Supporting Information

Cellulose Nanocrystal-Templated Tin Dioxide Thin Films for Gas Sensing

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Table S1. Composition and molar ratios of $SnCl_4$ solutions prepared for NMR analysis.

Sample	$SnCl_4$ ml	EtOH ml	H_2O ml	NH_4OH 2M ml	$HCl_{conc.}$ ml	Molar ratio Sn^{4+}/EtOH/H_2O/OH^-/HCl
neutral	0.35	4.0	-	-	-	1/28.72/0/0/0
neutral + H_2O	0.35	4.5	0.2	-	-	1/27.57/3.72/0/0
acidic	0.35	-	-	-	1.0	1/22.98/0/0/10.25
basic 1	0. 35	4.95	0.2	0.3		1/28.43/3.72/0.20/0
basic 2	0.4	4	0.4	0.59	-	1/20.09/6.50/0.35/0
basic 3	1.8	4	0.8	2	-	1/4.5/3.0/0.26/0

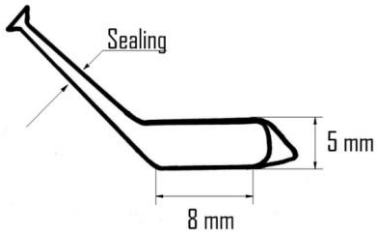

Figure S1. Schematic of a glass ampule used as a sample container for the ^{119}Sn static solid-state NMR measurements.

Table S2. ^{119}Sn shift values of different tin compounds

Species	$\delta(^{119}Sn)$/ppm	Reference	Remarks
$(C_2H_5)_3SnCl$	-153	1	
	-151	2	
$CH_3Sn(OC_2H_5)_3$	-434	3	
$R_2Sn(OR')_3$	-160	3	five coordinated
	-30	3	four coordinated
$(C_2H_2)_2SnCl$	-62	2	in $(CH_3)_2CO$
SnO_2	-604.3	4	MAS
$SnCl_4$	-150	1, 3, 5	
$Sn(OH)_4$	-590	6	$Sn(OH)_4$ in perchloric acid
	-580..-630	6	OH- bridged structures
$Sn(OH)_6^{2-}$	-590	7	
$[Sn(NCS)_6]^{2-}$	-842	8	in CH_2Cl_2
$[Sn(CN)_6]^{2-}$	-916	8	in CH_2Cl_2
$[SnCl(H_2O)_5]^{3+}$	-620	6	
$[SnCl(NCS)_5]^{2-}$	-810	8	
$[SnCl_2(H_2O)_4]^{2+}$	-623	7	
	-627..-621	7	
$[SnCl_2(NCS)_4]^{2-}$	-783	8	cis
$[SnCl_2(CN)_4]^{2-}$	-800	8	Cis

Species	$\delta(^{119}Sn)$/ppm	Reference	Remarks
$[SnCl_3(H_2O)_3]^+$	-631..-636	[6]	
	-614	[7]	cis
	-618	[7]	trans
	-600	[7]	
$[SnCl_3(NCS)_3]^{2-}$	-765	[8]	mer
	-767	[8]	fac
$[SnCl_3(CN)_3]^{2-}$	-760	[8]	mer
	-773	[8]	fac
$[SnCl_4(H_2O)_2]$	-648	[6]	
	-647	[6]	cis
	-669	[6]	trans
	-655	[9]	
	-658	[9]	
	-630	[9]	
$[SnCl_4(NCS)_2]^{2-}$	-740	[8]	trans
	-749	[8]	cis
$[SnCl_5(H_2O)]^-$	-677	[6]	
	-660	[7]	
$[SnCl_5(NCS)]^{2-}$	-734	[8]	
$[SnCl_5(CN)]^{2-}$	-728	[8]	
$[SnCl_6]^{2-}$	-720	[6]	
	-732	[9]	
	-700	[7]	
	-731	[8]	
	-734	[8]	
$SnBr_4$	-638	[2, 1]	
	-623	[9]	
$[SnBr(H_2O)_5]^{3+}$	-722	[6]	
$[SnBr(NCS)_5]^{2-}$	-946	[8]	
$[SnBr(CN)_5]^{2-}$	-1052	[8]	
$[SnBr_2(H_2O)_4]^{2+}$	-873	[6]	
	-895	[6]	
$[SnBr_2(NCS)_4]^{2-}$	-1098	[8]	trans
$[SnBr_2(CN)_4]^{2-}$	-1168	[8]	cis
	-1094	[8]	trans
$[SnBr_3(H_2O)_3]^+$	-1094	[6]	
	-1105	[6]	
	-1162	[6]	
$[SnBr_3(NCS)_3]^+$	-1311	[8]	fac
	-1295	[8]	mer
$[SnBr_3(CN)_3]^{2-}$	-1308	[8]	fac
	-1285	[8]	mer
$[SnBr_4(H_2O)_2]$	-1350	[6]	
	-1358	[6]	cis
	-1455	[6]	trans
$[SnBr_4(NCS)_2]^{2-}$	-1515	[8]	trans
	-1547	[8]	cis

