Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

SUPPORTING INFORMATION for

Current Promoted Micro-Annealing in Anodic TiO_2 Tube Arrays and Its Application in Sensitized Solar Cells

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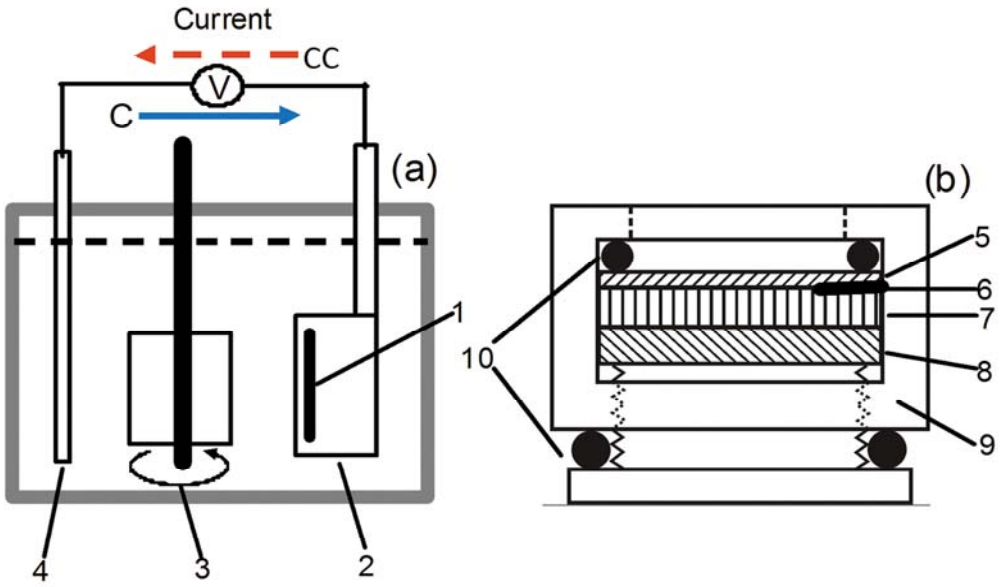

Figure S1 Schematic diagram of CPMA experiments: (a) side view of the setup: (1) Ti sheet, (2) sample chamber, (3) stirrer, (4) Cu electrode, (C) anodization mode, (CC) current injection mode; (b) sample chamber: (5) Ti sheet, (6) thermocouple, (7) copper electrode, (8) copper plate, (9) outer shell, (10) rubber O-ring.

The anodization of Ti was carried out in a two-electrode system shown in Figure S1 The Ti was mounted in a sample chamber made with Teflon. The polarity of the two electrodes could be switched in the anodization and current injection, respectively. A type K thermocouple was located beneath the Ti sheet to measure the temperature during the experiments.

