

Metal Electroplating of Three Dimensional (3D) Electrode in Electrolyte-less Dye Sensitized Solar Cells (ELDSC)

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ABSTRACT

The first Electrolyte-less dye sensitized solar cell (ELDSC) is proposed with the architecture of FTO-TiO₂-dye-metal. In the ELDSC design, the most significant contact is the TiO₂-dye-metal interface, whereby the metal electrode acts as the charge replenishment layer as well as the external electrode. In previous work, ELDSC has an inferior Fill Factor (FF) due to insufficient metal coverage from top-down physical vapor deposition. In this work, a three dimensional (3D) metal network plated through the mesoporous TiO₂ network is achieved through bottom-up metal electroplating. This study focuses on the characteristics of electro deposition onto insulating planar TiO₂ as well as mesoporous TiO₂ network. For planar TiO₂, gold (Au) islands form readily, becoming worm-like structures as they coalesce, subsequently becoming a continuous layer. (The plated metal on the insulating TiO₂ layer is made possible by plane defects within the insulator layer that serve as the conductive supply path.) In contrast, electroplating carried out on a FTO-planar TiO₂-mesoporous TiO₂ substrate results in a 3D Au network within the mesoporous TiO₂, where Au cords were observed as the connections among Au islands. This study demonstrates that a continuous metal layer can be electroplated onto an insulating TiO₂ layer, borrowing its intrinsic planar defect network. Further, applying the same principle, a 3D metal network can be formed within mesoporous TiO₂.

INTRODUCTION

There are 6 main components in a typical Dye Sensitized Solar Cell (DSSC) [1]: conductive oxide substrate, photoanode, dye, electrolyte and counter electrode. The volatile solvents in the liquid electrolyte typically used in standard DSSC systems require robust encapsulation, prompting searches for substitutes such as ionic liquids [2-6]. Ionic liquids, on the other hand, are limited by inefficient penetration into the mesoporous titanium dioxide (TiO₂) due to high viscosity. Thus the issue of the electrolyte in a DSSC still awaits an optimized solution.

In 2011, the first Electrolyte-less dye sensitized solar cell (ELDSC) with the architecture of TiO₂-dye-metal [7] was introduced to be the all-solid state organic solar cell. In previous work, the ELDSC device performed below the standard predicted from the energy band diagram

[7]. This was because the ELDSC device suffered from insufficient coverage of metal electrode in the mesoporous TiO_2 structure resulting from top-down metal deposition [8]. Hence, the ELDSC device, where the metal electrode was deposited through sputtering, has an inferior Fill Factor (FF) that affects the device's performance. In order to improve the performance of the ELDSC, a three dimensional (3D) metal network that evenly spread through and coat the mesoporous TiO_2 is essential (as illustrated in Figure 1(a)). Clearly, in the ELDSC design, the most significant contact is the mesoporous TiO_2 -dye-metal interfaces (refer to Figure 1(b)), whereby the metal electrode acts as the charge replenishment layer as well as the external electrode. Hence, an innovative metal deposition method – bottom-up metal electroplating, is proposed in this work.

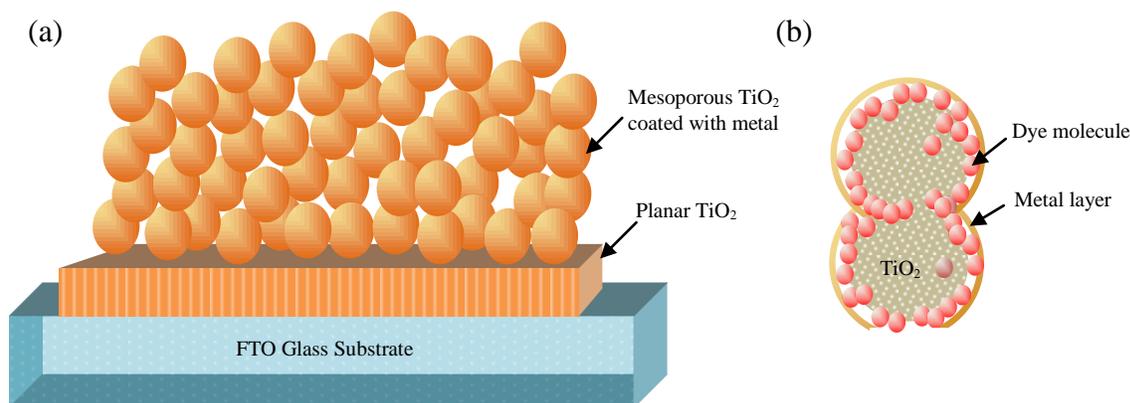


Figure 1 The illustration of the cross section view of (a) the visualized Electrolyte-less dye sensitized solar cell (ELDSC) and (b) the metal-dye- TiO_2 interface in ELDSC.