Species	δ(^{119}Sn)/ppm	Reference	Remarks
$[SnBr_4(CN)_2]^{2-}$	-1543	8	trans
	-1482	8	cis
$[SnBr_5(H_2O)]^-$	-1650	6	
$[SnBr_5(NCS)]^{2-}$	-1786	8	
$[SnBr_5(CN)]^{2-}$	-1691	8	
$[SnBr_6]^{2-}$	-2064	9	
	-2067	8	
	-2076	8	
	-2073	6	in CH_2Cl_2
	-1965	6	in water with LiBr

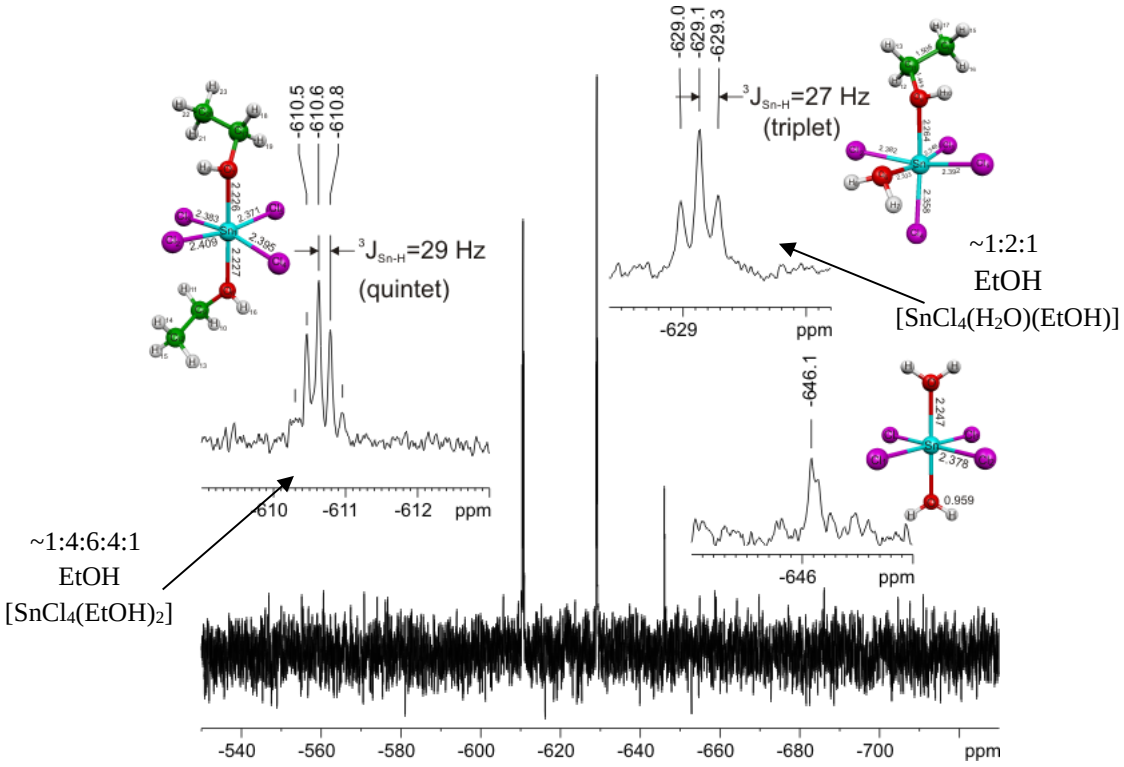

Figure S2. ^{117}Sn MAS NMR of $SnCl_4$ in ethanol measured at 210 K, sample spinning frequency 1000 Hz.