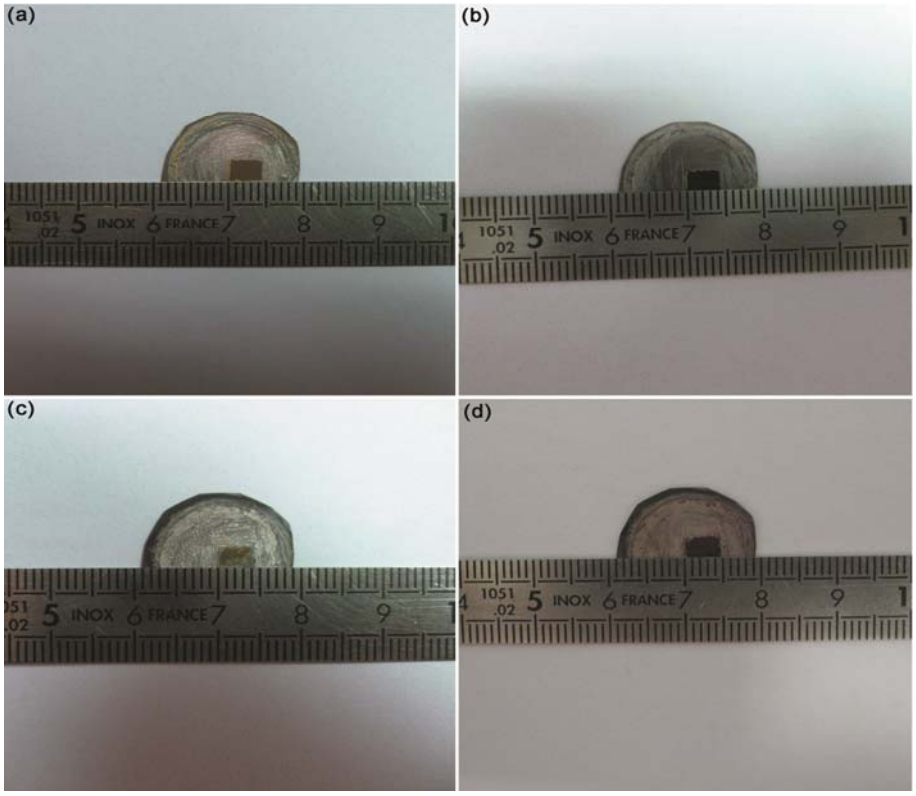

Figure S2 Digital images of TiO_2 NTs at different fabricating processes: (a) TiO_2 NTs grown on a Ti substrate after the secondary anodization, (b) TiO_2 NTs treated by HF aqueous solution, (c) crystallized TiO_2 NTs after the current annealing, (d) sensitized TiO_2 NTs with N719 solution.

Highly ordered TiO_2 NTs were prepared by anodization of a Ti sheet. The second anodization was performed at 160 V/160±5 V at 5 ^{o}C for 10 min. After being rinsed and aired as shown in Figure S2(a), the anodized Ti sheet was treated by HF. Obviously, as shown in Figure S2(b), the color of the TiO_2 NTs turned to black from yellow after HF treatment, which indicates the fluorination reaction occurred. After the current annealing, the TiO_2 NTs were crystallized into anatase and became translucent as shown in Figure S2(c). Sensitized by N719 solution for 12 h, the TiO_2 NTs looked deep-carmine [see Figure S2(d)] due to the tubes and their secondary structures were full of dye molecule.

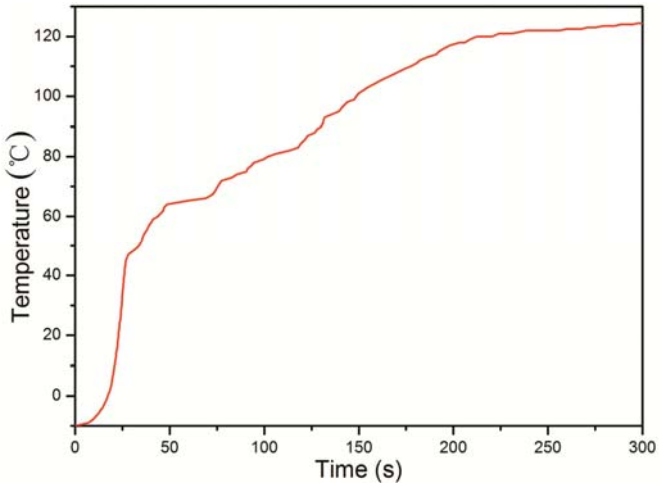

Figure S3 TiO_2 NTs sample temperature during current annealing in medium solution.

The typical temperature inside the sample chamber is shown in Figure S3, which was measured by a thermocouple implanted in the chamber below the Ti sheet. The sample temperature curve shows that the maximum temperature of the sample is less than 130 ^{o}C, while the low-temperature micro-annealing is happening during the process.

