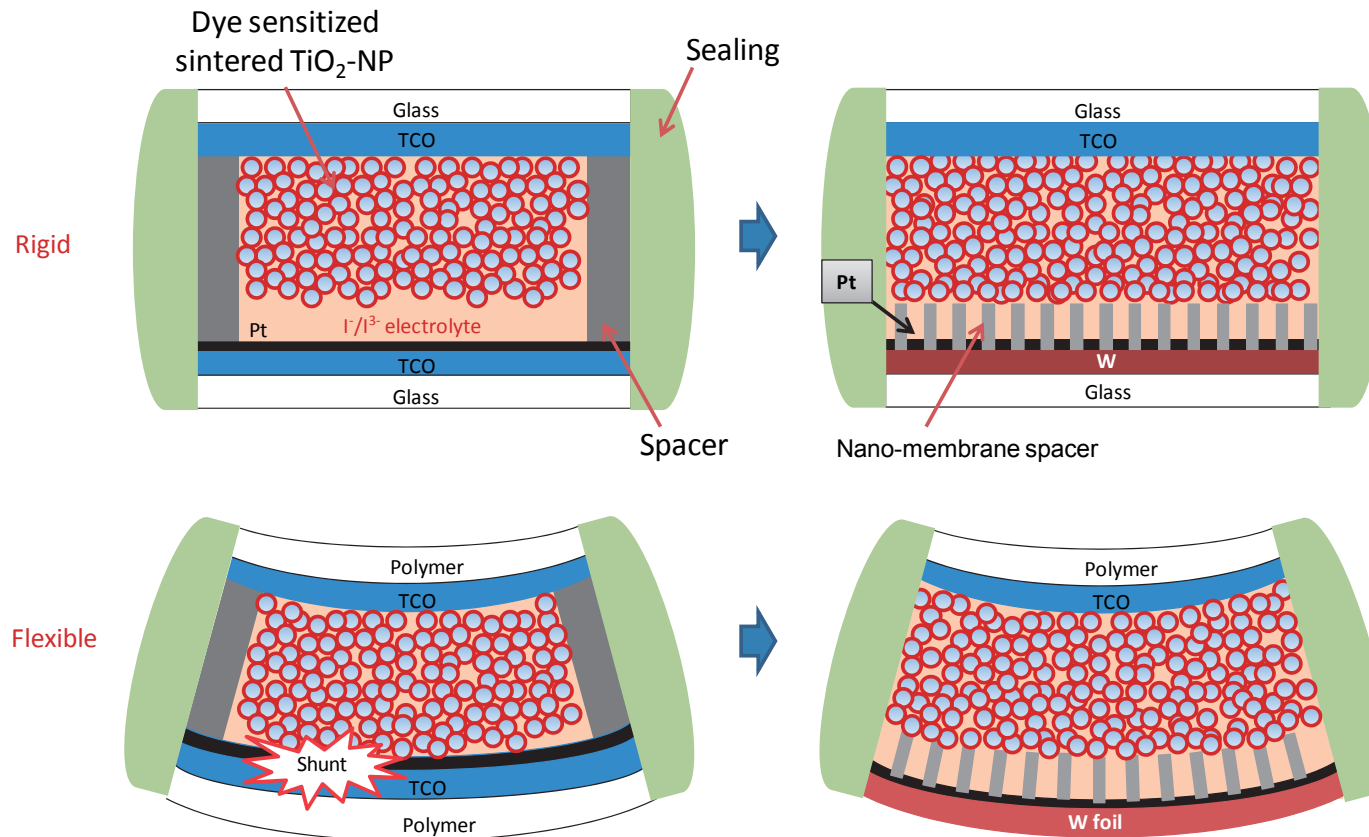# Nanostructured Photoelectrodes for Dye Sensitized Solar Cells

Ivan Turkevych, Koji Matsubara and Michio Kondo

Research Center for Photovoltaic Technologies
National Institute of Advanced Industrial Science and Technology

DSSC with nano-membrane spacer

Conventional DSSC has a sandwich structure, which consists of working electrode (usually 10 micron thick sintered and sensitized mesoporous TiO_2-NPs on TCO) and a counter electrode (usually TCO coated with Pt clusters that catalyze iodine redox couple reaction) separated by spacer. Therefore a part of the DSSC area is always sacrificed to spacer, which significantly decreases the efficiency of the module.

