

Supplementary Materials

Results

X-ray powder diffraction (XRPD): Williamson-Hall plot

Table S1. Position of peaks used for the construction of Williamson-Hall plot for the CeO₂ powder. The data in shaded raw are excluded from linear fit.

2θ [°]	$4 \sin(\theta)$	$\beta \cos(\theta)$
28.5312	0.98567	0.00241
33.0699	1.1384	0.00226
47.4758	1.61021	0.00226
56.3354	1.88822	0.00212
59.082	1.97218	0.00215
69.4087	2.27737	0.00203
76.695	2.48172	0.00227
79.0669	2.54611	0.00215
88.4175	2.7891	0.00225

Table S2. Position of peaks used for the construction of Williamson-Hall plot for the TiCe-1 powder.

2θ [°]	$4 \sin(\theta)$	$\beta \cos(\theta)$
28.5433	0.98689	0.00874
33.0817	1.13974	0.00679
47.4823	1.61176	0.01237
56.3368	1.88989	0.012
59.1046	1.97254	0.01252
69.3972	2.27893	0.01141
76.6847	2.4841	0.01798
79.0563	2.54679	0.01631
88.4002	2.79088	0.01798
95.3733	2.96007	0.01736

Table S3. Position of peaks used for the construction of Williamson-Hall plot for the TiCe-2 powder. The data in shaded raw are excluded from linear fit.

2θ [°]	$4 \sin(\theta)$	$\beta \cos(\theta)$
28.5306	0.98634	0.01036
33.0621	1.13902	0.00894
47.4673	1.61114	0.01388
56.3194	1.88936	0.01419
59.0678	1.97038	0.02211
69.3752	2.2783	0.0122
76.6909	2.48422	0.0219
79.0275	2.54608	0.02233

88.4121	2.79061	0.0225
95.3737	2.95981	0.01813

Table S4. Position of peaks used for the construction of Williamson-Hall plot for the TiCe-3 powder. The data in shaded raw are excluded from linear fit.

2θ [°]	$4 \sin(\theta)$	$\beta \cos(\theta)$
28.6108	0.98893	0.01342
33.128	1.14116	0.01196
47.5507	1.61375	0.01505
56.3942	1.89158	0.01551
59.2151	1.97512	0.01445
69.4557	2.28082	0.01258
76.732	2.48549	0.02047
79.0753	2.54738	0.02171
88.4733	2.79284	0.02164
95.4498	2.96163	0.01921

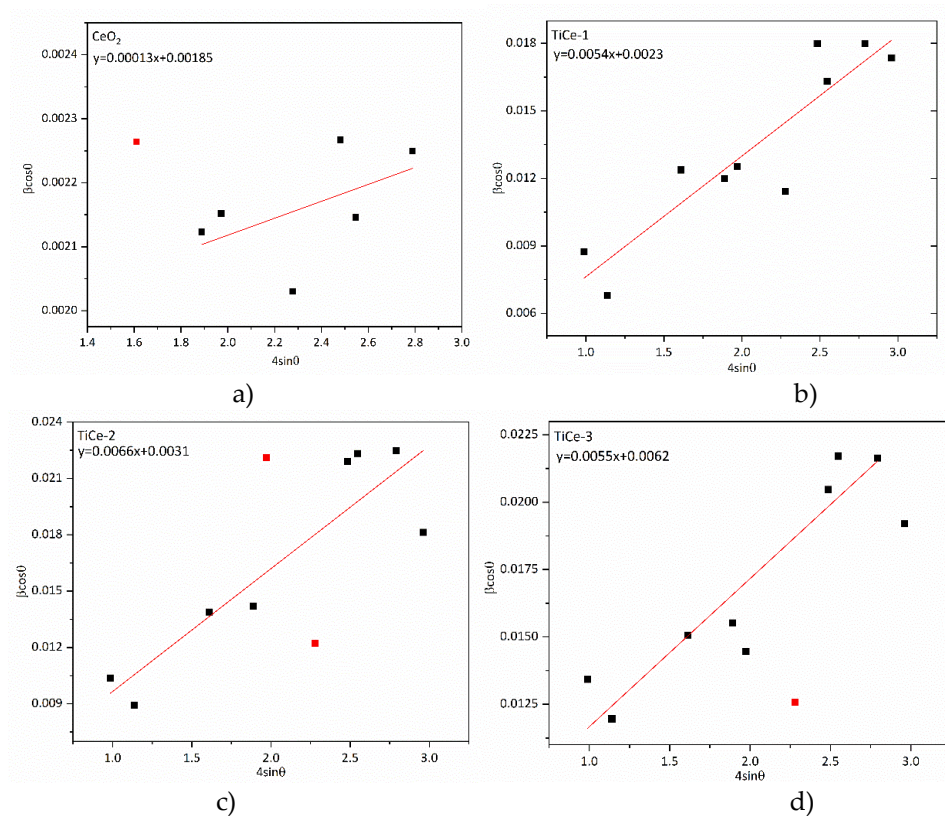


Figure S1. Williamson-Hall plot for: a) CeO_2 and b-d) mixed oxides. Dots marked red are excluded from linear fit.

