Supporting Information

Electrochemical Monitoring of TiO_2 Atomic Layer Deposition (ALD) by Chronoamperometry and Scanning Electrochemical Microscopy (SECM)

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Scheme S1. The protocol used to deposit TiO_2 films of different thicknesses

Serial number	Instruction	Position	Value	Unit
0	Flow of nitrogen	Nitrogen valve	20	sccm
1	Heat	Trap/pump line	150	deg C
2	Heat	Stop valve	150	deg C
3	Heat	Precursor manifold	150	deg C
4	Heat	Precursor cylinder	75	deg C
5	Heat	Outer chamber	150	deg C
6	Heat	Inner chamber	150	deg C
7	Stabilize	Trap/pump line		
8	Stabilize	Stop valve		
9	Stabilize	Precursor manifold		
10	Stabilize	Precursor cylinder		
11	Stabilize	Outer chamber		
12	Stabilize	Inner chamber		
13	Wait		300	sec
14	Pulse	Precursor cylinder	0.1	sec
15	Wait		20	sec
16	Pulse	Water cylinder	0.015	sec
17	Wait		20	sec
18	Go to	14	$25^{\$}$	cycles
19	Flow	Nitrogen valve	0	sccm

[\$] Number of this cycle was changed to have TiO_2 films of different thicknesses.

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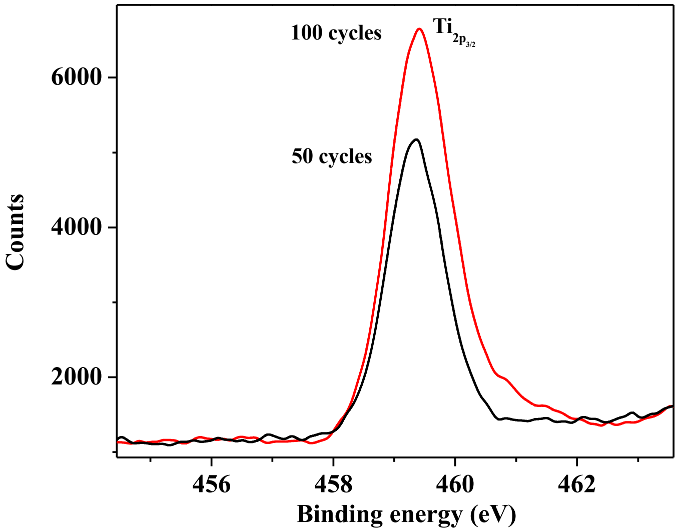

Figure S1. XPS result of TiO_2 deposited on ITO substrate for 50 and 100 cycles. XPS results have shown the signature of the Ti in the TiO_2 films deposited by ALD cycles.