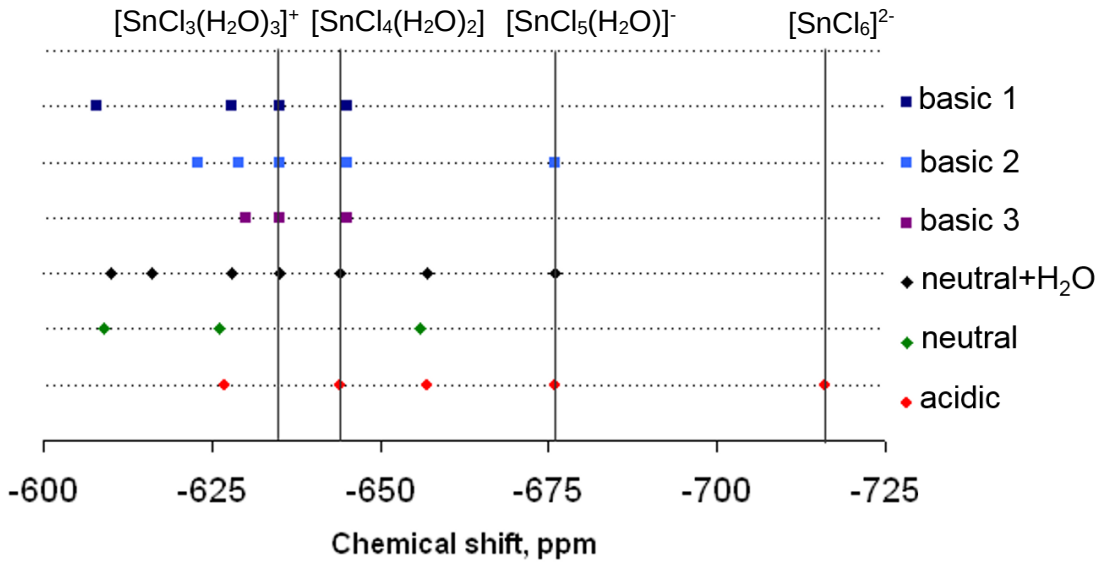

Figure S3. ^{119}Sn static low-temperature NMR signal maxima at 190 K recorded on tin (IV) chloride solutions dissolved in ethanol (neutral), with addition of water (neutral+H_2O), base (basic 1,2,3) or acid (acidic).

