Low temperature atomic layer deposition of cobalt oxide as an effective catalyst for photoelectrochemical water splitting devices

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Table of Contents

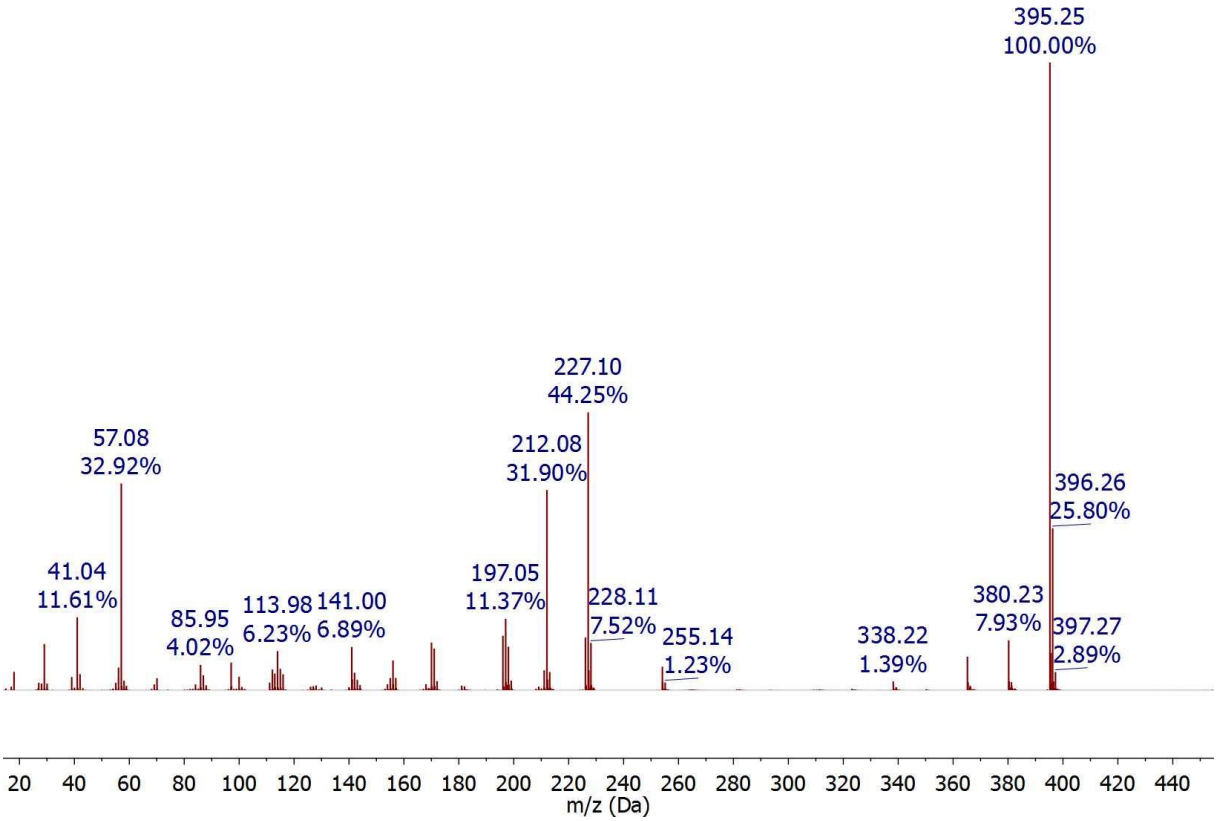
Figure S11 AFM image of Co_3O_4 deposited over 10 cycles at 120 °C on Si (100) substrate.

Figure S12 XPS spectra of Co_3O_4 thin films deposited over 10 cycles on Si and TiO_2 at 120 °C.

Figure S13 XRD patterns of TiO_2 deposited at 275 °C over 2000 cycles on FTO glass

Table S1 XPS surface distribution of Co, O, C, Ti and Si on samples deposited over 10 and 50 cycles on a 100 nm thick TiO_2 film and Si (100).

Figure S1 EI-MS fragmentation pattern of [Co(^{tBu2}DAD)$_2$].



The electron ionization mass spectrometry clearly identifies [Co(^{tBu2}DAD)$_2$] molecular ion peak at m/z 395.3.

Figure S2 Schematic depiction of the reaction chamber of F-120 ALD reactor (cassette configuration).