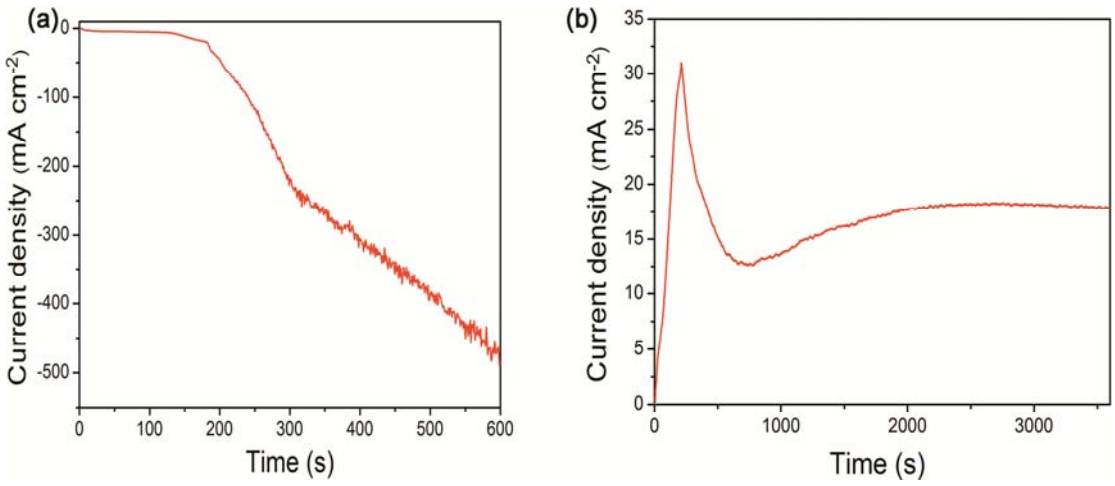

Figure S4 J-t curves during different processes of TiO_2: (a) during inversed current injection, at 300 V under -10 ^{o}C; (b) during spontaneous micro-annealing process, at 210 V under 5 ^{o}C.

The J-t curves were recorded during the anodization and current annealing experiments. Figure S4(a) has given the typical J-t characteristics during the current treatment. It can be seen that very strong current intensity has resulted during the short treatment. For comparison, Figure S4(b) has given the typical J-t curve during the spontaneous micro-annealing, in which the current was much lower.

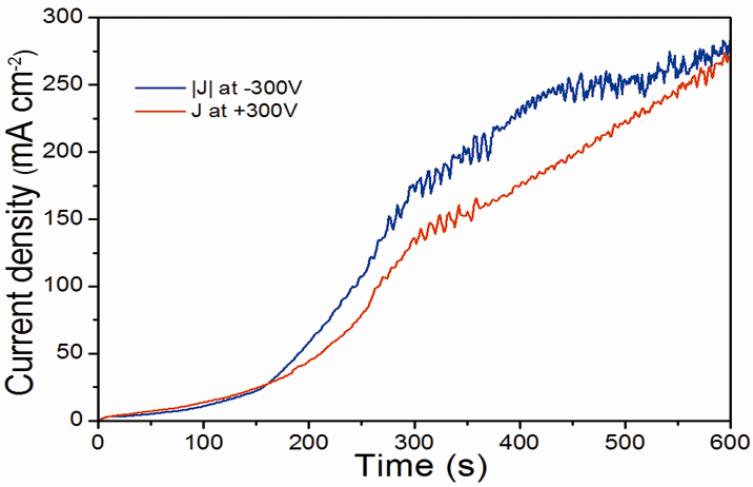

Figure S5 J-t curves with high potential applied from different directions on the electrochemical pool, t_{total} = 300s, plus 300s ramping at 1V/s.

To investigate possible influence from the semiconducting nature of the TiO_2 layer and Ti/TiO_2 interface on the conductance, +300V was also applied on the sample chamber and the J-t curve was recorded for comparison with the result from the inversed current injection of -300V. As shown in Figure S5, apparently there is no significant reduction if the sample chamber voltage was negatively biased compared to the case with positively biased voltage. The current was even a bit higher when the sample was negatively biased than the way vice versa.

Table S1 Data of photovoltaic characteristics of DSSCs in the work. [a]

	growth and chemical treatment conditions	J_{SC}/ mA cm^{-2}	V_{OC}/ V	FF (%)	η (%)
Plain cell	CV [b], -5 °C	7.71	0.47	40.48	1.34
	CV, -10 °C	11.24	0.52	35.82	2.05
HF treatment	CV, 0.05%HF, -10 °C	12.70	0.51	33.69	2.15
	CV, 0.10%HF, -10 °C	15.93	0.56	33.58	2.74
	CV, 0.15%HF, -10 °C	12.44	0.53	34.34	2.38
	CV, 0.20%HF, -10 °C	7.88	0.57	32.18	2.03
	CV, 0.35%HF, -10 °C	6.80	0.56	30.76	1.38
Modulated conditions	MV [c], 0.10%HF, -10 °C	13.02	0.66	45.30	3.51
	MV,0.10%HF, 450 °C	10.25	0.61	38.60	2.25

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

[b] constant voltage

[c] modulated voltage

Data of the DSSCs were included in the Table S1 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.