One of the challenges in ELDSC fabrication is to generate the TiO_2 -metal contact, which requires a continuous metal layer throughout the 3D mesoporous TiO_2 . Metal electroplating process is selected to fabricate the metal electrode in ELDSC because solution processing may be able to uniformly penetrate into porous structures, hence providing an equal opportunity for metal nucleation to occur both within and on the surface on mesoporous TiO_2 layer. This work reports on the characteristics of metal nucleation and growth on both planar and mesoporous TiO_2 .

EXPERIMENT METHODOLOGY

Sample Preparation

The fluorine doped conductive tin oxide (FTO) glass substrate was cleaned with glassware soap in ultrasonic bath for 30 minutes, followed by rinsing with deionized (DI) water, ethanol, acetone, and isopropyl alcohol (IPA) (30 minutes each). Next, titanium (Ti) was sputtered on the FTO, followed by oxidation of Ti to achieve the planar TiO_2 layer. After that, TiO_2 mesoporous network was Doctor Bladed on top of the planar TiO_2 layer. Lastly, sintering of mesoporous TiO_2 was carried out at 450°C .

Metal Electroplating

The bath solution (Techni Gold (Au) 25 ES RTU) was stirred at 200 revolutions-per-minute with a maintained temperature of 60°C during the electroplating process. In this plating set-up, the anode is Platinum (Pt) plate while the cathode is the sample to be plated. By controlling the plating duration, Au with different microstructures was electroplated on both the planar and mesoporous TiO₂ layers.

Material Characterizations

Field emission scanning electron microscopy (FESEM) and Transmission electron microscopy (TEM) techniques were used to carry out the study of the Au nucleation and growth on planar TiO₂ and mesoporous TiO₂ network. In addition, Focused Ion Beam (FIB) instrument was used to prepare the plated samples for TEM study.

RESULTS AND DISCUSSION

Electroplating on a structurally perfect insulator is infeasible. In this work, we are able to deposit metal on an insulator, TiO₂. This can be explained by the TiO₂ columnar structure, which is the key for electroplating on TiO₂ layer. The columnar TiO₂ generates defects through the TiO₂ layer and allows electron flow from the FTO substrate to the TiO₂ surface. The existence of electron paths across TiO₂ layer allows electron flow and leads to the achievement in electro-depositing of Au on TiO₂ layer.

Nucleation and Growth of Au on Planar TiO₂

The TiO₂ surface was first cleaned with IPA before electroplating. Both specimens (represented in Figure 2 and Figure 3) had a UV-Ozone treatment after the IPA cleaning step. The plating durations were controlled to obtain different stages of Au deposition on TiO₂. On the planar TiO₂ plated specimen, Au islands were observed to form after 2 seconds of electroplating. Figure 2 shows the top view of planar TiO₂ layer with nucleation sites and Au islands. As illustrated in Figure 3, these Au islands coalesce and form worm-like structures when the electroplating duration was increased to 2 minutes.

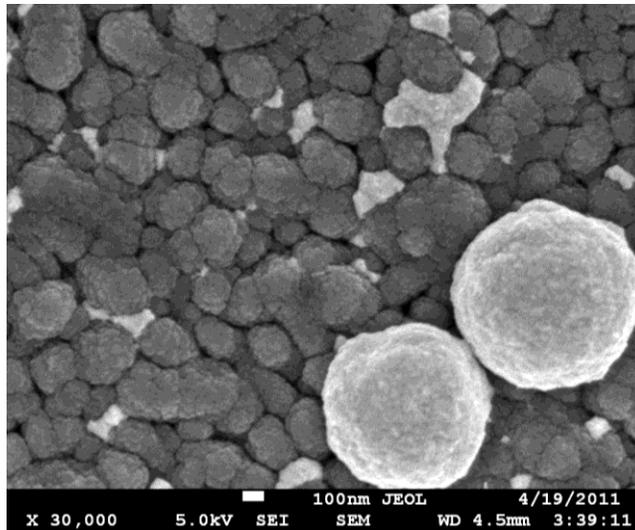


Figure 2 Top view of Au islands nucleated on the planar TiO₂ thin film. The TiO₂ thin film was cleaned by UV-Ozone treatment (20 minutes) before Au electroplating (10 seconds).