2D profilometry of sensing layers

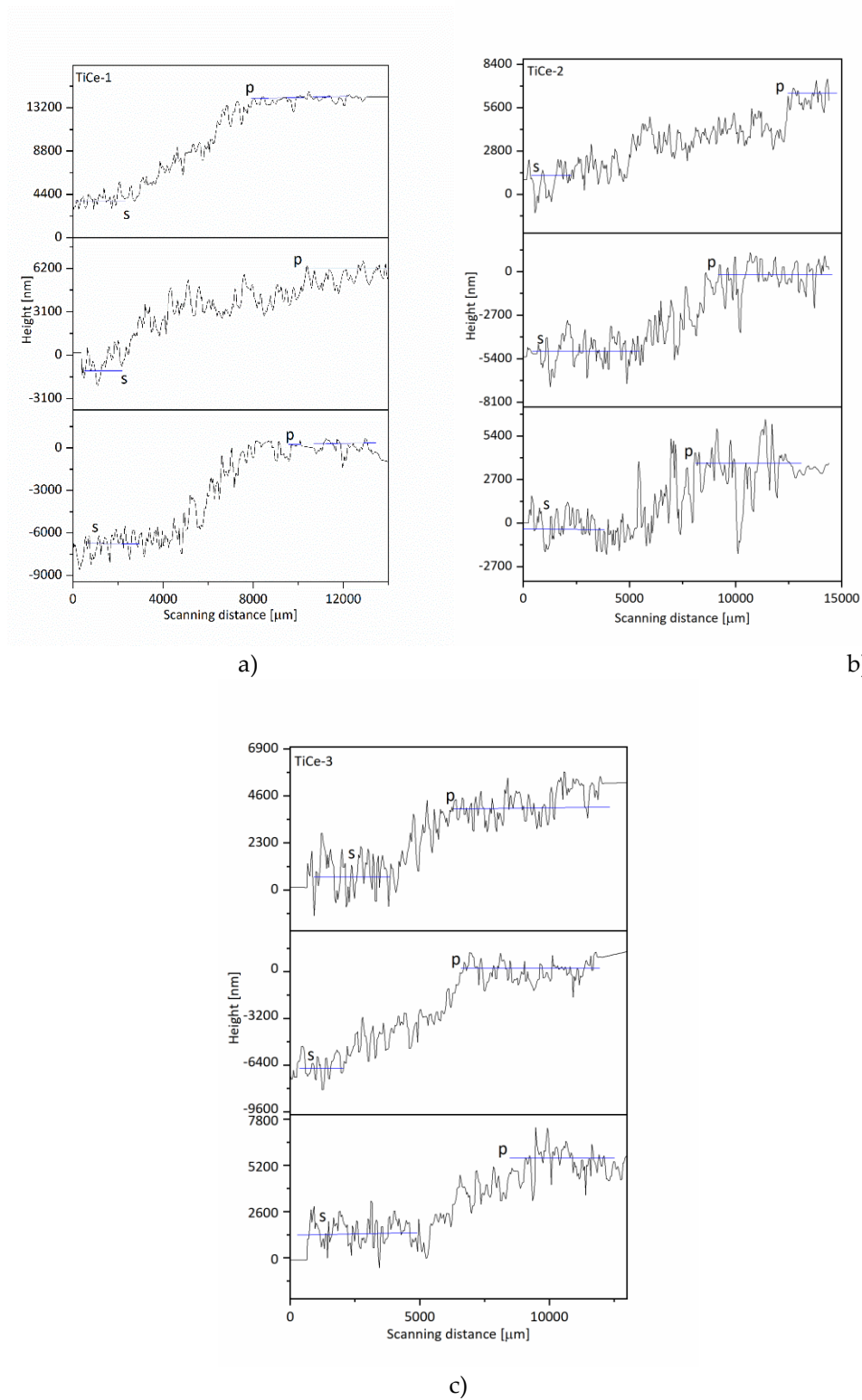
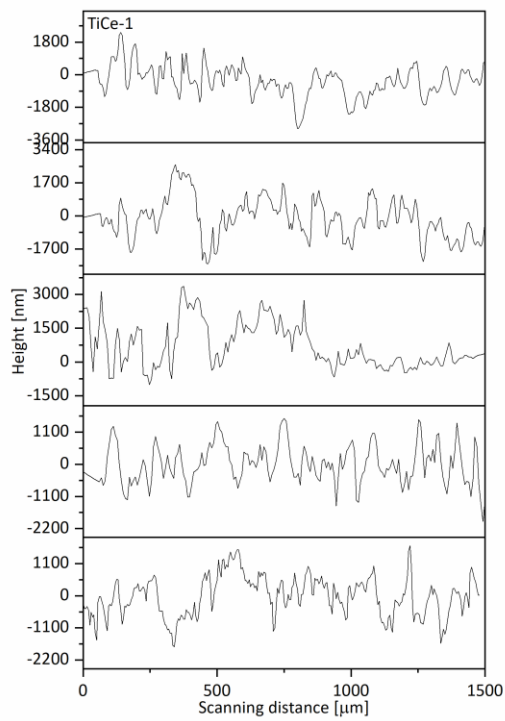
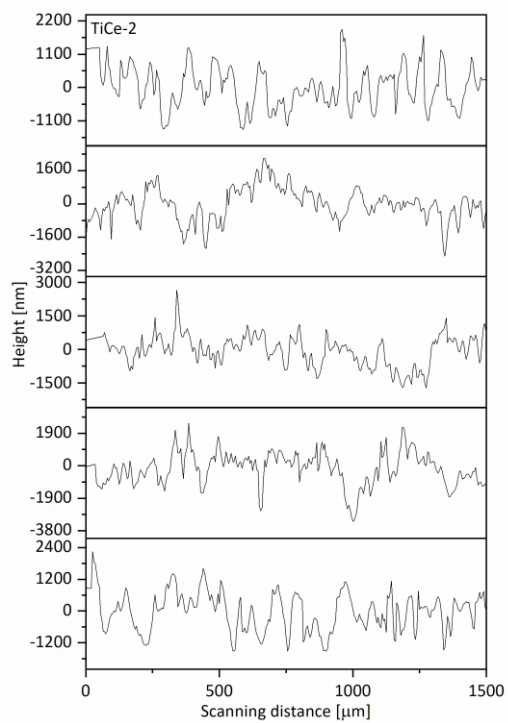