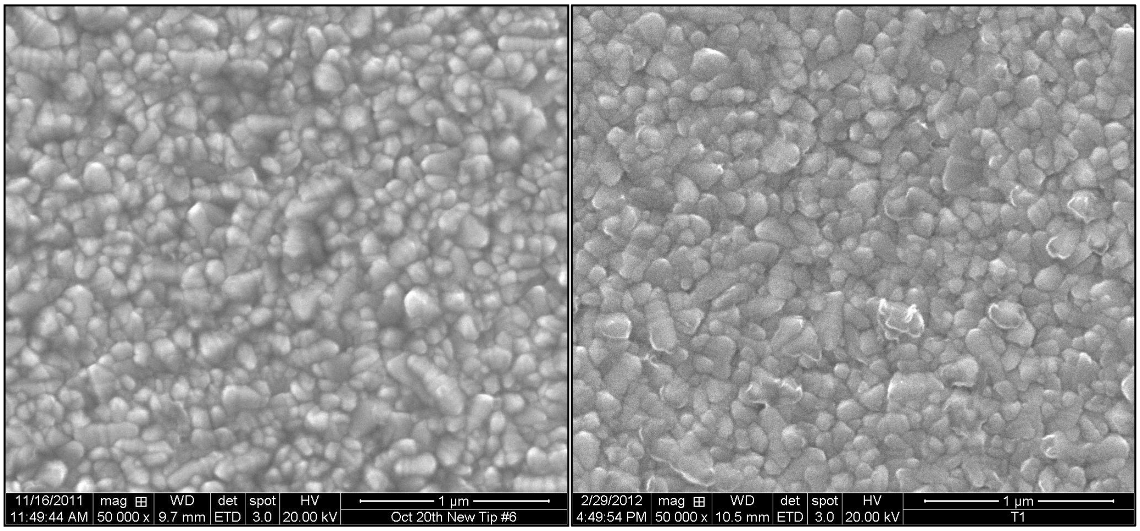

Figure S2. *Left*: SEM image of a Bare FTO substrate. *Right*: SEM image of TiO_2 deposited on FTO substrate after 50 ALD pulses.

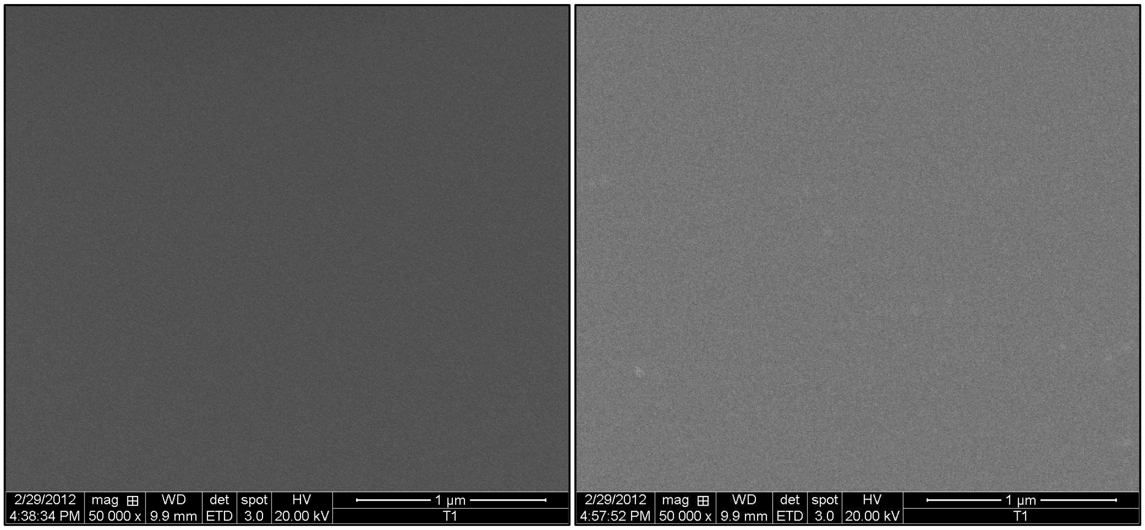

Figure S3. *Left*: SEM image of 30 nm thick Pt film deposited by sputtering on Si. *Right*: SEM image of TiO_2 deposited on same Pt substrate after 50 ALD pulses.

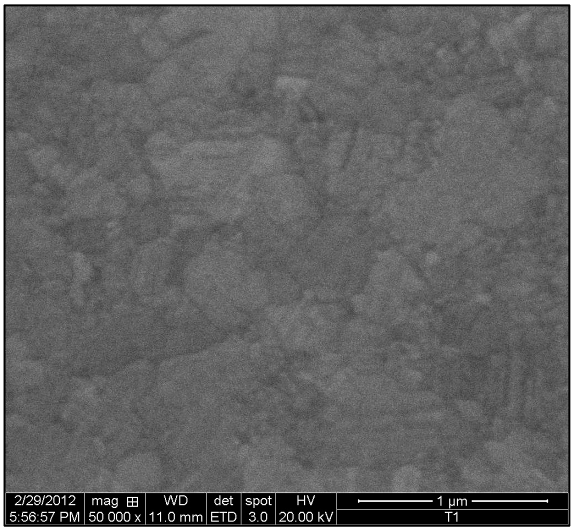

Figure S4. SEM image of TiO_2 deposited on 65 nm thick Ag film (on Si substrate) after 50 ALD pulses.

