

SUPPORTING INFORMATION

WO₃ Nanorolls Self-Assembled as Thin Films by Hydrothermal Synthesis

S. Vankova^a, S. Zanarini^{a*}, J. Amici^a, Fernando Cámara^{b,c}, Rossella Arletti^{b,c},
S. Bodoardo^a, N. Penazzi^a

^a Department of Applied Science and Technology - DISAT, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy.

^b Dipartimento di Scienze della Terra, Università di Torino, via Valperga Caluso 35, 10125, Torino, Italy.

^c NIS Centre of Excellence, Università di Torino, Via Giuria 7, 10125 Torino, Italy.

Characterization techniques

CH Instrument 600D Station (galvanostat/potentiostat, CHI instruments, Austin, USA) was used for electrochemical and opto-electrochemical measurements, by registering current vs. potential and current vs. time curves. Cyclic voltammeteries of the cathodes were registered in 1 M Lithium bis-trifluoromethanesulfonimide (LiTFSI) in Propylene Carbonate (PC) with a standard three electrode cell with WO₃ nanorolls thin film on ITO glass as working electrode, a Platinum plate as counter electrode and an Ag/AgCl electrode as reference. Spectro-electrochemical measurements were carried out by placing the custom-made cell in the sample compartment of a Varian Cary 500 UV-VIS spectrophotometer. Two different types of measurement were performed by coupling the spectrophotometer with the CH 600D potentiostat. The first type of experiment was the registration of the complete UV-VIS absorption spectrum as function of applied potential; the second type of experiment consisted in the acquisition of the visible light absorption at a specific wavelength as function of time during potential modulation i. e. repeated bleaching and coloring cycles. The switching time for Bleaching (ST_B) and the switching time for coloring (ST_C) can be easily calculated from the T% vs. time curves by the time necessary after bias inversion to reach the 80% of the maximum (bleaching, oxidation) or minimum (coloring, reduction) T% starting from

previous potential step minimum or maximum T% respectively. The electrochemical impedance spectroscopy (EIS) response was analyzed in the frequency range 10 mHz - 1 MHz at the open circuit potential, using the previously described CH 600D potentiostat equipped with a proprietary fitting software.

The morphology of the products was observed by field emission scanning electron microscopy (FESEM, Hitachi S-4300SE). The crystallographic phases of the fabricated thin films were examined by X-ray diffraction (XRD, Philips X'pert MRD diffractometer) using Cu K α radiation. The size and crystal structure of the hydrothermally-grown WO₃ nanorolls were also confirmed by high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) using a JEOL Jem 3010 uhr, working at 300 kV, a LaB6 source and a Gatan CCD camera attached. Sample was dropped on a copper mounted holey carbon film.

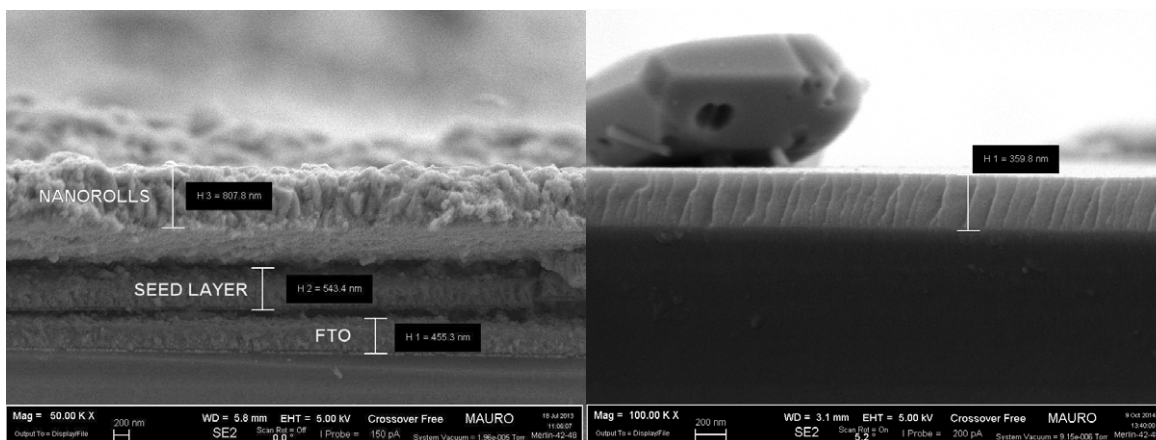


Figure S1. (left) FESEM micrograph showing the typical layer-by-layer aspect of the thin layer of WO₃ nanorolls obtained here. The seed layer was obtained with PVA of 85-124 000 u. m. a. ; (right) Cross section of a thin layer of WO₃ nanorolls with seed layer obtained with PVA of 31000-50000 u. m. a. .