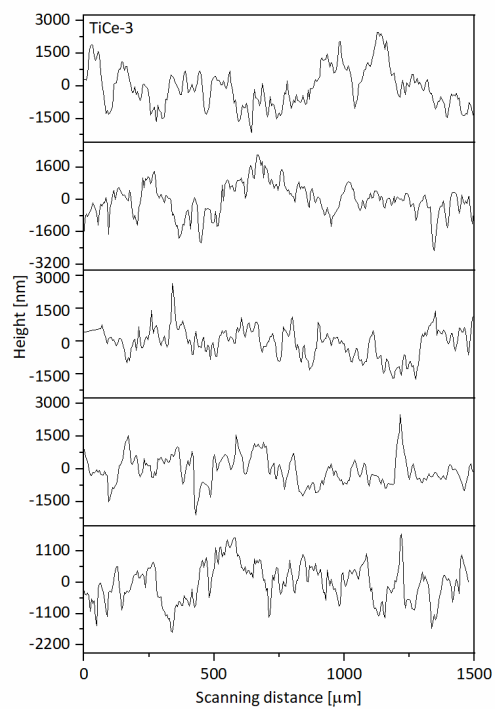
Figure S2. Thickness measurements of: a) TiCe-1; b) TiCe-2, and c) TiCe-3 film using a 2D profilometer; “s” indicates mean line of the substrate, while “p” is mean line of the paste.



a)



b)



c)

Figure S3. Surface roughness of: a) TiCe-1; b) TiCe-2, and c) TiCe-3 measured on five different regions.

Paste (ink) parameters are not the only, and certainly not the most important, factor in determining the dimensions of the layer. Four parameter settings are found to be crucial in tuning the printing process: snap-off distance, squeegee angle, squeegee speed, and the force pressing the squeegee onto the screen. Given the manual method of deposition employed, the random variation of these parameters over the different printing strokes is unavoidable. The fluctuation of printing conditions then affects the thickness of a printed film [1]. However, the significant difference in thickness between sample TiCe-1 and another two samples can hardly be attributed solely to the fluctuation of these parameters. The packing density of the particles increases as the particle size distribution broadens, thereby reducing the space available for the particles of the additional layer, and the thickness of the resulting material grows [2]. Indeed, the variation in thickness seems to follow the change in span of the particle size distribution (Tabel 1): the samples made of the powder with similar span (TiCe-2 and TiCe-3) were found to have comparable thicknesses, while the thickness of TiCe-1 is significantly bigger, as well as the particle size span of its corresponding precursor. The roughness parameters of sample TiCe-1 were estimated at a slightly higher value compared to the remaining two samples, which are characterized by a reduced mean particle size. Namely, surface roughness and irregularity are affected by particle agglomeration: smaller particles allow denser packing compared to larger ones, resulting in a smooth film surface [3].