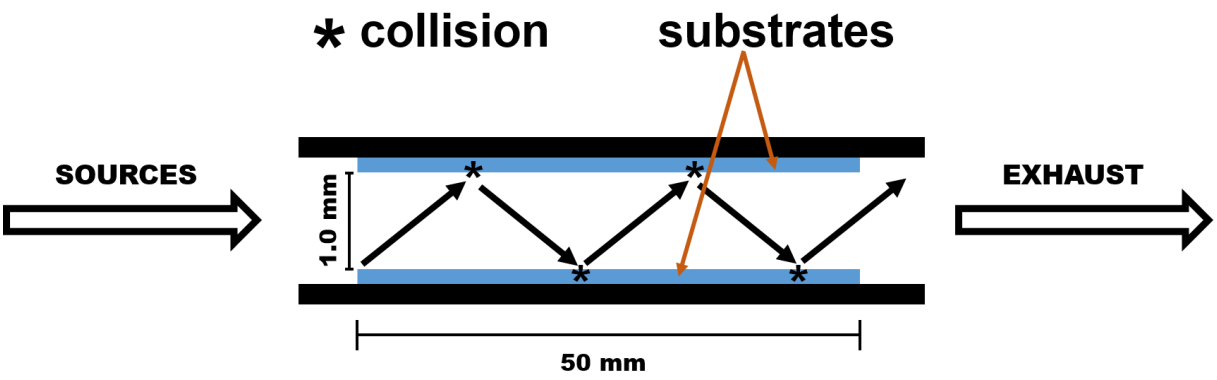


Figure S2. A schematic representation of the reaction chamber of the F-120 ALD reactor in the "cassette configuration". The dimensions of the schematic are not to scale.

Figure S3 Co_3O_4 film thickness vs distance from leading edge of the 5 x 5 cm^2 silicon substrate depending on the deposition temperature. All the samples were applied 300 deposition cycles.

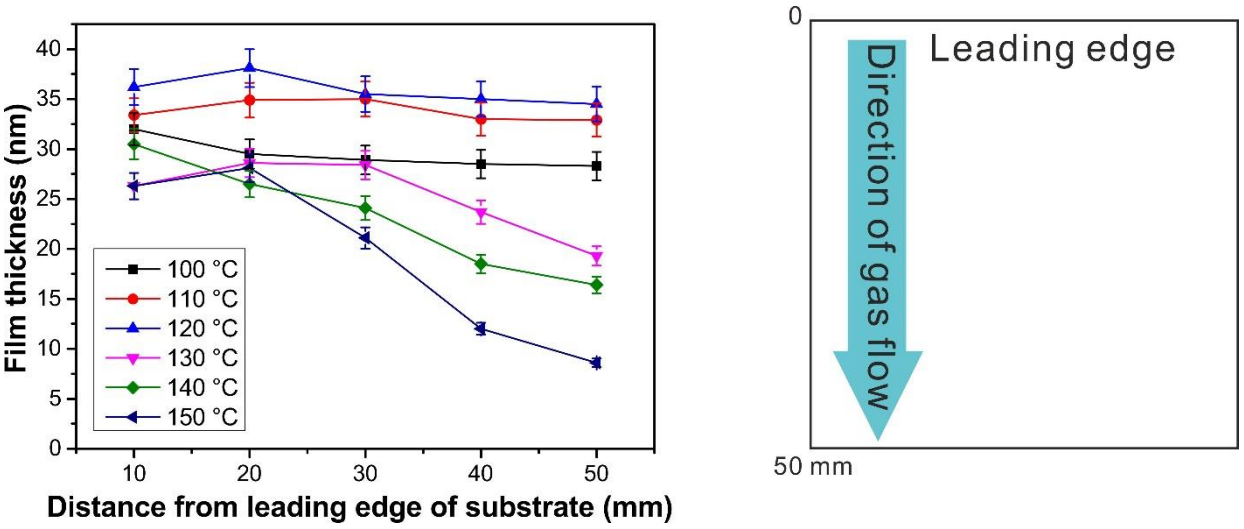
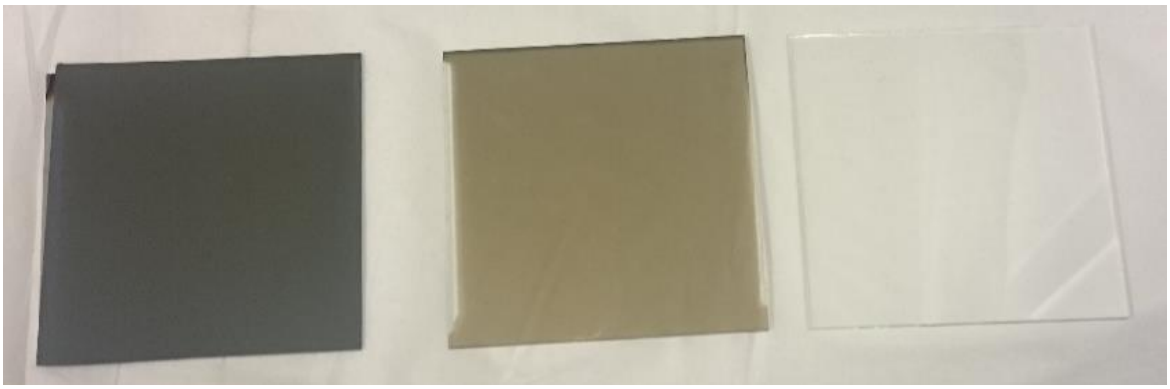


