during diffusion, the
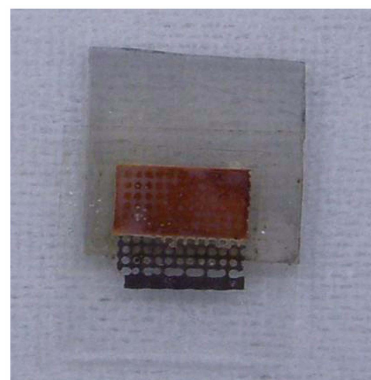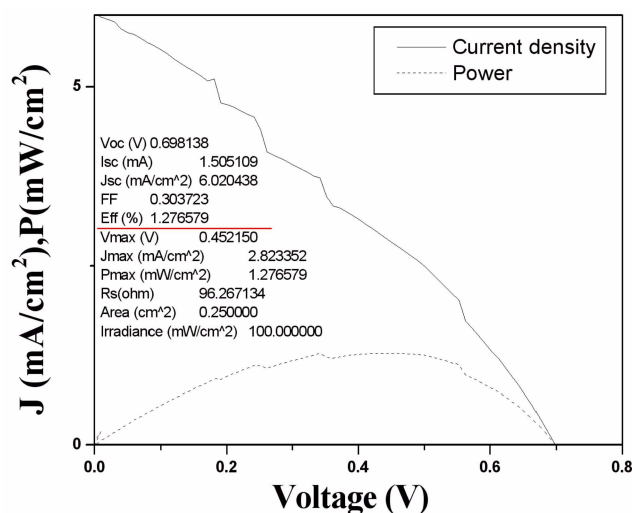

Fig. 5. Photocurrent (I) and photovoltage (V) characteristics of DSC using the photoanode of TiO_2-nanoparticle/Ti-mesh under 100 % AM 1.5 illumination.

current density will decrease. As the hole size of the Ti-mesh increases, the length of the TiO_2 particle networks becomes longer. The longer the distance for electron diffusion, the fewer electrons reach the Ti-mesh metal, resulting in lower photocurrent density. Thus, by controlling the hole size and wire diameter of Ti-mesh, the cell performance can increase significantly.

The second factor for improvement in this work is the fill factor of 0.303. The fill factor is reduced with increasing series resistance. The series resistance will be increased, and hence fill factor is reduced by increasing the thickness of Ti mesh and by poor contact between the TiO_2 particles and the Ti-mesh metal. The thickness of Ti mesh can easily be further reduced either by a chemical or mechanical thinning of mesh, and by the employment of thinner wires. The solid contact between the TiO_2 particle oxide and the Ti-mesh metal can only be accomplished by sintering; however, high

temperature sintering for a longer time is not possible due to the glass and dye molecules, which are vulnerable to heat. Adhesion between the oxide and metal at lower temperatures can be enhanced by forming a TiO_2 nanolayer on Ti-mesh, which can easily be done by simple electrochemical anodic oxidation of Ti-mesh. As mentioned above, both the photocurrent and the fill factor can be improved by the control of mesh dimensions and anodized oxide formation, which are the focus of on-going research.

5. CONCLUSIONS

Dye-sensitized solar cells (DSCs) using Ti-mesh electrodes were fabricated for high-efficiency, low-cost solar cell application. The Ti-mesh can replace TCO in the photoanode of DSC; thus the cell structure is composed of a glass/dye sensitized TiO_2 layer/Ti-mesh electrode/electrolyte/metal counter electrode. Thin Ti-mesh (~40 μm in thickness) electrode material is processed using the rapid prototype method. Electrical performance of as-fabricated DSC is characterized. Both the photocurrent and the fill factor are low; these low values are attributed to the large pore size of the mesh, and the thickness of Ti mesh and poor contact between the

TiO_2 particles and the Ti-mesh metal, respectively.

ACKNOWLEDGEMENTS

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