Energy dispersive spectroscopy (EDS): Mapping of sensing layers

1. TiCe-1

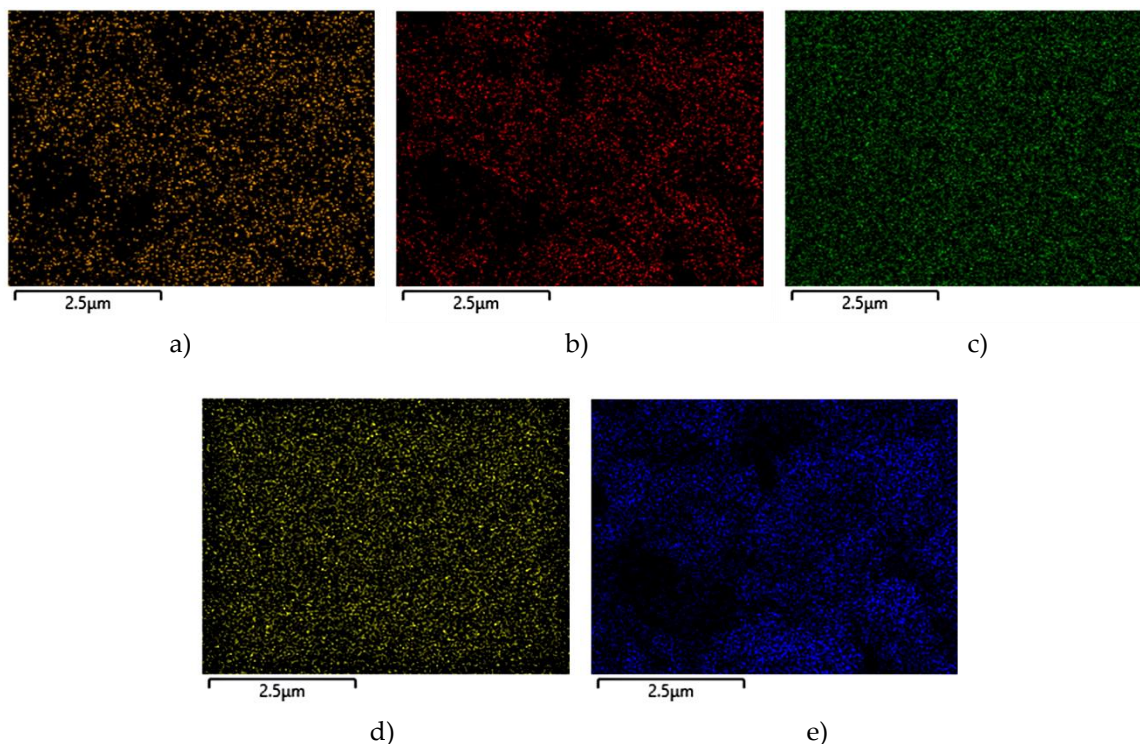


Figure S4. Elemental EDS mapping of: a) Al K series; b) C K series; c) Ce L series; d) Ti K series; e) O K series on the center of the TiCe-1 film.

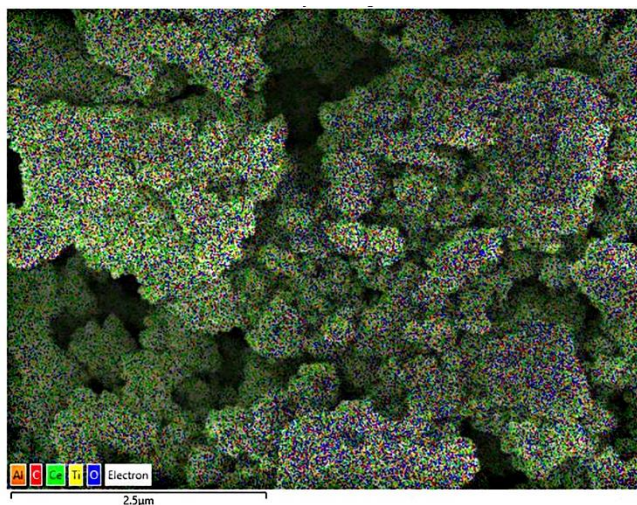


Figure S5. EDS layered image taken in the center of the TiCe-1 film.

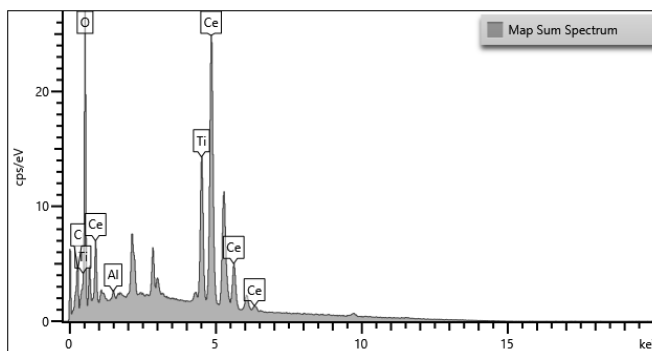


Figure S6. EDS map spectrum of the TiCe-1 film taken from the center.

Table S5. Data obtained from EDS mapping for sample TiCe-1.

Map Sum Spectrum									
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.18	0.00179	5.99	0.27	20.10	C Vit	Yes	
O	K series	2.37	0.00798	20.79	0.20	52.39	SiO2	Yes	
Al	K series	0.03	0.00022	0.29	0.04	0.43	Al2O3	Yes	
Ti	K series	2.00	0.02000	11.00	0.11	9.26	Ti	Yes	