Figure S4 The photograph of Co_3O_4 thin film on Si and soda lime glass deposited at 120 °C over 300 cycles.



Co_3O_4 on Si (100) Co_3O_4 on soda lime glass Soda lime glass

Figure S5 Plane view SEM of Co_3O_4 thin film deposited over 1000 cycles at 120 °C.

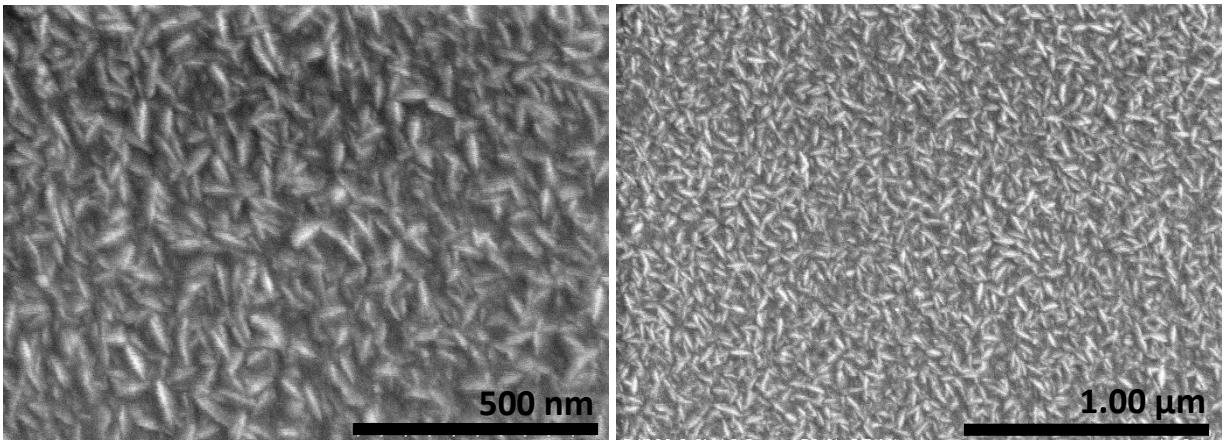
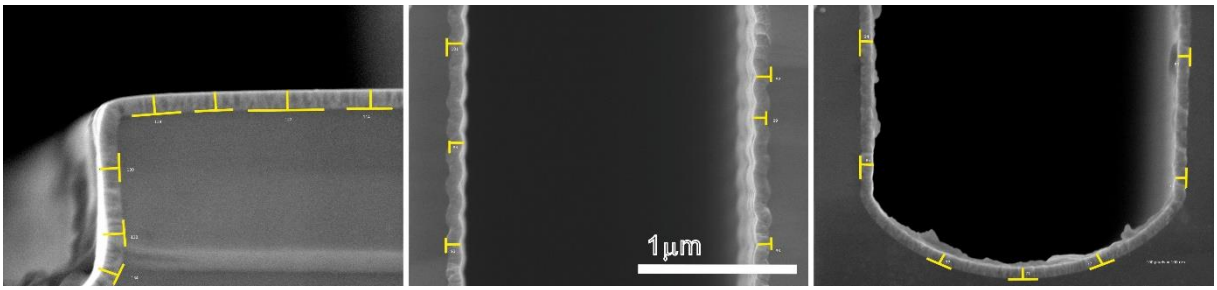


Figure S6 SEM image of Si trench with an aspect ratio of 20:1 (depth 40 µm, width 2 µm). Co_3O_4 film has been deposited over 1000 cycles at 120 °C using pulse lengths of 6 seconds for both $Co(^{tBu2}DAD)_2$ and ozone. The purge length for both precursors was 10 seconds.