In this work we propose a concept of a counter electrode with integrated nano-membrane spacer, which has a through-hole structure and allows penetration of the iodine electrolyte to the Pt catalyst underneath. In this case the working electrode can be placed directly on top of the counter electrode without risk of shortcut, which is important for flex-DSSCs.

Nano-membrane spacer
Nanoporous anodic alumina (NPA)

∅100 nm
P 300 nm
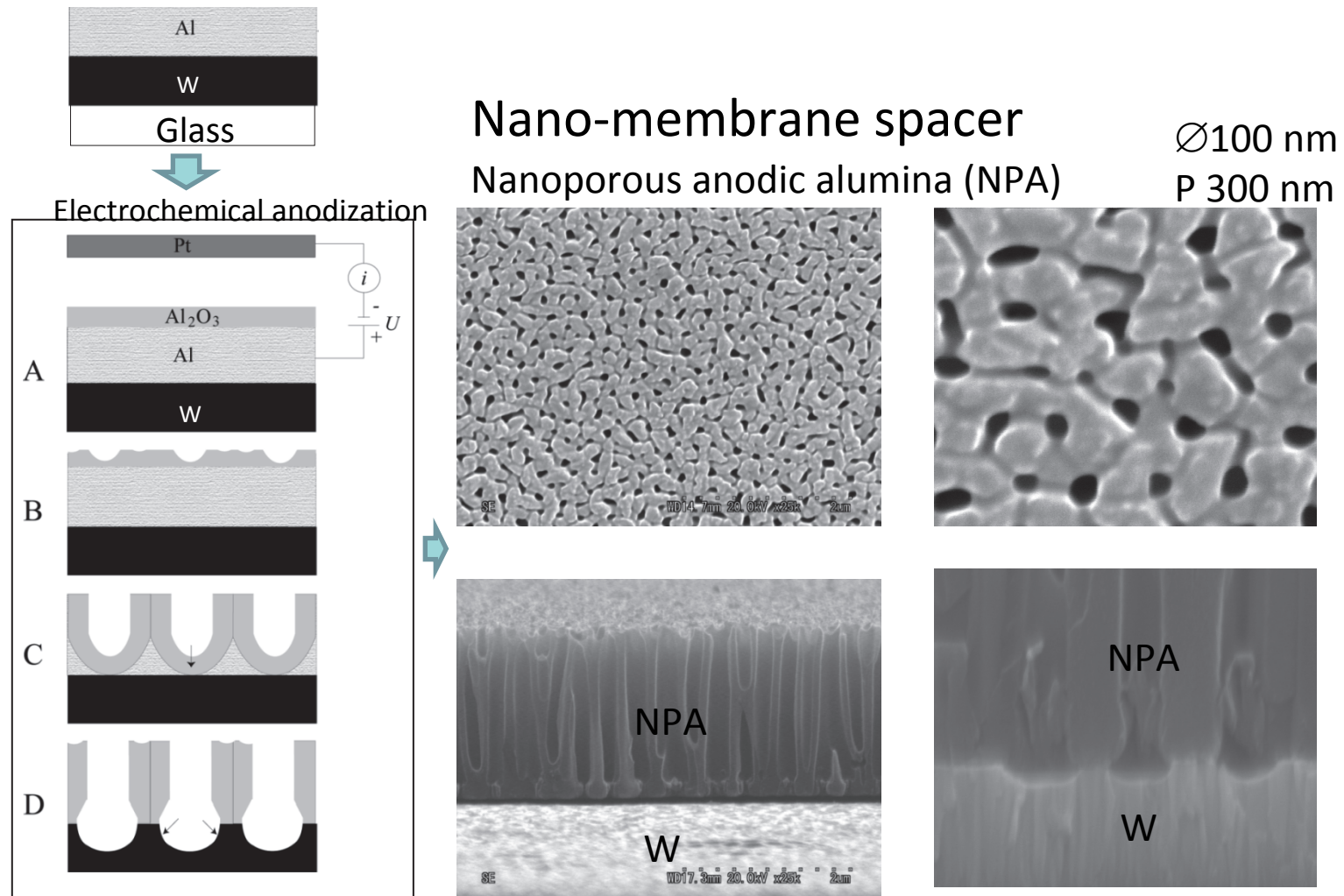
The fabrication process starts from the deposition Al layer on W. Then the anodization of Al results in the formation of nanoporous alumina (NPA) with through hole structure. The anodization process is characterized by a complete conversion of Al into NPA, i.e. there will be no Al in contact with the iodine electrolyte in DSSC. When the anodization front approaches the W/Al interface