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Electronic Supplementary Information for "Chemical Assisted Formation of Secondary Structures towards High Efficiency Solar Cells Based on Ordered TiO_2 Nanostructures"

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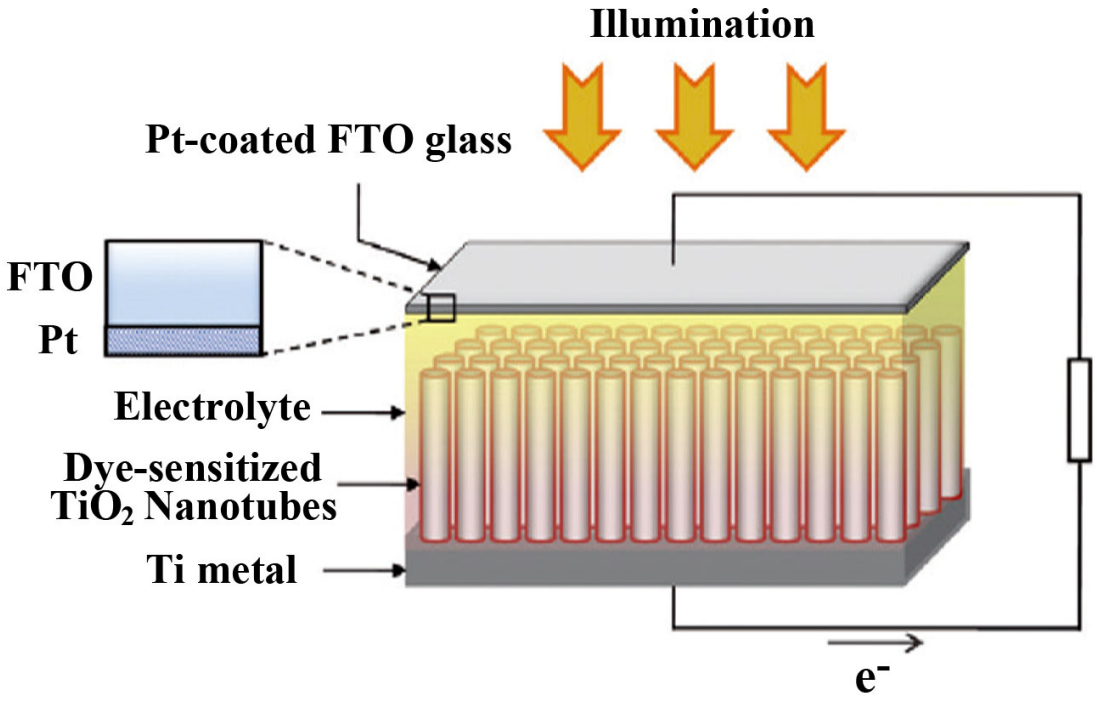

Figure 1. Schematic diagram of the back-side illuminated cell based on TiO_2 NTs grown on a Ti substrate.

From the direction of the incident light, the cell consists of the counter electrode with platinum black, electrolyte, dye-sensitized TiO_2 NTs, and Ti metal as the photoanode. The overall efficiency of this type of cell is suppressed due to the one-sided light injection mode and the relatively lower light transmission via the Pt black than the ITO. However, it offers a good platform for a systematic study of anodized TiO_2 NTs with identical initial conditions without harming the properties of any changes in the tubes.