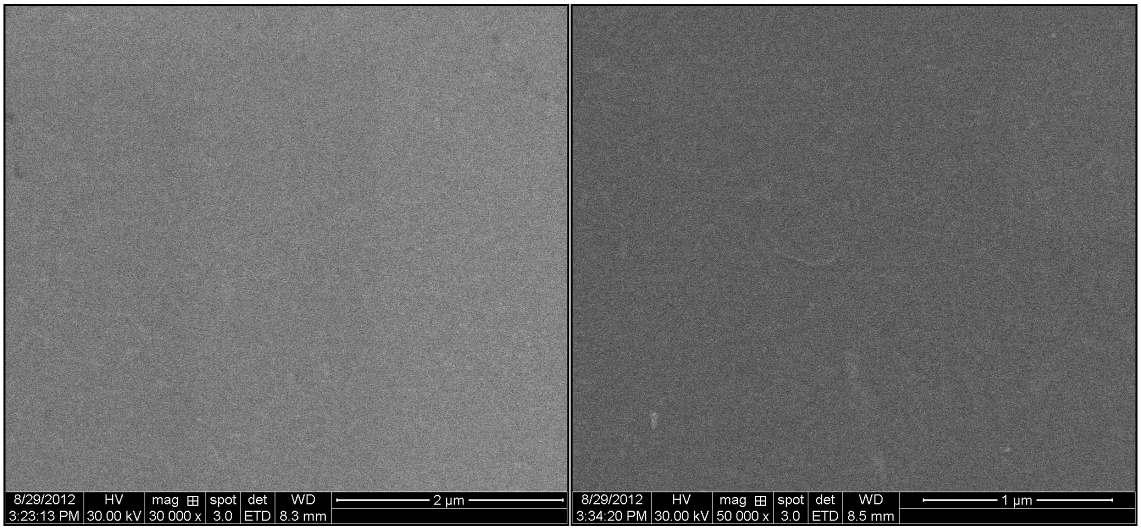

Figure S5. *Left*: SEM image of bare ITO substrate. *Right*: SEM image of TiO_2 deposited on ITO substrate after 50 ALD pulses.