Thickness(nm)	Top	Middle	Bottom
	114	101	84
	122	93	85
	111	93	77
	119	93	71
	130	89	77
	138	92	71
			80
Average thickness (nm)	122	94	78

Fully conformal Co_3O_4 films could not be deposited on 40 µm Si trenches (aspect ratio of 1:20) despite using 6 s pulse and 10 s purge times of both precursors. A conceivable explanation of for not achieving full conformality in the trench structure is the combined effect of ozone decomposing effect of Co_3O_4 and high surface area of the substrate.

Figure S7 XPS survey spectrum of Co_3O_4 thin film deposited over 1000 cycles at 120 °C.

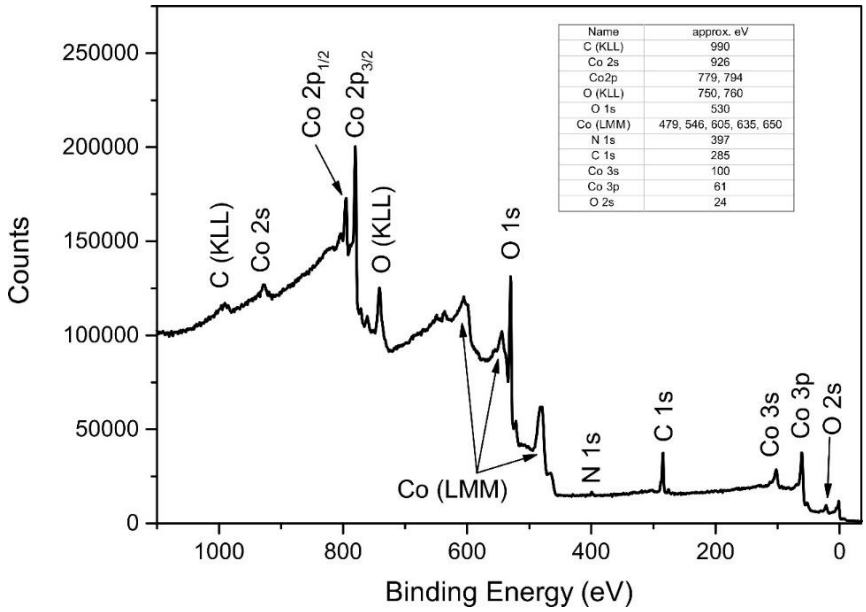
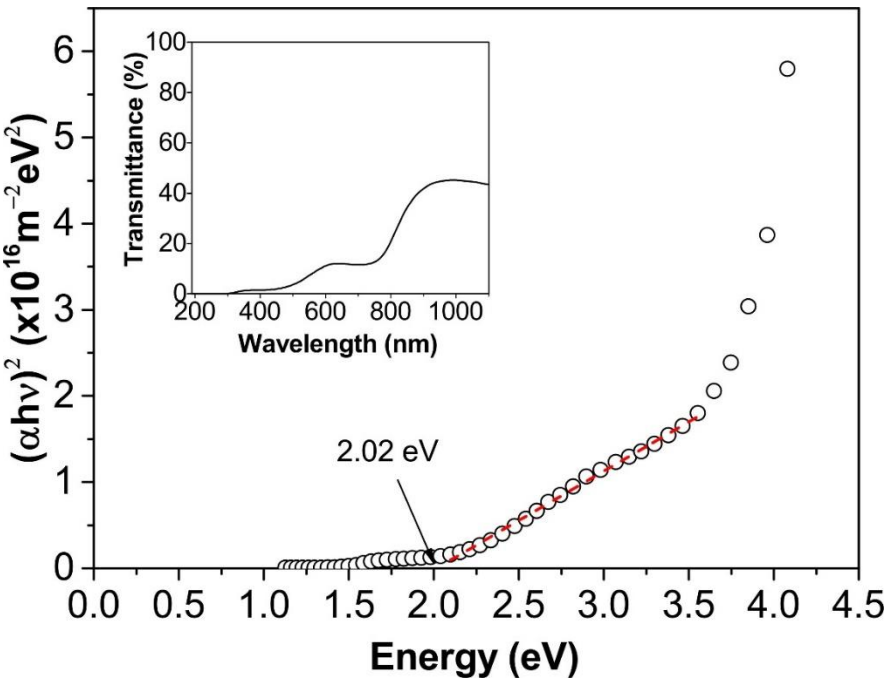