Ce	L series	10.49	0.09758	61.93	0.27	17.82	CeO2	Yes	
Total:				100.00		100.00			

2. TiCe-2

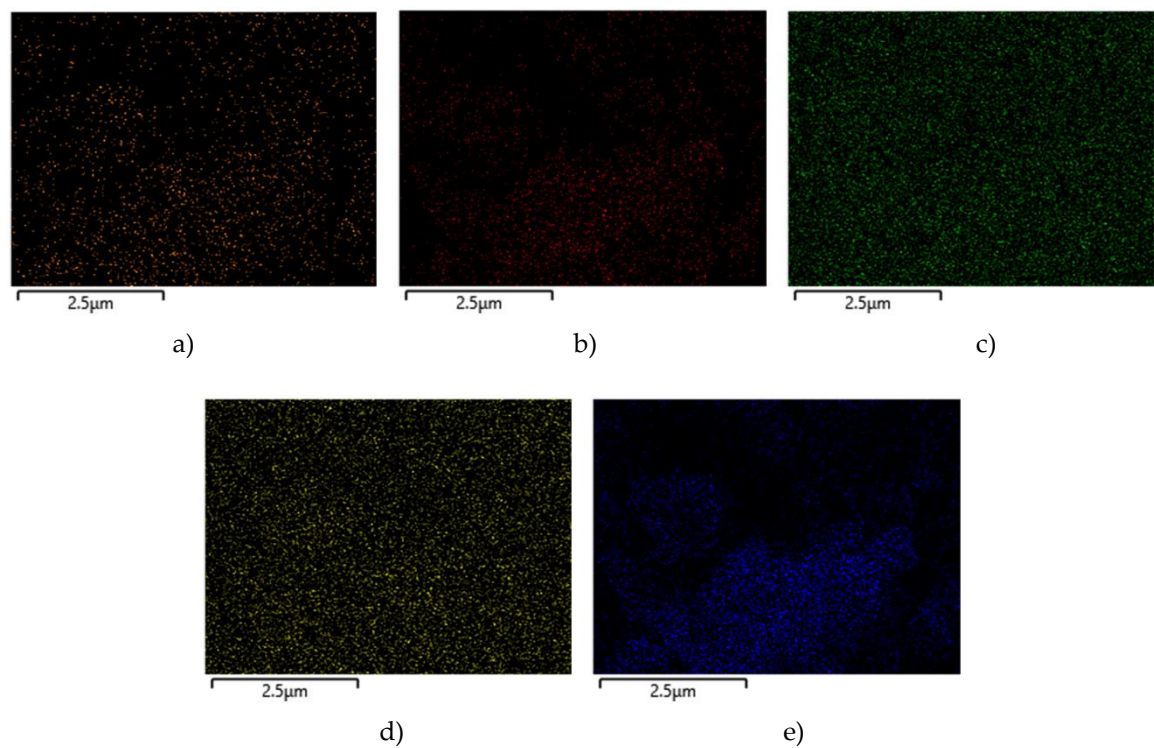


Figure S7. Elemental EDS mapping of: a) Al K series; b) C K series; c) Ce L series; d) Ti K series; e) O K series on the center of the TiCe-2 film.

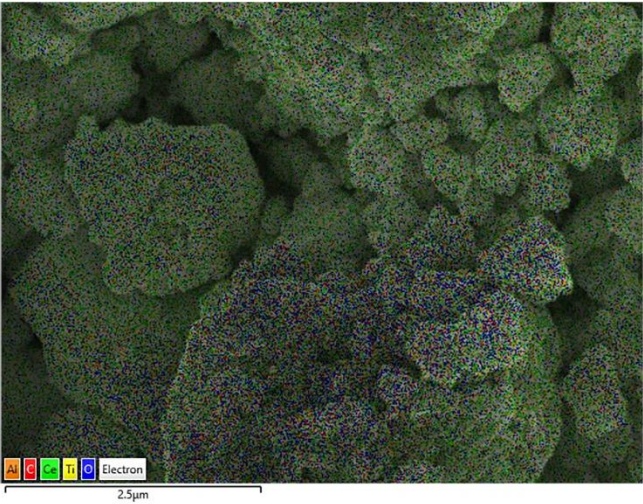


Figure S8. EDS layered image taken in the center of the TiCe-2 film.

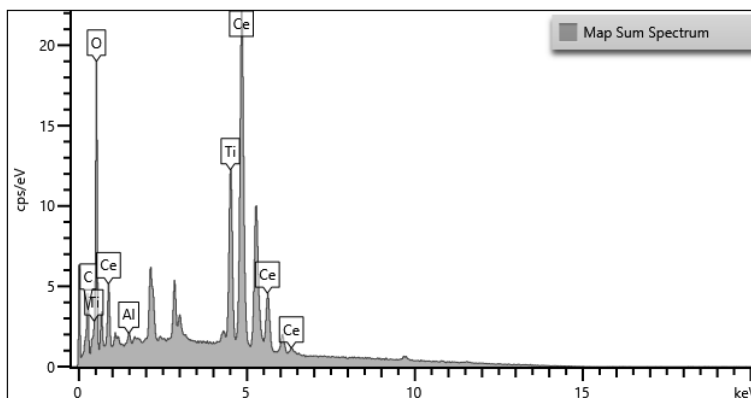


Figure S9. EDS map spectrum of the TiCe-2 film taken from the center.

Table S6. Data obtained from EDS mapping for sample TiCe-2.

Map Sum Spectrum									
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.15	0.00148	5.96	0.34	21.44	C Vit	Yes	
O	K series	1.68	0.00564	17.77	0.25	47.98	SiO2	Yes	
Al	K series	0.03	0.00021	0.33	0.05	0.52	Al2O3	Yes	
Ti	K series	1.73	0.01732	11.23	0.14	10.12	Ti	Yes	
Ce	L series	9.30	0.08658	64.71	0.34	19.94	CeO2	Yes	
Total:				100.00		100.00			