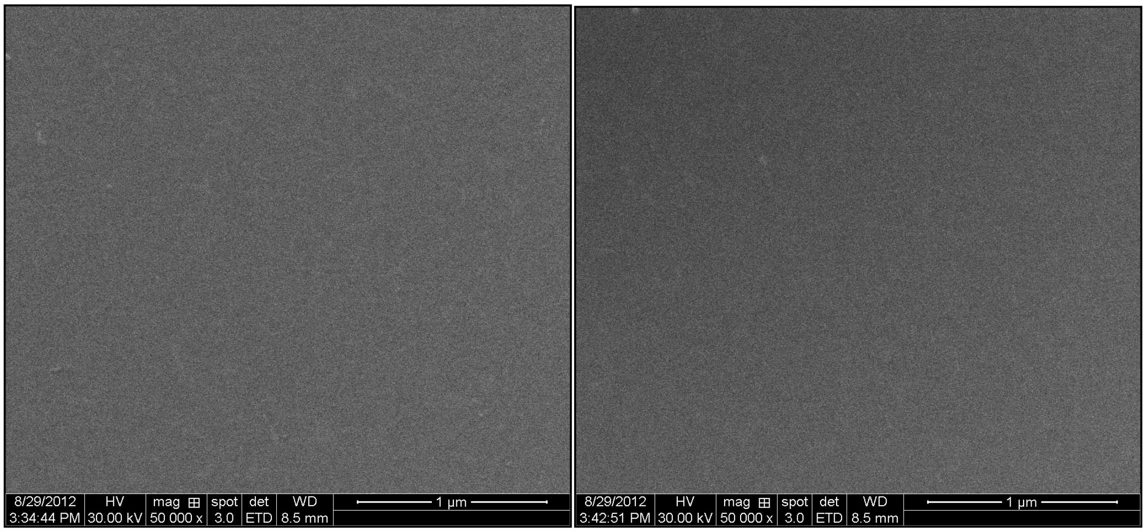

Figure S6. SEM image of TiO_2 deposited on ITO substrate after 75 (left) and 100 (right) ALD pulses.

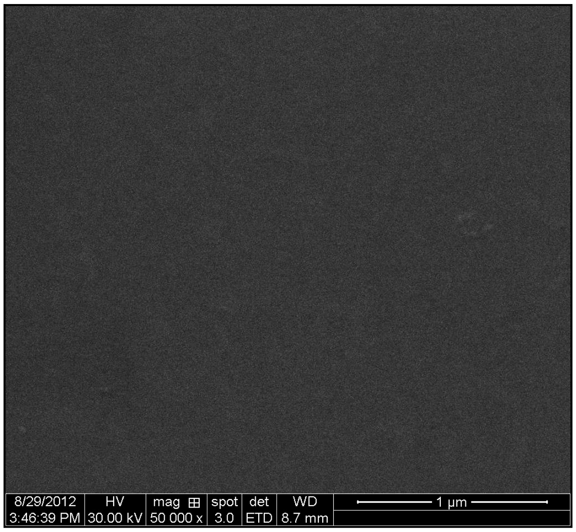

Figure S7. SEM image of TiO_2 deposited on ITO substrate after 125 ALD pulses.