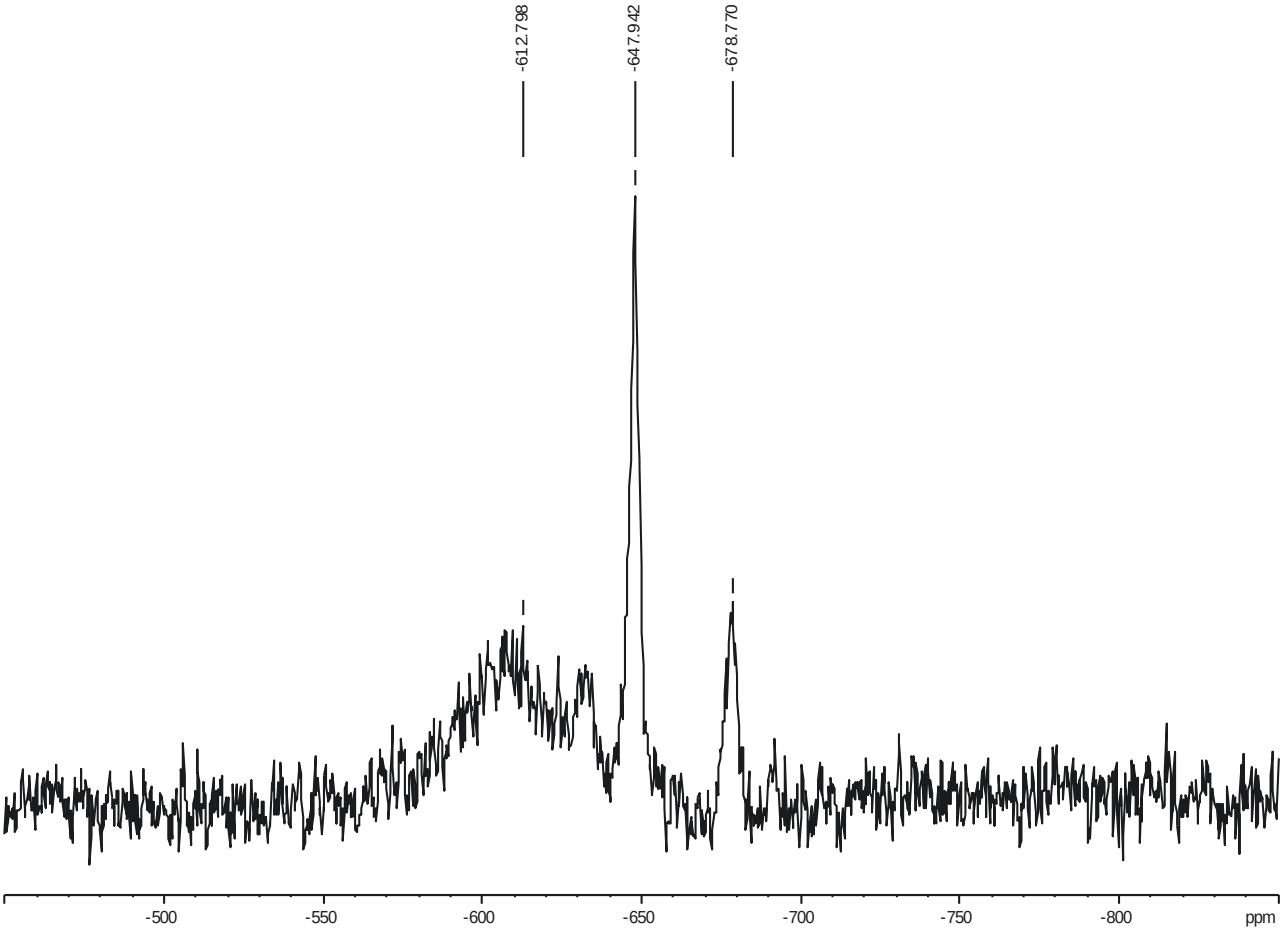

Figure S4. ^{119}Sn static NMR at RT of a "basic 3" sample ($SnCl_4$/EtOH/H_2O/NH_4OH).

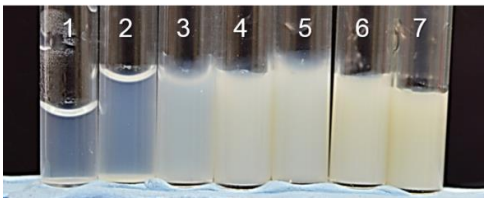

Figure S5. A photograph showing mixed CNC-tin tetrachloride colloids in glass vials (d=0.5 cm): (1) 2 wt% CNCs in water, (2) 0.2 M $SnCl_4$ in water, (3) 0.2 M $SnCl_4$ and 2 wt% CNCs in water, (4) 0.2 M $SnCl_4$ and 2 wt% CNC in EtOH, (5) 0.2 M $SnCl_4$, CNC 2 wt% and 0.5 M HCl, (6) 0.2 M $SnCl_4$, CNC 2 wt% and 0.5 M NaOH, (7) CNC and $SnCl_4$ in water after overnight stirring, 0.2 M $SnCl_4$, CNC 2 wt%.

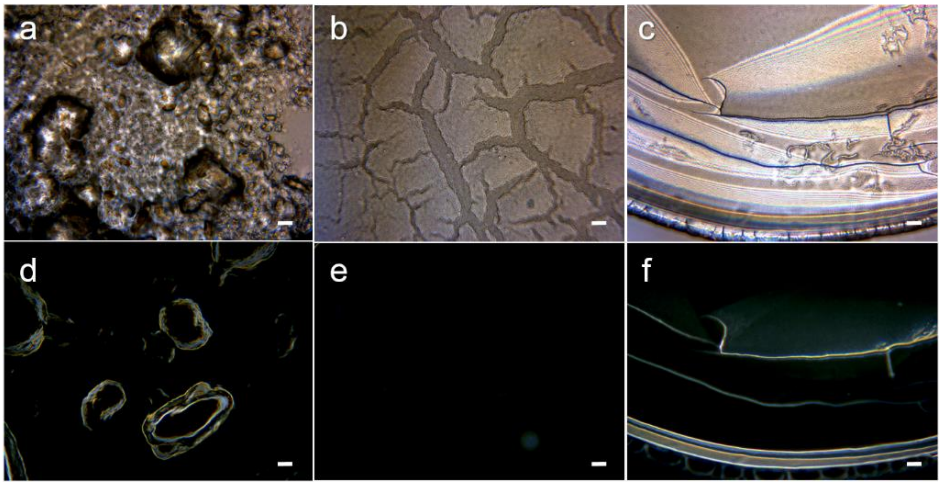

Figure S6. Optical microscopy bright (a-c) and dark field (d-f) images of tin tetrachloride and CNC aqueous suspension (0.2 M $SnCl_4$, 2 wt% CNC) cast on a glass slide after 1 h (a) and overnight stirring (b, c). Samples were imaged in the middle of a dried droplet (a, b) and at the edge (c). The dark field images reveal aggregates (d) and film cracking at the edge of the dried droplet (f). Scale bars: 0.2 mm.