Figure S6 displays the XPS survey scan of Co_3O_4 that is dominated by cobalt and oxygen photopeaks. No Ar+ sputtering experiment was performed.

Figure S8 UV-Vis transmission spectrum and corresponding Tauc plot of Co_3O_4 thin film deposited over 1000 cycles at 120 °C.



UV-Vis spectroscopy was performed on the as-deposited Co_3O_4 film grown on soda-lime glass to determine the optical bandgap of Co_3O_4 thin films via Tauc plot. Obtained data indicated a direct band gap value of 2.02 eV.

Figure S9 UV-Vis transmittance plots of a 100 nm TiO_2 film (pristine TiO_2) modified by the depositing series of Co_3O_4 (10, 50, 100, 300, 500, and 10000 cycles) on the TiO_2 films.

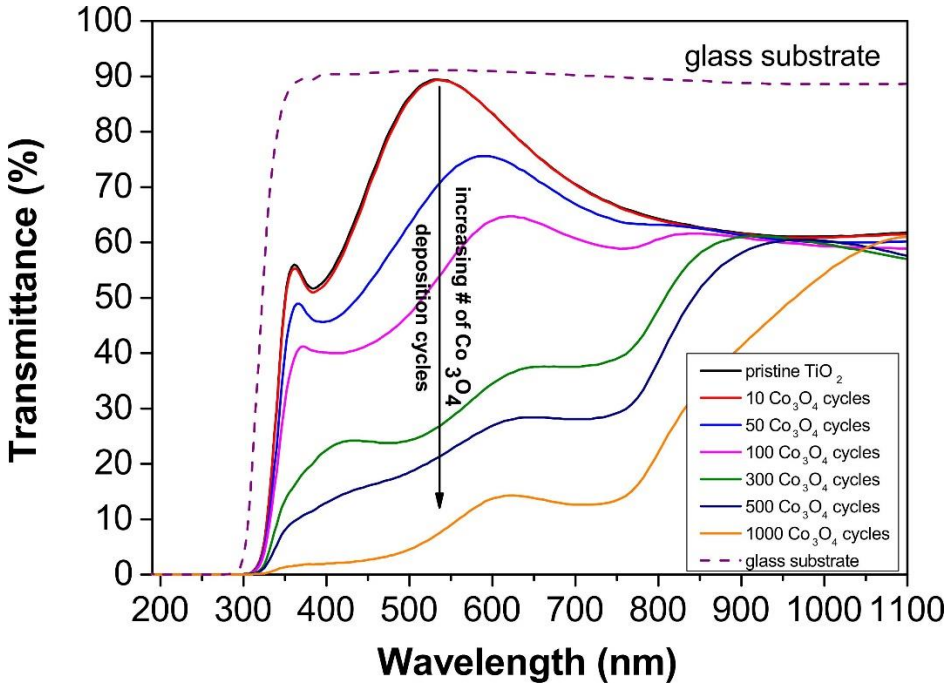


Figure S10 Photocurrent transients of TiO_2/Co_3O_4 structures on FTO glass with varying number of ALD cycles (10 – 1000) under irradiation at different wavelengths (a), selected transients (b, c), and the corresponding photoaction spectra (d) measured in KOH (0.1 M) at 1.48 V vs RHE at TiO_2 and TiO_2/Co_3O_4 photoanodes.