3. TiCe-3

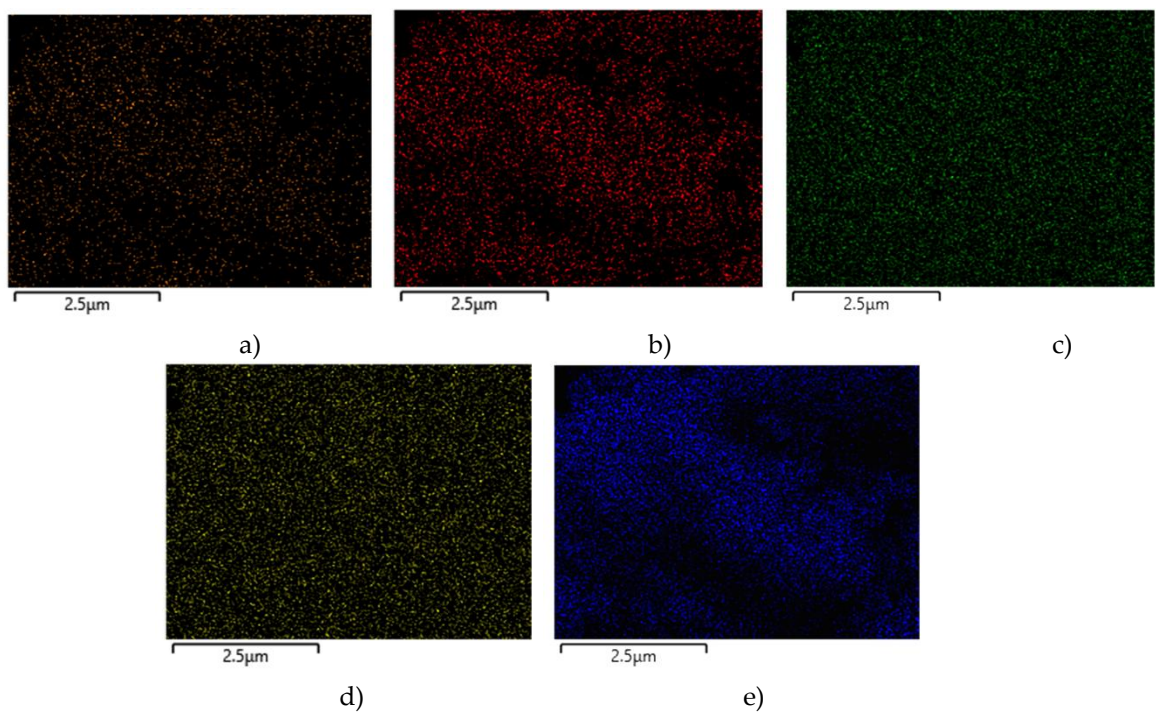


Figure S10. Elemental EDS mapping of a) Al K series; b) C K series; c) Ce L series; d) Ti K series; e) O K series on the center of the TiCe-3 film.

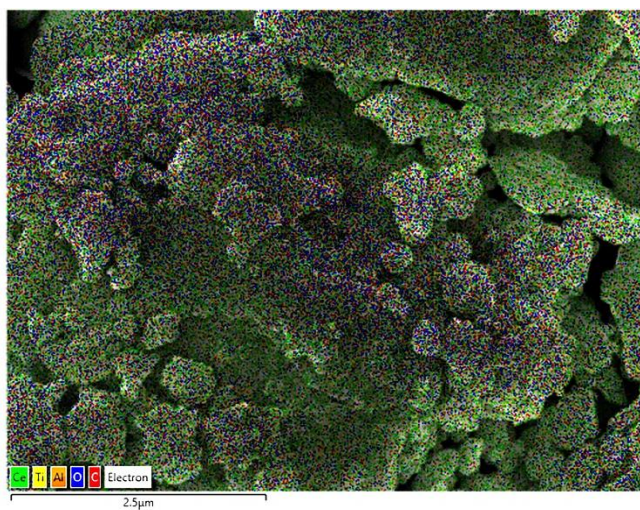


Figure S11. EDS layered image taken in the center of the TiCe-3 film.

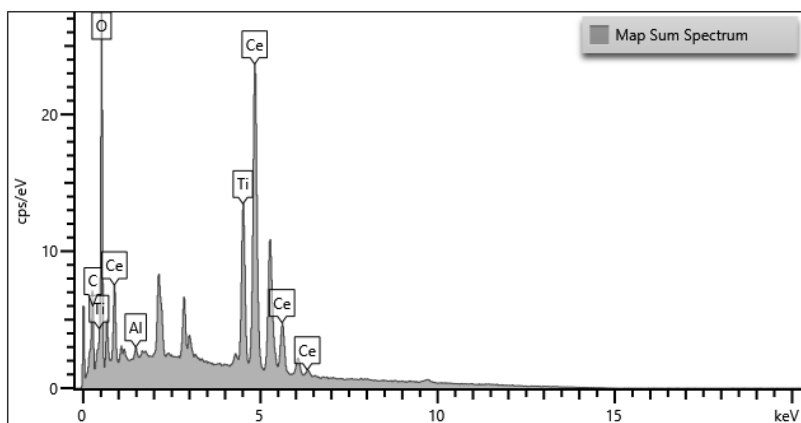


Figure S12. EDS map spectrum of the TiCe-3 film taken from the center.

Table S7. Data obtained from EDS mapping for sample TiCe-3.

Map Sum Spectrum									
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.25	0.00246	8.12	0.35	25.38	C Vit	Yes	
O	K series	2.40	0.00807	21.28	0.25	49.94	SiO2	Yes	
Al	K series	0.04	0.00026	0.33	0.05	0.46	Al2O3	Yes	
Ti	K series	1.88	0.01879	10.44	0.13	8.19	Ti	Yes	
Ce	L series	10.01	0.09319	59.83	0.33	16.04	CeO2	Yes	
Total:				100.00		100.00			