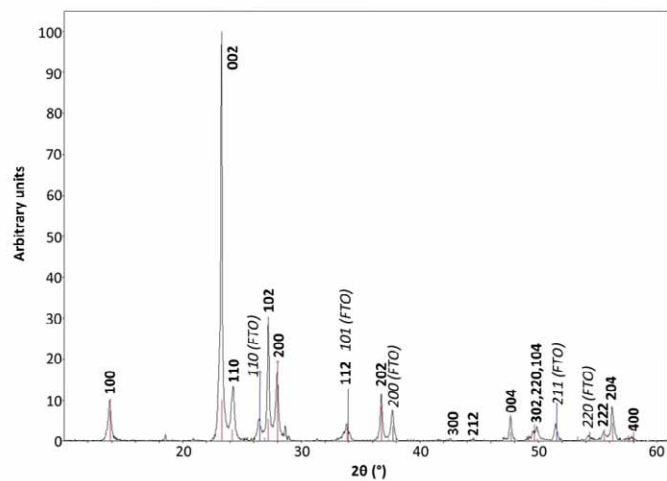


Figure S2. Typical XRD pattern of WO_3 nanorolls thin film on FTO/glass substrate.

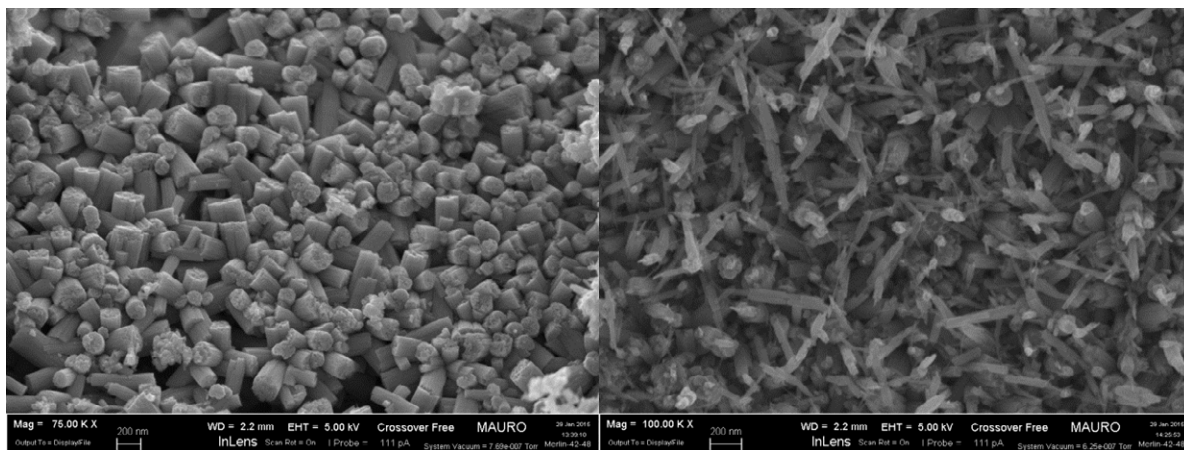


Figure S3. (Left) FESEM Picture showing the typical firewood-like fragmented WO_3 nanorolls (shorter PVA Chain) obtained by scratching away the thin layer on Lacey Carbon/200 nm Cu mesh; (right) FESEM shot showing the typical elongated and thinner structure of WO_3 NR on FTO glass (longer PVA chain).