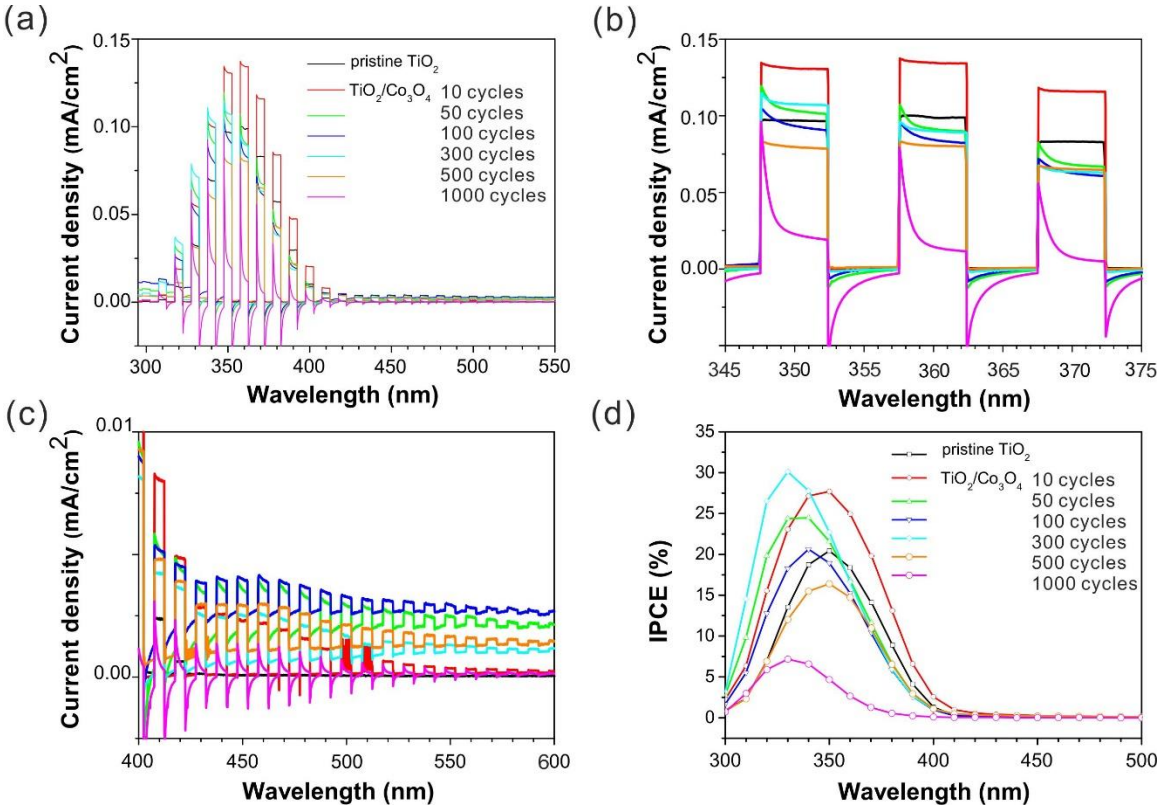

(a)
Current density (mA/cm2)
Wavelength (nm)
pristine TiO2
TiO2/Co3O4 10 cycles
50 cycles
100 cycles
300 cycles
500 cycles
1000 cycles
(b)
Current density (mA/cm2)
Wavelength (nm)
(c)
Current density (mA/cm2)
Wavelength (nm)
(d)
IPCE (%)
Wavelength (nm)
pristine TiO2
TiO2/Co3O4 10 cycles
50 cycles
100 cycles
300 cycles
500 cycles
1000 cycles

Figure S11 AFM images of Co_3O_4 deposited over 10 cycles (a,b) and 50 cycles (c,d) at 120 °C on Si (100) substrate. After 10 deposition cycles, island-like nanoparticles are formed instead of a closed film. After 50 deposition cycles, the island-like features are no longer present and a homogeneous and smooth surface is observed, indicating that a closed film has been formed. Images (a) and (b) were captured from different positions of a sample deposited over 10 cycles. Images (c) and (d) were captured from different positions of a sample deposited over 50 cycles.