X-ray photoelectron spectroscopy (XPS): Quantitative analysis

It is possible to calculate the relative intensities of different photoelectron lines, including all their contributions, when the spatial distribution of all chemical phases is known. In several practical cases simple analytical approaches can provide very good results. This allows solving the inverse problem: deducing surface structure from XPS measurements starting from few premises, realistic or obtained using other experimental techniques. Intensity of a photoelectron line '*i*' originating from a phase AB can be expressed in the following form:

$$I_i = J_x \cdot \Delta t \cdot n_i \cdot \sigma_i \cdot T(E_i) \cdot L_{Qi}^{AB} \quad (S1)$$

where J_x is the flux of X-ray photons, Δt is the acquisition time for a particular energy (dwell time), n_i is atomic concentration of 'i' element in AB, σ_i is photoionization cross-section, T is the transmission of the energy spectrometer which, and L_{Qi}^{AB} is attenuation length for quantification. Attenuation length depends on both the kinetic energy of photoelectrons and the electronic structure of the phase AB, but these two dependencies are, to a very good approximation, decoupled. If we consider a monoatomic sample A covered by a monoatomic layer B of thickness d , which here represents a hydrocarbon overlayer, the line intensities I_A and I_B can be expressed as:

$$I_A = J_x \cdot \Delta t \cdot n_A \cdot \sigma_A \cdot T(E_A) \cdot L_{QA}^A \cdot e^{-\frac{d}{L_A^B}} = I_{A0} \cdot e^{-\frac{d}{L_A^B}} \quad (S2)$$

and

$$I_B = J_x \cdot \Delta t \cdot n_B \cdot \sigma_B \cdot T(E_B) \cdot L_{QB}^B \cdot \left(1 - e^{-\frac{d}{L_B^B}}\right) = I_{B0} \cdot \left(1 - e^{-\frac{d}{L_B^B}}\right), \quad (S3)$$

where L_A^B and L_B^B are 'practical' effective attenuation lengths of photoelectrons from elements 'A' and 'B' traveling through material 'B'. Then, I_{A0} and I_{B0} are the intensities of lines 'A' and 'B' when d equals 0 and infinity, respectively. These equations are starting points for the estimation of an overlayer thickness using XPS results.

For quantitative analyses, the hydrocarbon phase (partially oxidized in all samples) is modeled as a paraffin layer of unknown thickness. The hydrocarbon thickness d can be estimated by comparing intensities I_A and I_B originating from the corresponding regions A and B. According to the expressions (2) and (3), the ratio between the two lines is:

$$\frac{I_A}{I_B} = \frac{n_A}{n_B} \cdot \frac{\sigma_A}{\sigma_B} \cdot \frac{T(E_A)}{T(E_B)} \cdot \frac{L_{QA}^A}{L_{QB}^B} \cdot e^{\frac{d}{L_A^B}} \cdot \left(1 - e^{-\frac{d}{L_B^B}}\right). \quad (S4)$$

The last equation can be easily solved numerically or by trial-and-error method since all quantities are known and measured except the thickness. With this approach we will estimate the thickness d on the top of the reference TiO_2 and CeO_2 using the intensities of the C 1s and Ti 2p (Ce 3d) lines. Although hydrocarbon contamination leads to attenuation of the sample signal, the known value of the thickness of the overlayer allows to estimate intensities of Ti 2p (Ce 3d) and parts of O 1s lines (peaks O1 and O2) before passing through it:

$$I_{i0} = I_{iexp} \cdot e^{\frac{d}{L_i^{HC}}}. \quad (S5)$$

Here, i signifies O, Ti or Ce, HC refers to the hydrocarbon layer, and I_0 is the intensity of the line without a presence of the overlayer, expressed by equation (1). Since we know the cross-sections, attenuation lengths for quantification, and the spectrometer transmission, we can calculate the composition of the samples, i.e. O: Ti and O: Ce ratio, directly from the set of equation such as (1), using Ti 2p and Ce 3d (or Ce 4d) line. When calculating O: Ti, the contribution of surface oxygen, O2, will be omitted. In the case of O: Ce, the total oxygen signal (O1+O2) will be considered, due to the existence of surface Ce^{3+} ions.

If we assume that TiO₂-CeO₂ are in-depth uniform and laterally non-uniform samples, we can write equation (1) as a function of the fraction of surface area occupied by a particular chemical phase or the surface coverage θ of one of the phases. Given the nature of the synthesis route, we expect the surface to consist of TiO₂ and CeO₂ patches, which must be included in quantification analysis. In a two-phase laterally non-uniform system consisting of patches A (TiO₂) and B (CeO₂), surface coverage is defined as θ_A and $\theta_B = 1 - \theta_A$. In that case, the corresponding oxygen line intensities can be expressed by a slight modification of the equation for the photoelectron line intensity:

$$I_A = J_x \cdot \Delta t \cdot n_A \cdot \theta_A \cdot \sigma_A \cdot T(E_A) \cdot L_{QA}^A \quad (S6)$$

and

$$I_B = J_x \cdot \Delta t \cdot n_B \cdot (1 - \theta_A) \cdot \sigma_B \cdot T(E_B) \cdot L_{QB}^B. \quad (S7)$$

From these two equations we can eliminate the X-ray flux, which is always unknown quantity, and express the coverage θ_A as

$$\theta_A = \frac{k}{1+k}, \quad (S8)$$

where

$$k = \frac{I_A}{I_B} \cdot \frac{n_B}{n_A} \cdot \frac{\sigma_B}{\sigma_A} \cdot \frac{T(E_B)}{T(E_A)} \cdot \frac{L_{QB}^B}{L_{QA}^A}. \quad (S9)$$