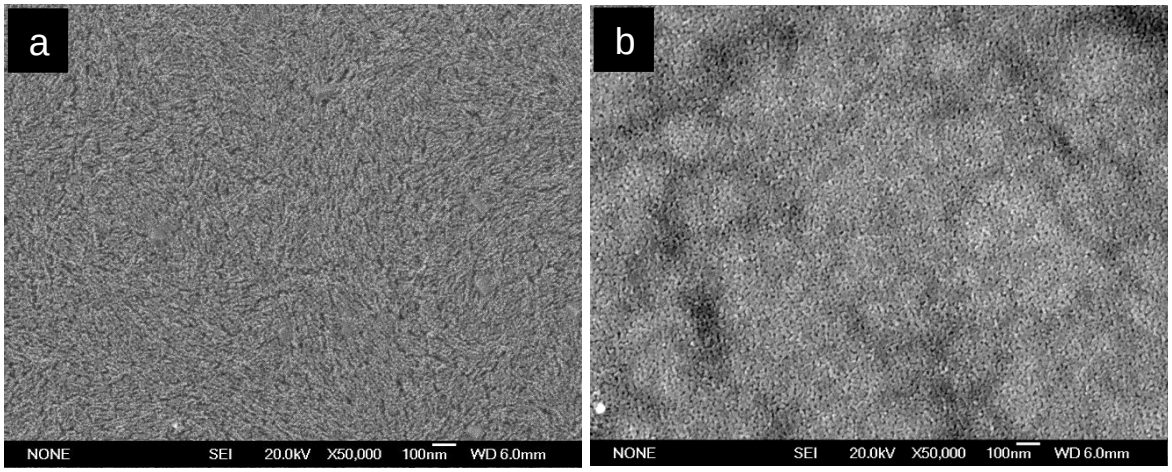

Figure S7. SEM top-view images of tin oxide prepared from 0.1 M (a) and 0.3 M (b) tin tetrachloride in 2 wt% CNCs in water. The suspension was spin-coated on a silicon wafer and calcined at 400 °C.

