

Supporting information:

Branched double-shelled TiO₂ Nanotube Networks on Transparent Conducting Oxide Substrates for Dye Sensitized Solar Cells

Jijun Qiu,^{a,b} Xiaomin Li,^b Xiangdong Gao,^b Xiaoyan Gan,^b Binbin Weng,^a Lin Li,^a Zijian Yuan,^a Zhisheng Shi*^a and Yoon-Hwae Hwang^c*

^a School of Electrical and Computer Engineering, University of Oklahoma, Norman, Oklahoma 73019, USA.

^b State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

^c Department of Nanomaterials Engineering & BK 21 Nano Fusion Technology Division, Pusan National University, Miryang 627-706, Korea

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Figure S1 shows the growth direction of ZnO branches.

Figure S2 shows a narrow diameter distribution of ZnO branches.

Figure S3 shows a scattering effect at top of 1D TiO₂ nanotube arrays and 3D TiO₂ nanotube networks.

Figure S4 shows the connection between TiO₂ nanotubal stems and the FTO substrate before LbL-AR deposition.

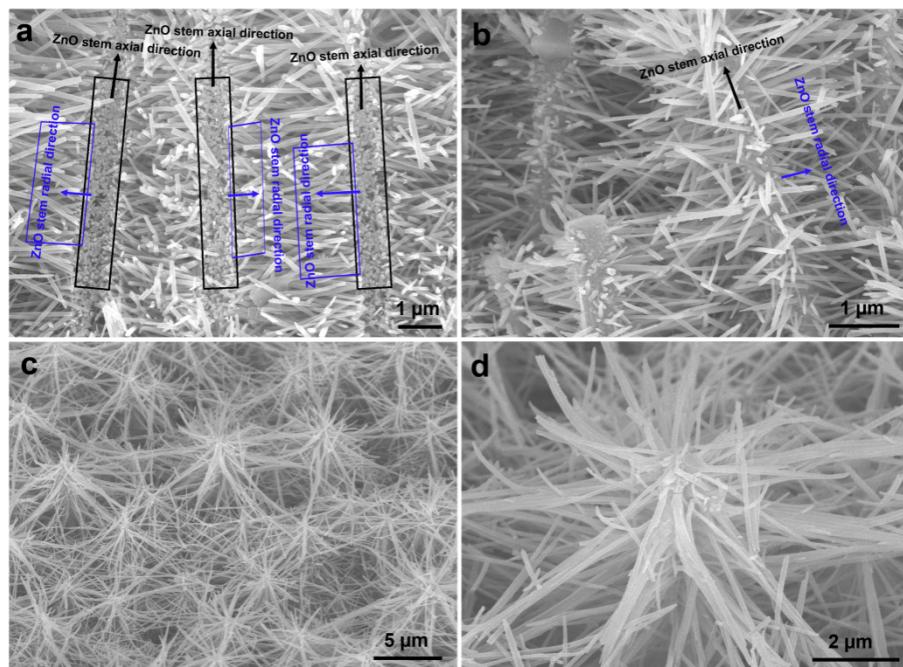


Figure S1 Side-view FESEM ZnO branches a) without and b) with ZnO stems. Tiled top-view FESEM images of TiO₂ 3D NTNs with c) low and d) high magnification

Figure S1 a shows a typical FESEM images of ZnO branches without ZnO stems, which had been peeled during the cutting process. Only transverse section profiles of ZnO branches' bottoms could be observed in the axial direction of ZnO stems (as indicated by black rectangles in Figure S1 a), and the ZnO nanowires are parallel or thereabout in the radial direction of ZnO stems (as indicated by the blue rectangles), indicating a little angle between ZnO branches and stems. Same phenomena also could be observed in the FESEM image of ZnO branches grown from ZnO stems, as shown in Figure S1 b. Tiled top-view FESEM image of TiO₂ nanotube networks with different magnification, as shown in Figure S1 c and d, also show that TiO₂ nanotubal branches are perpendicular to the TiO₂ tubal stems, indicating vertical growth direction of ZnO branches.

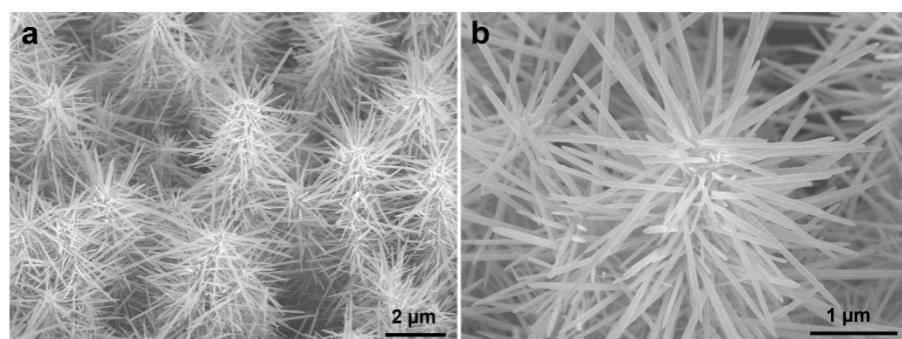


Figure S2 Tiled top-view of branched ZnO template with a) low and b) high magnification.