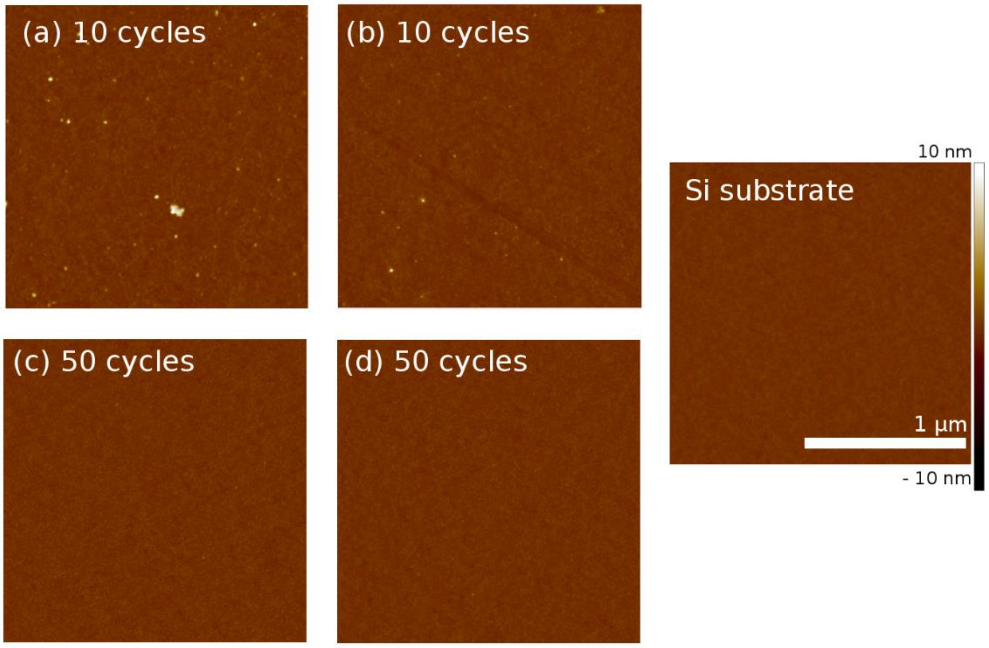


Figure S12 XPS spectra of cobalt oxide deposited over 10 and 50 cycles on a 100 nm thick TiO_2 layer and on Si (100) substrate at 120 °C.