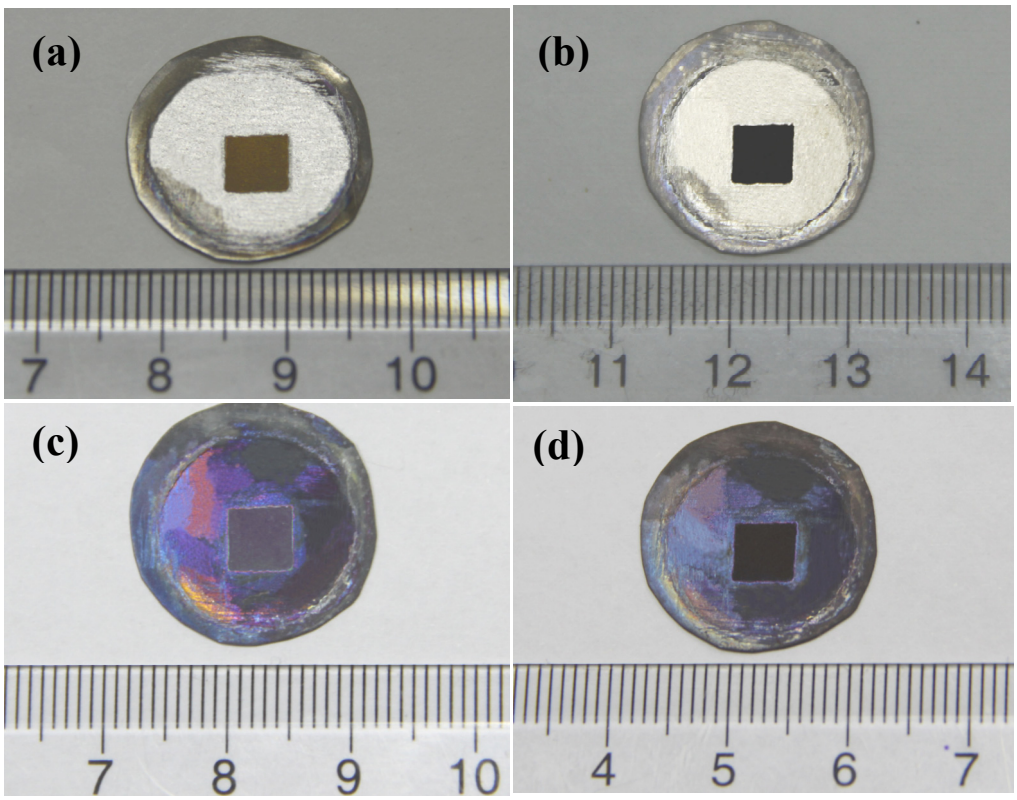

Figure 2. Digital images of TiO_2 NTs at different fabricating processes: (a) TiO_2 NTs grown on a Ti substrate after a secondary anodization, (b) TiO_2 NTs treated by HF aqueous solution, (c) crystallized TiO_2 NTs after the annealing, and (d) sensitized TiO_2 NTs with N719 solution.

Highly ordered TiO_2 NTs were prepared by anodization of a Ti sheet. The second anodization was performed at 180 V/180±5 V at 5 ^{o}C for 10 min. After being rinsed and aired as shown in Figure 2(a), the anodized Ti sheet was treated by HF. Obviously, as shown in Figure 2(b), the color of the TiO_2 NTs turned to black from yellow after HF treatment, which indicates the fluorination reaction occurred. After the annealing in air at 500 ^{o}C, the TiO_2 NTs were crystallized into anatase and became translucent as shown in Figure 2(c). Sensitized by N719 solution for 12 h, the TiO_2 NTs looked deep-carmine [see Figure 2(d)] due to the tubes and their secondary structures were full of dye molecule.

Table 1 Other data of photovoltaic characteristics of DSSCs in the same work. [a]

	growth and chemical treatment conditions	J_{SC}/ mA cm^{-2}	V_{OC}/ V	FF (%)	η (%)
plain cell	CV [b]	7.08	0.60	47.8	2.02
	CV	7.09	0.63	45.2	2.03
HF treatment	CV, 0.1%HF	9.16	0.59	39.6	2.16
	CV, 0.2%HF	9.74	0.67	37.8	2.48
	CV, 0.35%HF	8.53	0.70	45.7	2.71
	CV, 0.35%HF	8.46	0.70	46.0	2.72
	CV, 0.35%HF	9.02	0.72	42.6	2.76
	CV, 0.5%HF	6.54	0.67	42.0	1.84
$TiCl_4$ treatment	CV, $TiCl_4$	10.60	0.64	40.5	2.76
	CV, $TiCl_4$	10.72	0.63	40.7	2.76
	CV, $TiCl_4$	10.78	0.65	38.9	2.74
	CV, 0.1%HF, $TiCl_4$	11.46	0.65	40.5	3.01
	CV, 0.2%HF, $TiCl_4$	13.37	0.64	39.2	3.35
	CV, 0.35%HF, $TiCl_4$	16.89	0.66	32.7	3.68
	CV, 0.35%HF, $TiCl_4$	16.97	0.67	32.3	3.67
	CV, 0.35%HF, $TiCl_4$	17.40	0.68	31.3	3.69
	CV, 0.5%HF, $TiCl_4$	13.32	0.62	40.6	3.36
modulated conditions	CV, 0.35%HF, 600 rpm	10.97	0.59	52.6	3.42
	MV, [c] 0.35%HF, 100 rpm	14.32	0.56	46.9	3.74
	MV, 0.35%HF, 600 rpm	12.67	0.58	47.1	3.48
	MV, 0.35%HF, 100 rpm, $TiCl_4$	15.13	0.62	46.3	4.35
	MV, 0.35%HF, 100 rpm, $TiCl_4$	15.42	0.65	42.9	4.30
	MV, 0.35%HF, 100 rpm, $TiCl_4$	13.69	0.71	45.1	4.37

[a] All data were acquired in back-side illuminated DSSCs.

[b] constant voltage

[c] modulated voltage

Except the data existing in the text of the manuscript, other data of the DSSCs were included in the Table 1 in the electronic supplementary information. To avoid impacts from uncertain factors and make sure the experimental results are systematic and repeatable, each condition was tested by various samples. The values under identical conditions are quite close, showing that the experimental results are suitably reproducible.