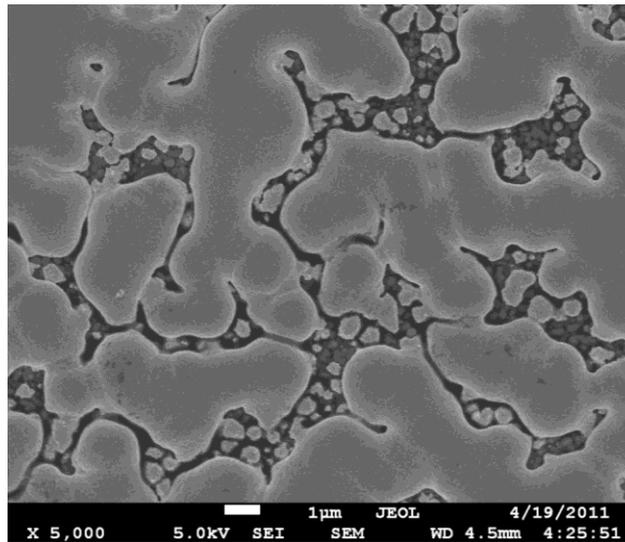


Figure 3 Top view of Au island coalescence on the planar TiO₂ thin film. The TiO₂ thin film was cleaned by UV-Ozone treatment (20 minutes) before Au electroplating (2 minutes).

Au Layer Formation on Planar TiO₂

Figure 4 shows a continuous layer of Au formed on the ultra-thin planar TiO₂. The plated Au is essentially a conformal thin film with some sub-micron-sized pin holes.

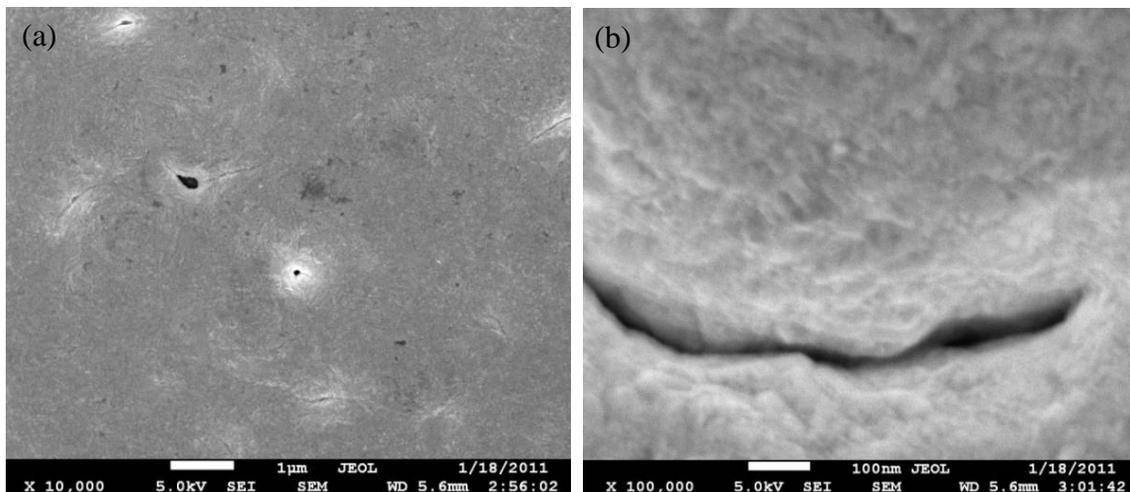


Figure 4 (a) Au layer formation on ultra-thin planar TiO₂ (Plating duration 2 minutes) and (b) Au layer with pin holes on planar TiO₂.

3D Metal Network in Mesoporous TiO₂

Referring to Figure 5(a), electroplating carried out on a FTO-planar TiO₂-mesoporous TiO₂ sample results in a 3D Au network within the mesoporous TiO₂. Figure 5(b) shows the mesoporous TiO₂ nanoparticles before Au electroplating was carried out. Currently, the Au electroplated in the mesoporous TiO₂ has yet to reach high metal coverage density. However, by increasing the plating duration, it is a straightforward method to obtain more Au in mesoporous TiO₂ network.

In addition, the spreading of Au cord was observed as the connection among Au islands in the mesoporous TiO₂. Figure 6 is a high resolution TEM image that shows a Au cord on TiO₂ nanoparticles. These Au cords are believed to be the growth directions of the Au throughout the mesoporous TiO₂ network. Currently we have not observed any preferential growth direction of the Au cords.