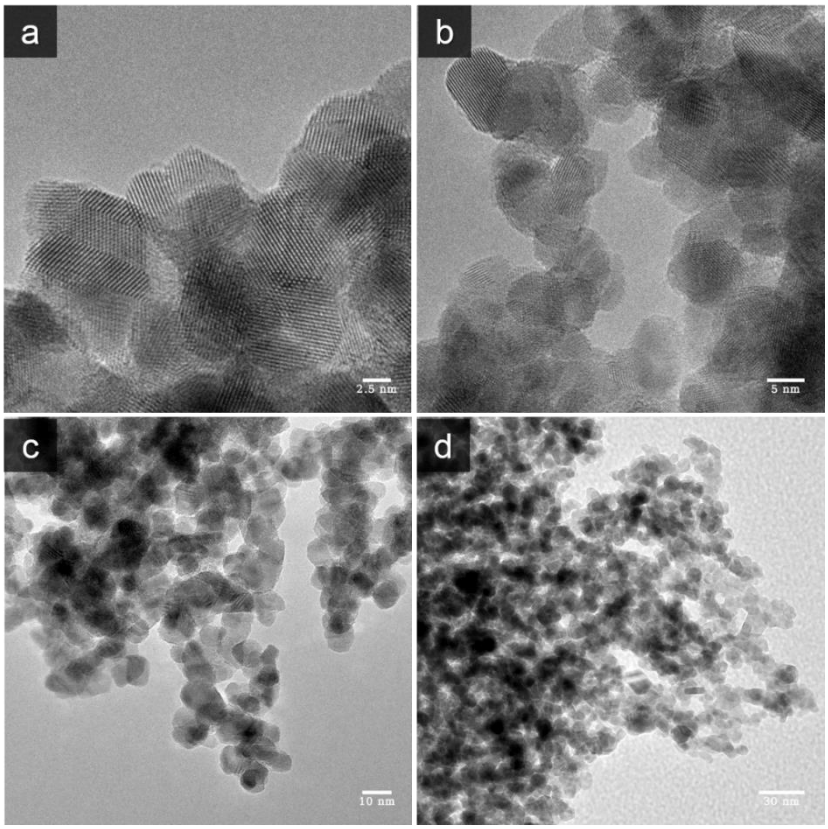

Figure S8. TEM images of CNC-templated tin oxide prepared from a precursor solution containing 0.2 M tin tetrachloride, 2 wt% CNCs and water. The suspension was coated on a silicon wafer and calcined at 400 °C. Scale bar: (a) 2.5 nm, (b) 5 nm, (c) 10 mn, (d) 30 nm.

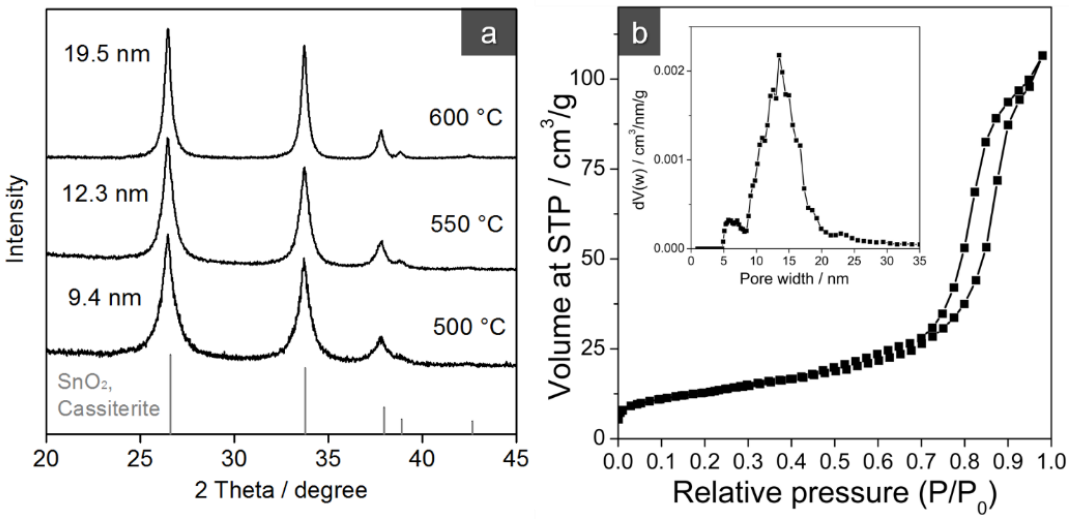

Figure S9. XRD patterns (a) and N_2 sorption isotherms (b) of CNC-templated tin dioxide prepared from tin tetrachloride and CNC colloids and calcined at different temperatures (500 – 600 °C (a), and 600 °C (b). Inset in (b): pore size distribution by using the Quantachrome Instruments Autosorb-1 software and a slit/cylindrical pore NLDFT equilibrium model. X-ray diffraction and nitrogen sorption analysis was performed on pulverized free-standing films obtained by casting and calcining precursor solutions.

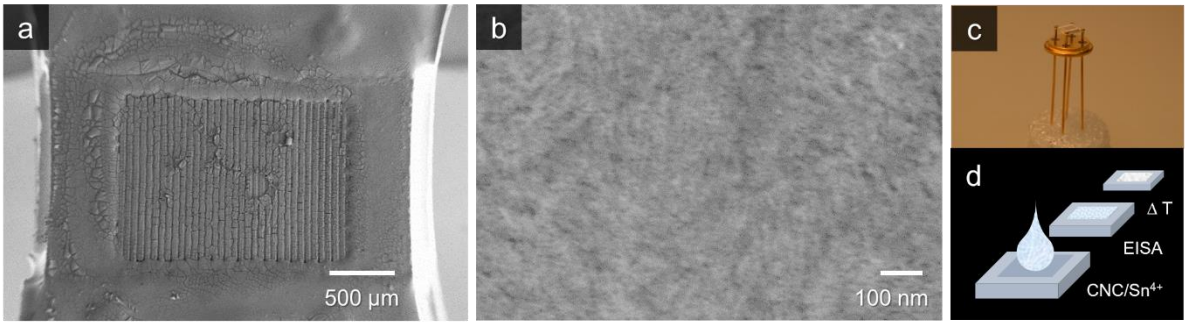

Figure S10. SEM images of the CNC templated tin dioxide directly coated on a sensor substrate and calcined at 400°C. (a) low magnification image, (b) high magnification image, revealing the nanoporous structure of the tin dioxide film. (c) Photograph of the sensor substrate, (d) Schematic of the fabrication procedure for the CNC-templated porous tin dioxide sensor. EISA: Evaporation-induced self-assembly.