it interacts with the W and forms etched concaves in the W underlayer. The NPA is seamlessly integrated on W, i.e. has an excellent adhesion to W and hardly can be remove even by intentional scratching.
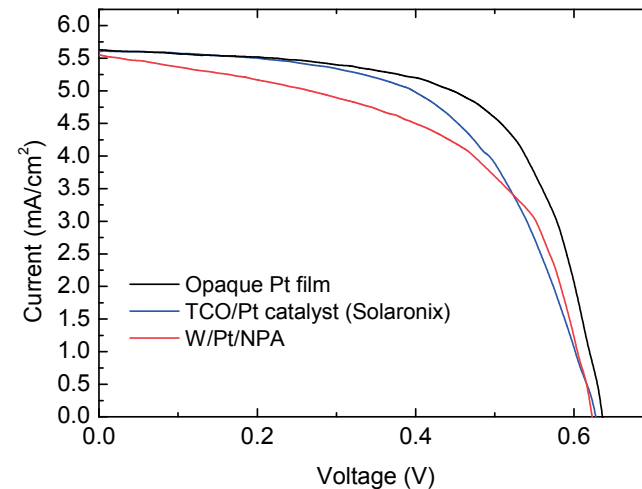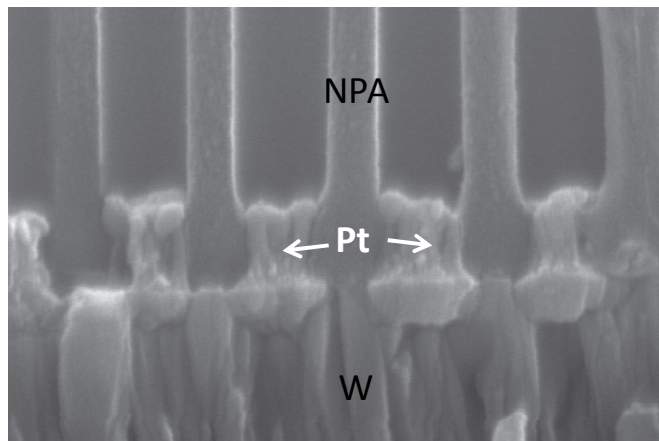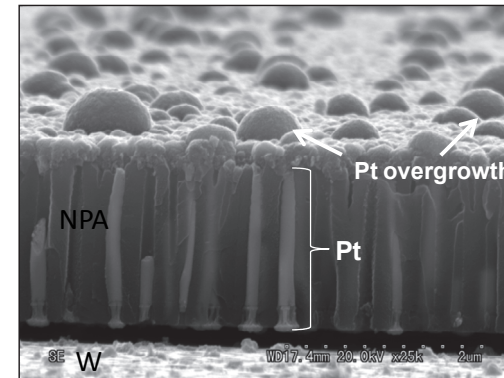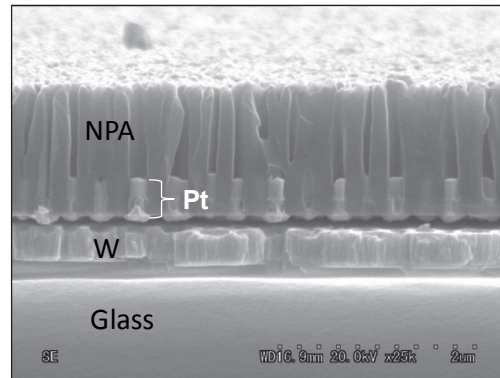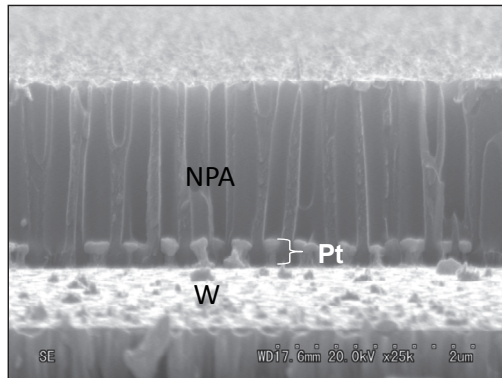
Pt pillars were fabricated on W under the NPA by electrochemical bath deposition. To avoid overgrowth of the pillars and deposition of Pt on the top of the NPA, their height must be controlled by adjusting electrochemical potential of the W in the electrolyte, its concentration, temperature and deposition time. As can be seen, Pt pillars actually cork up the channels in NPA, so the W is not going to be in contact with the iodine electrolyte in DSSC.