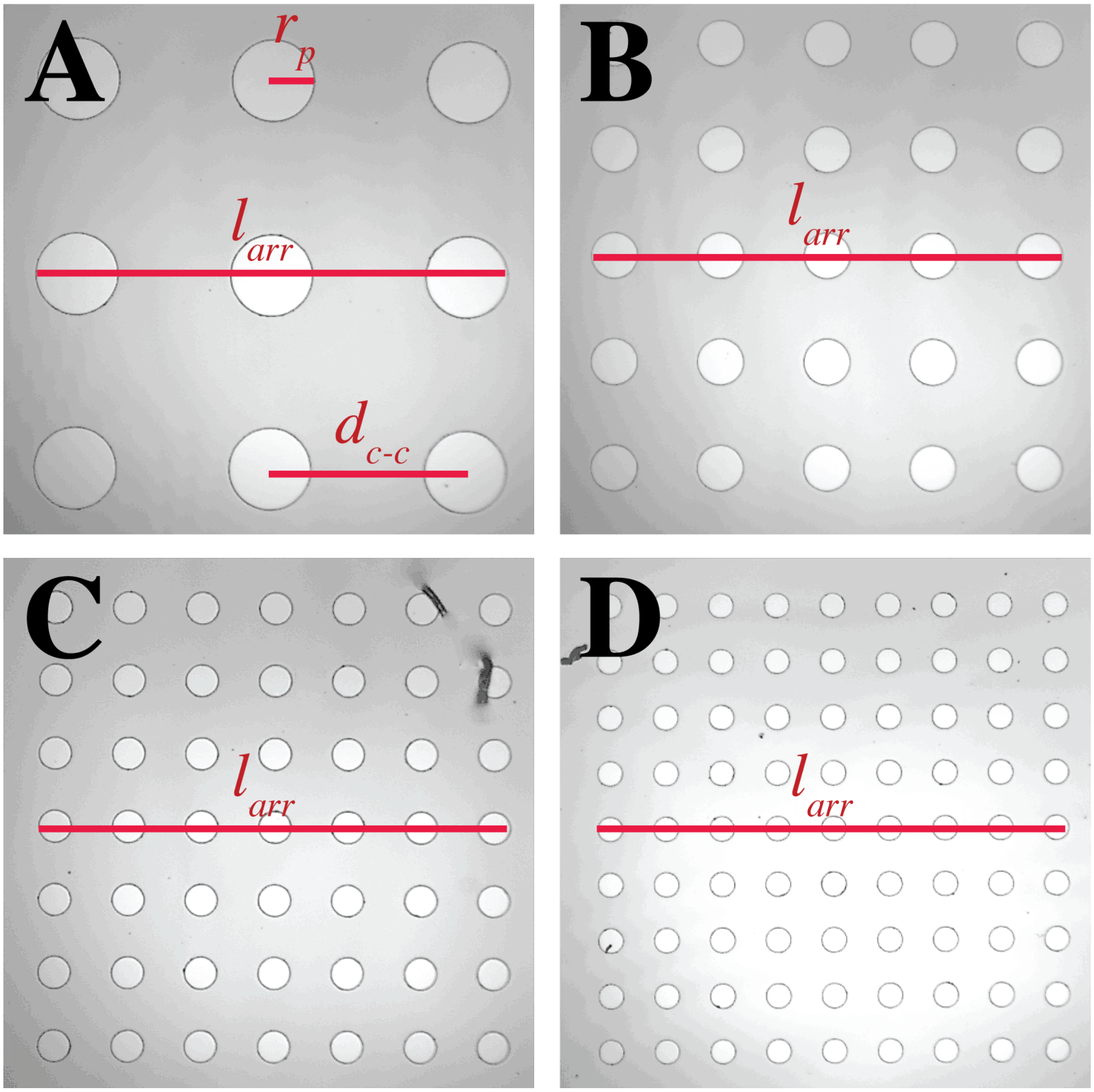

Figure S8. Optical images of microarray designs captured with a camera mounted on an inverted microscope. Each microarray has a defined number of pores, n_p: A = 9, B = 25, C = 49 and D = 81. The center-to-center distance separation between pores is $d_{\text{c-c}} = 5r_p$, where r_p is the radius of each pore. Pore radii varied as follows: A = 100 µm, B = 54.5 µm, C = 37.5 µm and D = 28.6 µm. The pore radii were adjusted to always give the same microarray length: l_{arr} = 600 µm. Dark features in images C and D are paper fibers that were not rinsed away before capturing the images.