Large size FESEM images of ZnO branches in Figure S2 shows that the different in diameter of branches is very small. At the same time, TiO₂ nanotubal branches also show a very narrow diameter distribution, as shown in Figure S1 c and d, indicating a uniform diameter of ZnO branch templates.

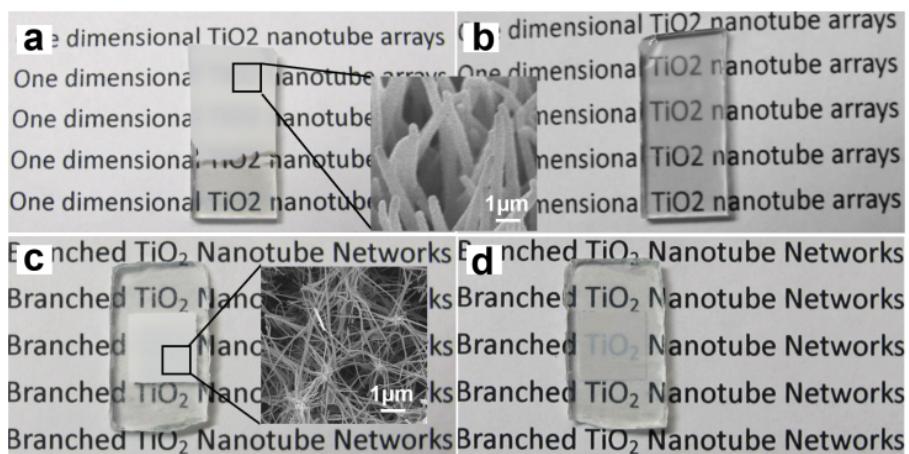


Figure S3 Photograph of the prepared one 1D TiO₂ nanotube array and 3D branched TiO₂ nanotube networks on FTO substrates. (a) top- and (b) back- view of 1D TiO₂ nanotube arrays; (c) top-and (d) back-view of 3D TiO₂ nanotube networks.

Figure S3 shows the real photo-images of TiO₂ nanotubal arrays and networks taken from front and back sides. An obvious transparent difference between front and back views could be observed from Figure S1c and S3d, indicating a strong scattering effect at the top surface of 3D branched TiO₂ nanotube networks. However, the 1D TiO₂ nanotube arrays also shows a scattering effect in Figure S3a and S3b. Therefore, in our opinion, the improved performance of 3D TiO₂ nanotube networks is mainly attributed to the increased surface areas resulted from TiO₂ nanotube branches with small size, rather than scattering effect.

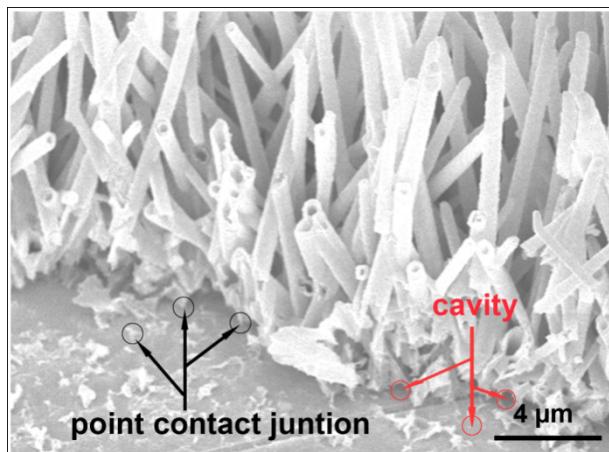


Figure S4 Tiled top-view FESEM images of double-shelled TiO_2 nanotubal stems.

ZnO seed layer, which connects the TiO_2 nanotubal stems with FTO substrates, will be etched together with ZnO stems after longer etching time for a low $[\text{Zn}^{2+}]$ and a high DSCs performance, forming lots of cavities or cracks in the places where were occupied by ZnO stems, as indicated by red circles in Figure S4, and the TiO_2 nanotubal stems connects with FTO substrate just by weak point contact junction (as indicated by black circles in Figure S4). The weak adhesion can't live through the brunt of low pH (high TiCl_4 concentration) and high temperature during the hot TiCl_4 solution treatment. May methods have been tried to solve this problem, including using TiO_2 seed layer and TiO_2/ZnO mixed seed layer et al. By now, only additional LBL-AR TiO_2 deposition can effectively prevent TiO_2 nanotubal stem peeling during TiCl_4 treatment. We believe that new LBL-AR TiO_2 deposition can fill the cavities and cracks with fine TiO_2 nanoparticles to form area contact, exceedingly enhancing the adhesion.