The W/Pt/NPA counter electrode showed performance comparable to other counter electrodes used in conventional DSSCs. It showed the same Voc and Jsc as opaque Pt film or semitransparent TCO/Pt counter electrodes, but lower FF. The cause for lower FF will be investigated in near future by impedance spectroscopy.

Nanostructured Photoelectrodes for Dye Sensitized Solar Cells

Ivan Turkevych, Koji Matsubara, Michio Kondo

Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology

Introduction

Conventional DSSC has a sandwich structure, which consists of working electrode (usually 10 micron thick sintered and sensitized mesoporous TiO_2-NPs on TCO) and a counter electrode (usually TCO coated with Pt clusters that catalyze iodine redox couple reaction) separated by spacer. The spacer is usually a 20-50μm thick polymer rectangle placed around the mesoporous TiO_2-NPs working electrode. After the assembly of this sandwich structure, a glue sealing is applied around the perimeter of the device to prevent electrolyte leakage. Sometimes spacer is made of a thermoplastic polymer and act as sealing as well.

The function of the spacer is to prevent a shortcut between two electrodes. Even in the case of rigid structure, spacer stripes should be applied at least every 10 cm, because 0.5 mm glass is still bendable enough to shortcut the device under a local pressure. In the case of flex-DSSC the situation is even more critical. Another function of the spacer is protection of a metal grid that is deposited on TCO to improve carrier collection, because most of the metals corrode in the iodine electrolyte. Therefore a part of the DSSC area is always sacrificed to spacer, which significantly decreases the efficiency of the module.

In this work we propose a concept of a counter electrode with integrated nano-membrane spacer (Fig.1.), which has a through-hole structure and allows penetration of the iodine electrolyte to the Pt catalyst underneath. In this case the working electrode can be placed directly on top of the counter electrode without risk of shortcut, which is important for flex-DSSCs.

Experimental

The fabrication process started from the deposition Al layer on W. The Al was deposited by r.f. magnetron sputtering at 5 sccm of Ar, and working pressure of 0.8 Pa. Then the Al layer was converted to nanoporous alumina (NPA) by anodization at 120V in diluted phosphoric acid. The concentration of the phosphoric acid was adjusted to get the right pH value that ensures a stable and uniform anodization process.

After complete conversion of the Al layer into NPA, the W underneath the NPA was exposed to the electrolyte containing Pt^{2+} complex. The Pt was deposited on the exposed W by electrochemical bath deposition. Three electrode configuration with the Ag/AgCl reference electrode was used to control the Pt deposition.

Three working electrodes with the area of 5x5 mm and thickness of 5μm were fabricated by screen-printing TiO_2-NPs paste (Solaronix) on TCO. After sintering at 450ºC for 3 hours, they were sensitized in N719 dye solution in ethanol for 5 hours. After that I-V characteristics were measured under solar simulator by using three different counter electrodes (i.e. opaque Pt film, TCO catalyzed by Pt clusters (Solaronix), and our W/Pt/NPA counter electrode.
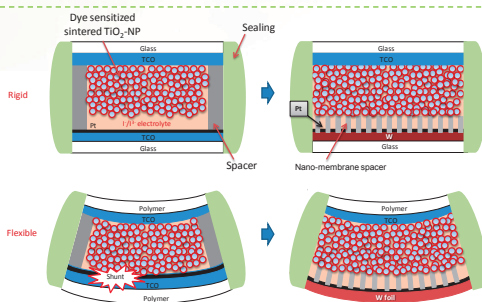
Results and discussion

Figure1. Demonstration of the nano-membrane spacer concept for rigid and flex-DSSCs.

Anodization of Al resulted in the formation of nanoporous alumina (NPA) with through hole structure. The average diameter of the nanopores was 100 nm and the average interpore distance was 300 nm. Thickness of the NPA is given by the thickness of the initial Al layer multiplied by 1.2 due to volume expansion of the aluminum oxide. The anodization process is characterized by a complete conversion of Al into NPA, i.e. later Al is not going to be in contact with the iodine electrolyte in DSSC.