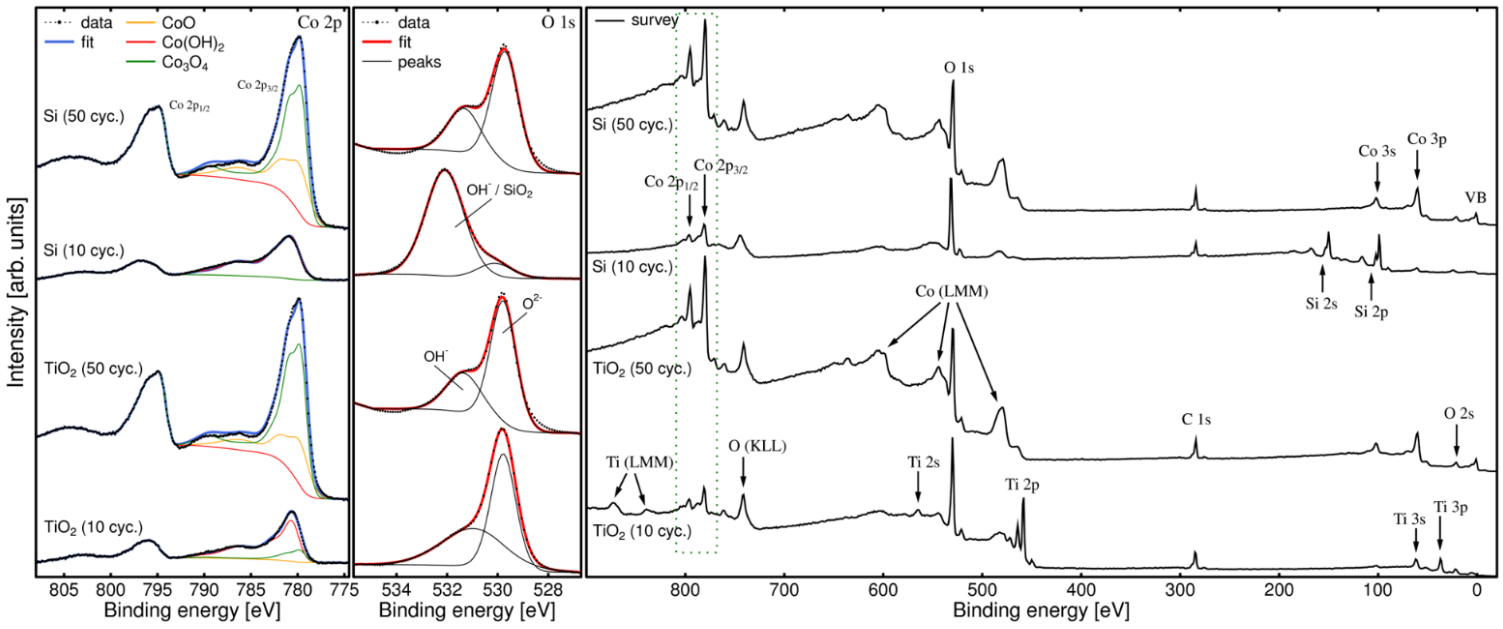
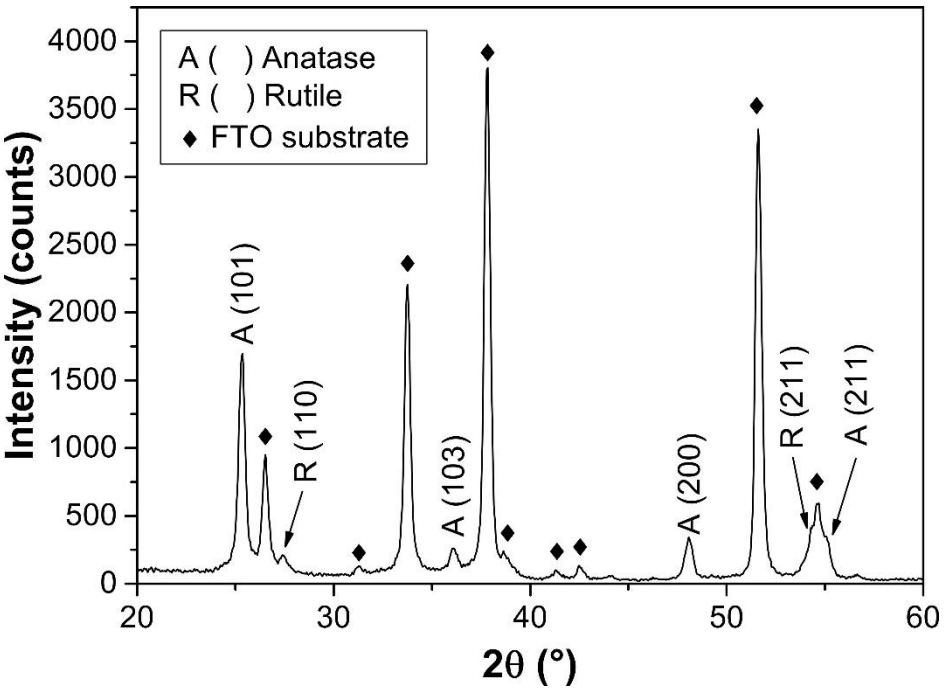


Table S1. XPS surface distribution of Co, O, C, Ti and Si on samples deposited over 10 and 50 cycles on a 100 nm thick TiO_2 film and Si (100).

In samples deposited over 10 cycles on Si (100) and TiO_2, the signal from the substrate is observed, indicating that the formed cobalt oxide film is not closed, but island-like nanoparticles are formed instead. After 50 deposition cycles on both Si (100) and TiO_2, the signal from the substrate is no longer observed, indicating that a closed layer has been formed.

							Co %			O %	
	Co	O	C	Ti	Si	Total	CoO	$Co(OH)_2$	Co_3O_4	O^{2-}	OH^-
10 cycles on TiO_2	4.82	44.38	41.38	9.43	0.00	100.01	24.90	52.28	22.82	51.17	48.83
50 cycles on TiO_2	14.41	47.92	37.37	0.00	0.00	100.00	50.94	0.00	49.06	41.39	58.31
10 cycles on Si (100)	3.80	33.01	25.34	0.00	37.86	100.01	35.53	57.37	7.11	16.69	83.31
50 cycles on Si (100)	13.15	47.42	39.43	0.00	0.00	100.0	39.62	0.23	60.15	37.03	62.97

Figure S13 XRD patterns of TiO_2 deposited at 275 °C over 2000 cycles on FTO glass



GI-XRD reflections of TiO_2 films deposited at 275 °C on FTO show mixed phases of anatase/rutile dominated by the anatase phase.[1]

References:

1. Ballirano, P.; Caminiti, R., Rietveld refinements on laboratory energy dispersive X-ray diffraction (EDXD) data. *J. Appl. Crystallogr*. **2001,** *34*, 757-762.