Table S3. Nitrogen sorption data of pulverized free-standing samples prepared from precursor solutions containing 0.2 mol L^{-1} $SnCl_4$ and 2 wt% CNC (corresponding to a SnO_2:CNC ratio of 1.5 g/g) and calcined at different temperatures.

Sample	T, °C	Domain size (XRD), nm	BET, m^2/g	Pore size, nm	Pore volume, cm^3/g
1	500	9	245	3	0.27
2	550	12	64	13	0.19
3	600	19	24	20	0.14

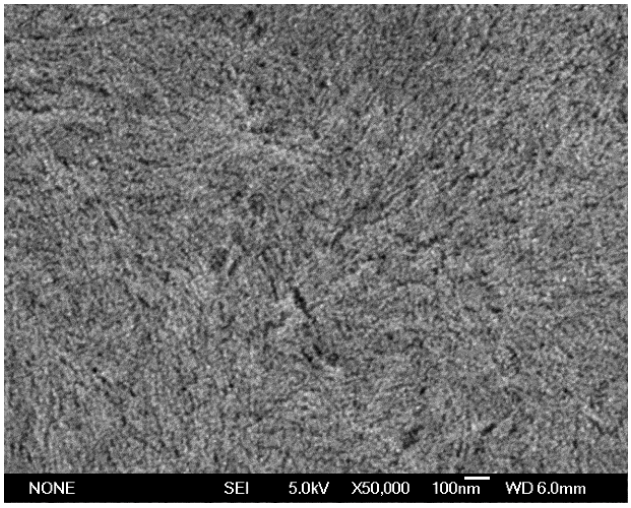

Figure S11. SEM top-view image of tin dioxide prepared from a precursor solution containing CNC and tin tetrachloride with a SnO_2:CNC ratio of 1.5 g/g. The suspension was spin-coated on a silicon wafer and calcined at 600 °C.

References:

1. Mitchell, T. N. On the Relation between Element NMR Chemical Shifts in the Fourth Main Group. *J. Organomet. Chem.* **1983**, *255*, 279-285.
2. Burke, J.; Lauterbur, P. Sn^{119} Nuclear Magnetic Resonance Spectra. *J. Am. Chem. Soc.* **1961**, *83*, 326-331.
3. Hani, R.; Geanangel, R. A. *Coord. Chem. Rev.* **1982**, *44*, 229-246.
4. Clayden, N.; Dobson, C.; Fern, A. High-Resolution Solid-State Tin-119 Nuclear Magnetic Resonance Spectroscopy of Ternary Tin Oxides. *J. Chem. Soc. Dalton Trans.* **1989**, 843-847.
5. Burke, J. J.; Lauterbur, P. C. Sn^{119} Nuclear Magnetic Resonance Spectra. *J. Am. Chem. Soc.* **1961**, *83*, 326-331.
6. Taylor, M.; Coddington, J. The Constitution of Aqueous Tin(IV) Chloride and Bromide Solutions and Solvent Extracts Studied by ^{119}Sn NMR and Vibrational Spectroscopy. *Polyhedron* **1992**, *11*, 1531-1544.
7. Mao, X.-A.; You, X.-Z.; Dai, A.-B. Study of hydrolytic kinetics of the hexachlorostannate anion by two-dimensional ^{119}Sn exchange spectroscopy *Magn. Reson. Chem.* **1989**, *27*, 836-840.
8. Dillon, K.; Marshall, A. Tin-119 Nuclear Magnetic Resonance Studies of some Pseudohalogeno-Derivatives of $[SnX_6]^{2-}$(X = Cl or Br). *J. Chem. Soc. Dalton Trans.* **1987**, 315-317.
9. Colton, R.; Dakternieks, D. Phosphorus-31 and Tin-119 NMR Studies on Tin(IV) Halides and Their Adducts. *Inorg. Chim. Acta* **1982**, *61*, 1-7.