When the anodization front approaches the W/Al interface it interacts with the W and forms etched concaves in the W underlayer. Fig. 2 shows a schematic of the anodization process and SEM images of the top and side views of the resulted W/NPA structure. The NPA is seamlessly integrated on W, i.e. has an excellent adhesion to the W and hardly can be remove even by intentional scratching.
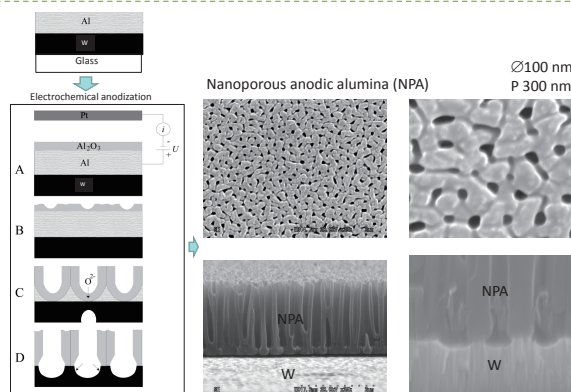

Figure 2. Schematic of the anodization process and SEM images of the top and side views of the resulted W/NPA structure.

Fig. 3 shows SEM images of the W/NPA with Pt pillars fabricated by electrochemical bath deposition. To avoid overgrowth of the pillars and deposition of Pt on top of the NPA, the height of the pillars must be controlled by adjusting electrochemical potential of the W in the electrolyte, concentration, temperature and deposition time. As can be seen from the SEM images, Pt pillars actually cork up the channels in NPA , so the W is not going to be in contact with the iodine electrolyte in DSSC as well.
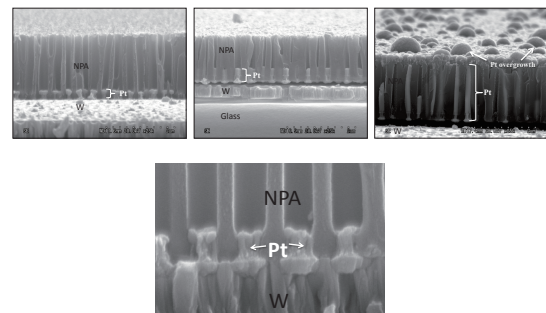

Fig.3. Electrochemical bath deposition of Pt into W/NPA

Fig. 4 shows I-V characteristics of three different counter electrodes, i,e. opaque Pt film, TCO catalyzed by Pt clusters, and our W/Pt/NPA counter electrode. In the case of Pt film and TCO/Pt counter electrodes a 20μm polymer spacer was used to separate them from the working electrode on the top. The working electrode was placed directly on our W/Pt/NPA counter electrode. Our counter electrode shows the same Jsc and Voc, as two other electrodes, and lower FF. Same Voc means that the electrochemical potential of our counter electrode is located at the same energy level as in other two cases, implying that W is not in contact with the iodine electrolyte and Pt pillars cork up the NPA channels effectively and uniformly. Same Jsc means that in all three cases we had the same performance of the working electrode. In future we are going to perform characterization of our counter electrode by impedance spectroscopy to reveal the cause for the lower FF.
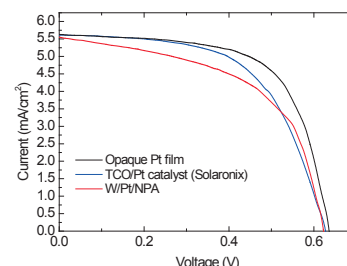

Figure 4. IV characteristics of counter electrodes made of opaque Pt film, TCO catalyzed by Pt clusters, and W/Pt/NPA.

Conclusions

In conclusion, we proposed a concept of a counter electrode with integrated nano-membrane spacer, which has a through hole structure and allows penetration of the iodine electrolyte to the Pt catalyst underneath.

The DSSC solar cell with the nano-membrane counter electrode was fabricated and showed performance comparable to other counter electrodes used in conventional DSSCs. The device showed same Voc and Jsc as opaque Pt film and/or semitransparent TCO/Pt counter electrodes, but lower FF.

The cause for lower FF will be investigated in a near future by impedance spectroscopy. The W/Pt/NPA structure is stable in iodine electrolyte. The techniques used for the fabrication of this structure are truly scalable, i.e. large substrates can be processed with a great degree of uniformity.