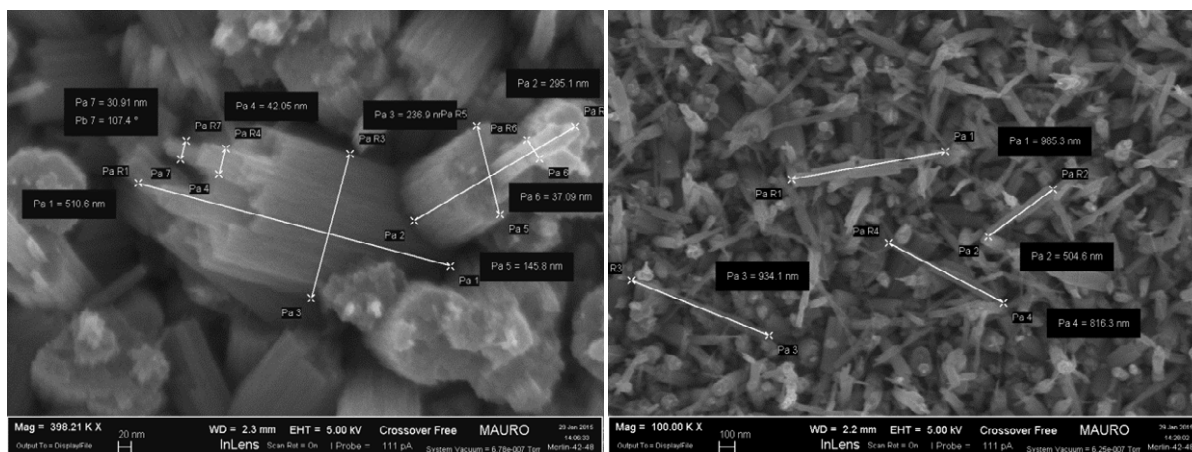


Figure S4. FESEM Pictures showing examples of measurement of diameter and length of the WO_3 NR obtained in different preparative conditions.

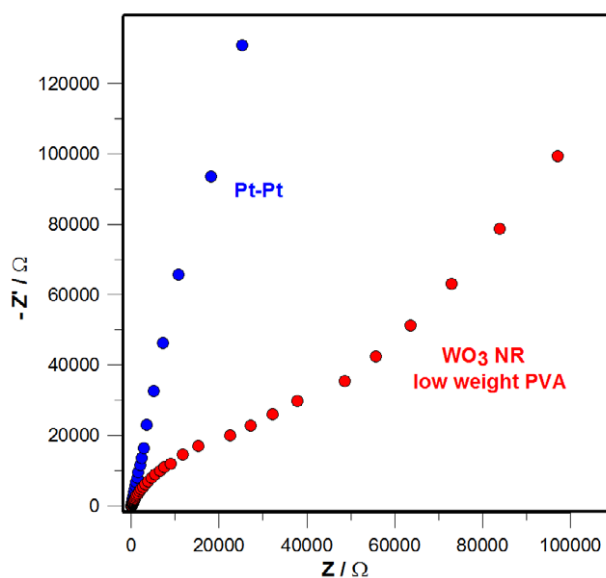


Figure S5. Typical Nyquist Plots at ambient temperature in PC 1M LiTFSi solution. Electrodes setup: (blue dots) Pt plate | Pt plate | Ag/AgCl reference and (red dots) WO_3 nanorolls/FTO | Pt plate | Ag/AgCl reference. Frequency range: 10 mHz - 1 MHz at the open circuit potential.

PVA Chain weight / UMA	Overall WO_3 NR length / nm	Log portion length / nm	Log portion diameter / nm	Tip portion diameter / nm
31000-50000	300-650	200-600	200-300	20-50
85000-124000	500-900	200-500	75-150	20-50
146000-186000	750-1300	650-1200	75-150	20-50

Table S1. Indicative diameter and length of WO_3 NR by varying PVA chain length in seed layer preparation. These range values are based on 20 single NR measurements taken by FESEM pictures.

WO ₃ NR/ glass FTO	Cycle nr. 5	Cycle nr. 2000
ST _B ^I	8 s	8 s
ST _C ^{II}	9 s	9 s
ΔT%(550 nm)	26 %	21 %
ΔT%(700 nm)	33 %	27 %

^I Switching Time of bleaching for 80% ΔT%max at 550 nm by applying a potential of -2 to 0V vs. Ag/AgCl.

^{II} Switching Time of coloring for 80% ΔT%max at 550 nm by applying a potential of 0 to -2V vs. Ag/AgCl.

Table S2. Effect of 2000 cycles of electrochemical switching on the ST_B, ST_C and ΔT% of WO₃ nanorolls . Electrolyte: LiTFSI 1 M in Propylene Carbonate. Electrodes setup: Nanorolls film on glass FTO (low M.W. PVA) as Working, Platinum plate as counter and Ag/AgCl electrode as reference. Potential program: E₁= +0 V, E₂= -2 V; t₁=t₂=40 s.

Nanocrystal type	Coloration Efficiency η (cm ² C ⁻¹) [*]
WO ₃ nanoflakes	60±8
WO ₃ nanorolls (M.W. PVA= 31000-50000)	67±6
WO ₃ nanorolls (M.W. PVA= 85000-124000)	53±5
WO ₃ nanorolls (M.W. PVA= 146000-186000)	39±7

* based on 5 different samples of each type

Table S3. Coloration Efficiency of the WO₃ NR produced by HT synthesis in different conditions and comparison with WO₃ nanoflakes produced by the Su method.