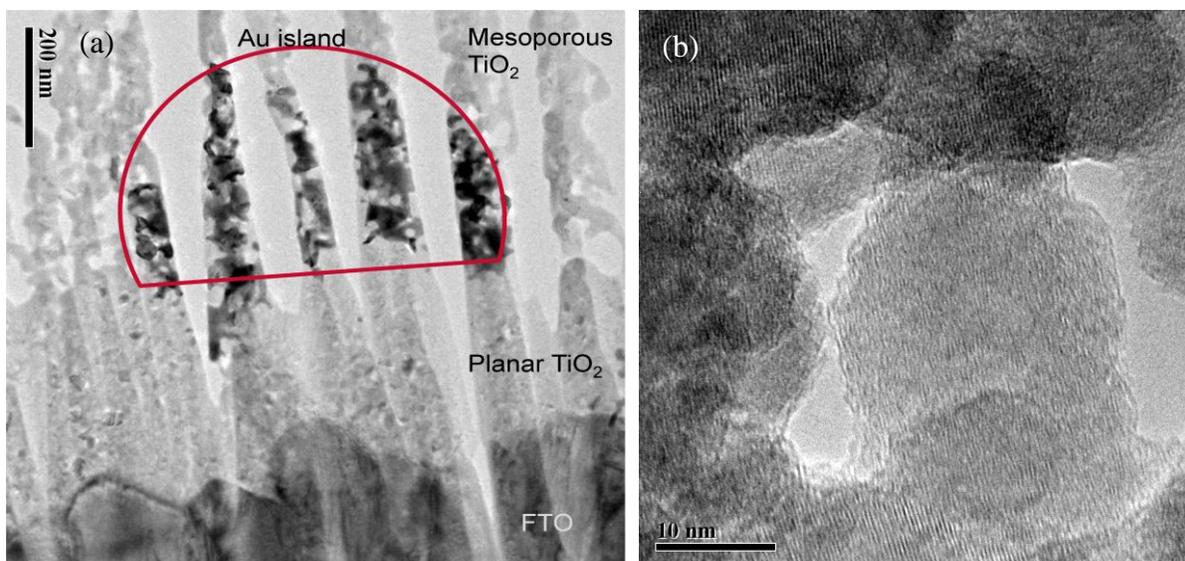


Figure 5 Cross section TEM images of (a) 3D metal electrode in mesoporous TiO₂ network after 1 minute of plating and (b) mesoporous TiO₂ network before electroplating.

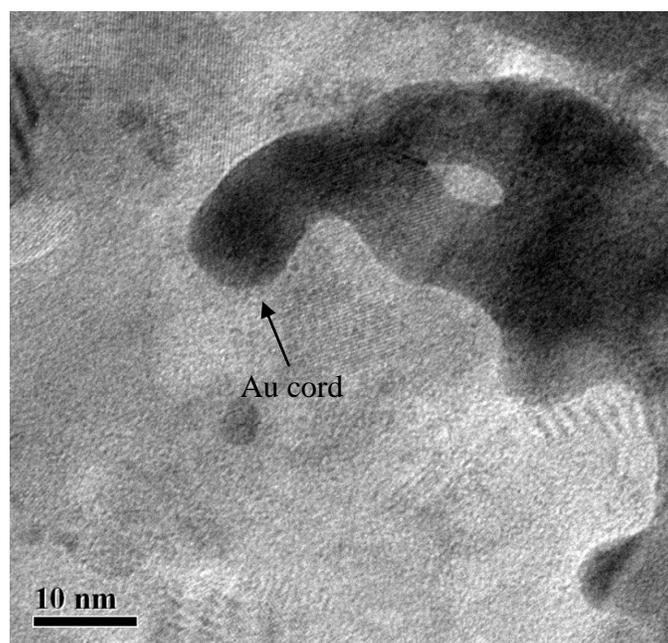


Figure 6 High resolution TEM image of Au cord on TiO₂ nanoparticles (Plating duration 1 minute).

CONCLUSIONS

In electrodeposition of Au onto insulating TiO₂, deposition begins with Au island nucleation, then island growth, followed by coalescence of islands to form worm-like structures which link further to form a metal layer eventually. (The plating is made possible by internal boundaries with the planar insulator.) This study demonstrates that a continuous metal layer can be plated on a columnar insulating TiO₂ structure. In addition, 3D metal network can be formed

in the mesoporous TiO₂. Further work will be carried out to decrease the thickness of the metal electrode as well as to increase the metal electrode coverage in the mesoporous TiO₂ network.

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