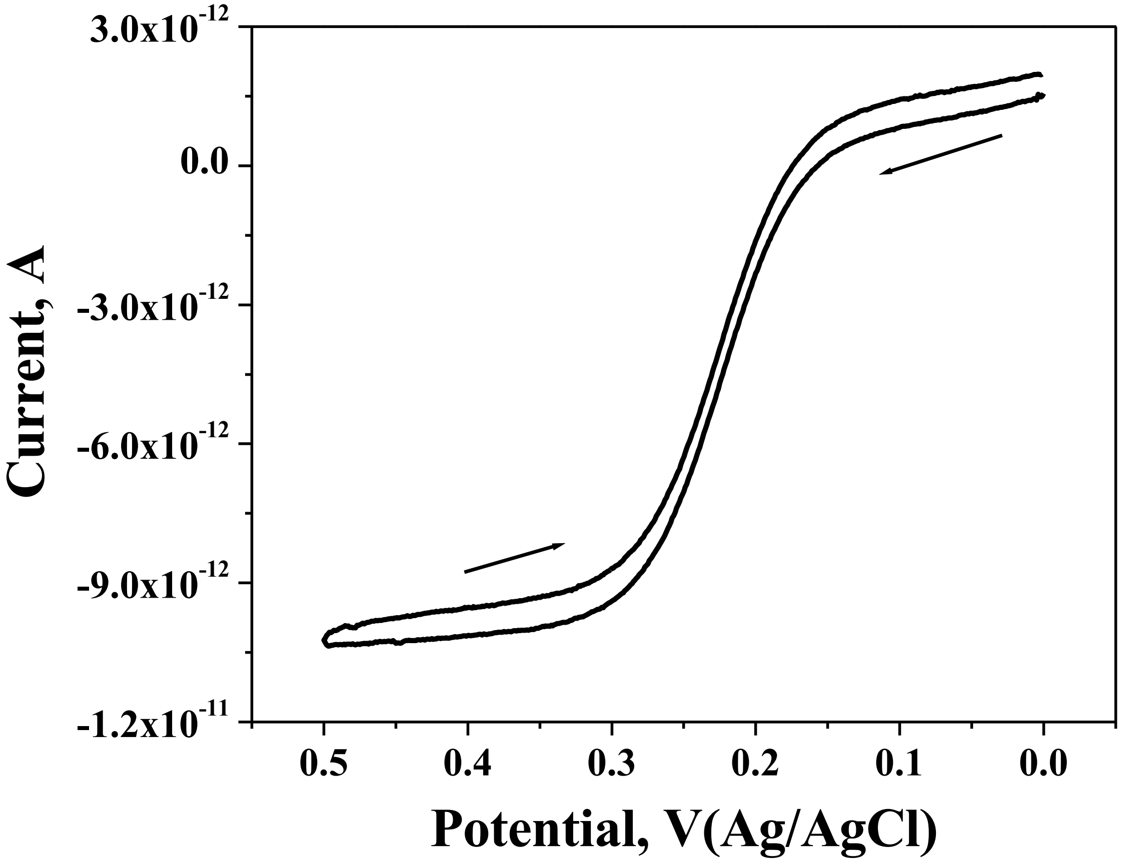

Figure S9. Cyclic voltammogram of 1 mM FcMeOH in 0.1 M $NaNO_3$ at Pt-nano electrode, *a* = 43 nm.

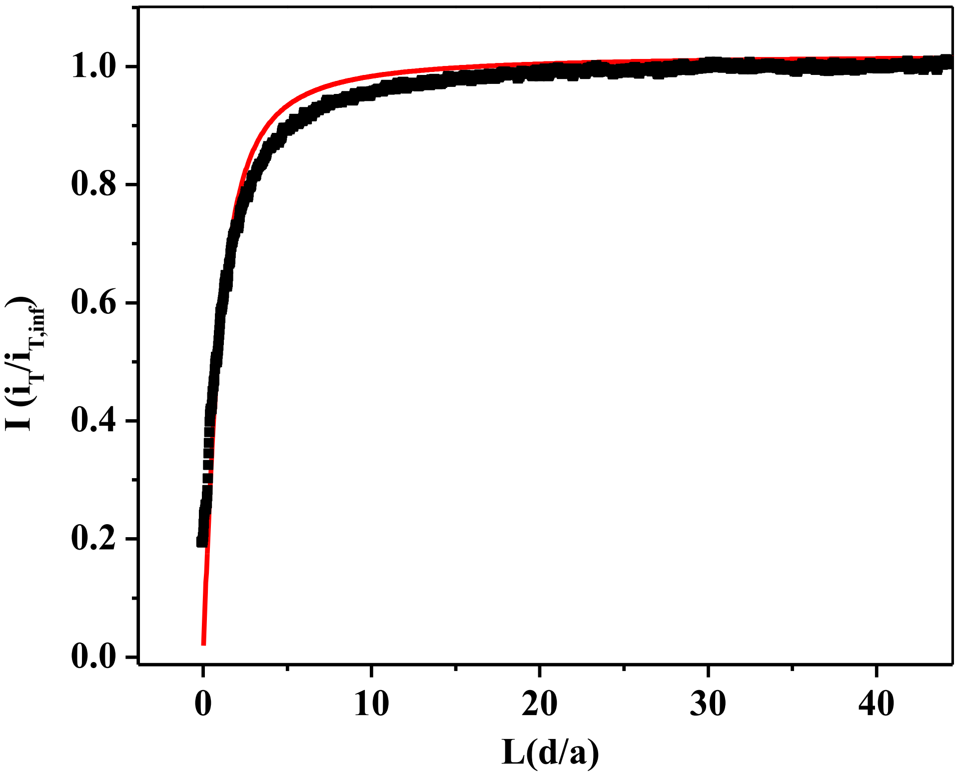

Figure S10. Approach curve with nano electrode, *a* = 43 nm, 1 mM FcMeOH in 0.1 M $NaNO_3$.

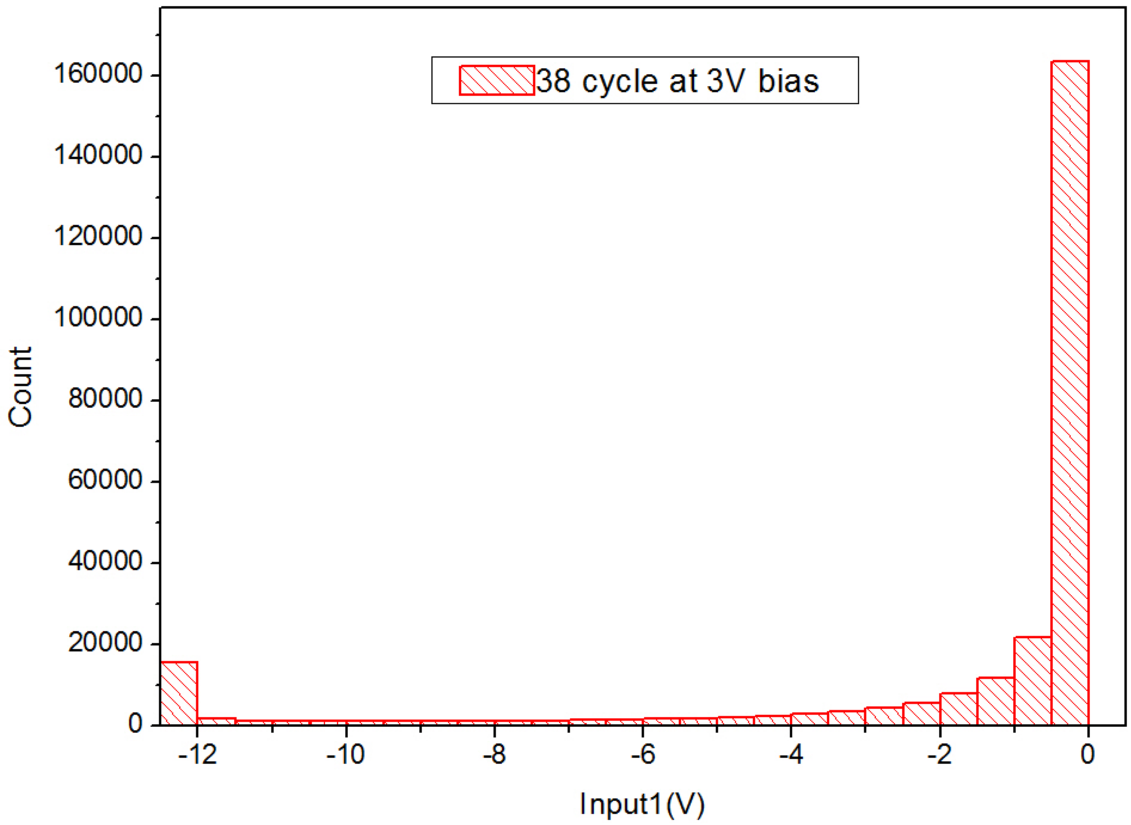

Figure S11. The AFM cantilever has scanned the TiO_2 on ITO surface measuring the voltage difference between the sample and the AFM tip. The imaged regions were 512 lines x 512 measurements per line, every 10 nm. So there are 262,144 points plotted in this figure. Voltages are converted to current by means of an I-V amplifier converter.