In this approach, it is assumed that all photoelectrons emitted from line A travel exclusively through region A, and vice versa. That is not certain for atoms located close to the A/B interface. In other words, the approach is correct as long as the size of separate islands is sufficiently large. To obtain a coverage ratio, as well as the contamination thickness, it is necessary to introduce a final assumption: the TiO₂ patches in mixed oxides have the same surface structure as the reference sample. TiO₂ is indeed expected to be more stable than CeO₂, which is known to have the lowest hardness value among ceramics. Therefore, the milling process is likely to have less effect on the TiO₂ than on the CeO₂ particles [4]. Starting from the last assumption and knowing the ratio of O1 to Ti 2p_{3/2} in TiO₂ (1.0671) and the ratio between the intensities O2:O1 = 0.3222, we can estimate the O1 and O2 intensities attributed to TiO₂ based on the Ti 2p_{3/2} intensity in the detailed spectra of mixed oxide. After that, we can calculate the contributions of CeO₂ to the two oxygen peaks and then finally apply equation (8) to calculate the coverage of TiO₂ and CeO₂. Once the surface coverage is known, the actual surface concentrations of Ti and Ce and the thickness of hydrocarbon contamination can be estimated. In the case of a mixed oxide, d can be expressed by the following equation:

$$d = \left(\frac{1}{L_{A2}^B} - \frac{1}{L_{A1}^B} \right)^{-1} \cdot \ln \left[\frac{I_{A1}}{I_{A2}} \cdot \frac{\sigma_{A2}}{\sigma_{A1}} \cdot \frac{T(E_{A2})}{T(E_{A1})} \cdot \frac{L_{QA2}^A}{L_{QA1}^A} \right], \quad (S10)$$

which is derived from equation (2). This approach includes two lines of the same element found exclusively in the bulk, labeled A1 and A2 (for example Ti 2p and Ti 3p). From the known overlayer thickness d and the known fraction of the O 1s line intensity related to CeO₂, we can calculate O: Ce ratio using the previously explained procedure.

Previous measurements clearly showed that the transmission function of the spectrometer we used has a 1/E dependence, with E representing the kinetic energy of a photoelectron. The total ionization cross sections and asymmetry parameters (the latter only being used to calculate the effective attenuation lengths, as the XPS setup operates under the 'magic angle') were obtained from the work of Yeh and Lindau [5]. Practical effective attenuation lengths (for thickness measurements) and attenuation lengths for quantification were calculated using the corresponding NIST database [6]. In this context, we employed

the TPP-2M empirical formula to calculate the inelastic mean free paths [7]. This formula requires, among other parameters, the number of valence electrons. For this purpose, we utilized 14 eV for the high-energy cut-off, as recommended by Seah et al [8].

Results of electrical measurements

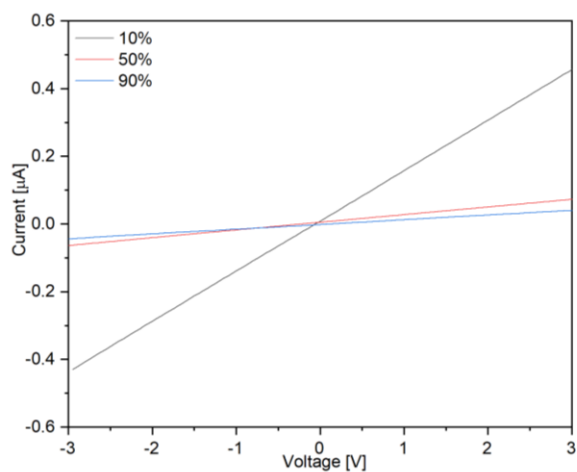


Figure S13. Current-voltage characteristics of a TiCe-1-based sensor at 10, 50 and 90 % of O₂ at 310 °C.

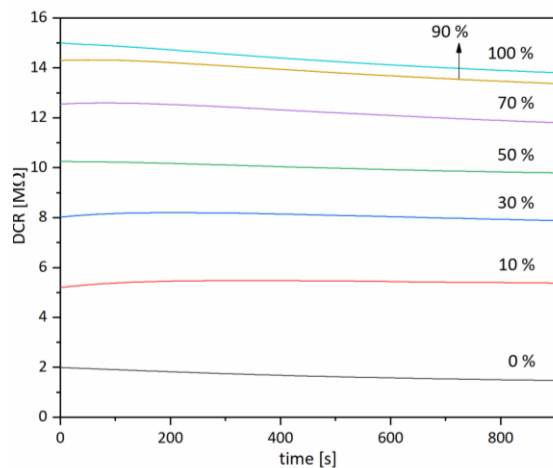


Figure S14. Example of resistance time tracking at different volume concentrations of O₂ for the sample TiCe-3.

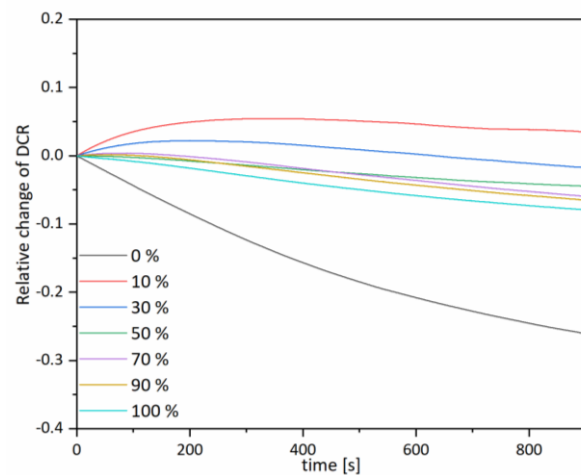


Figure S15. Relative change of resistance with for the sample TiCe-3. Derived from the data shown in Figure S13.

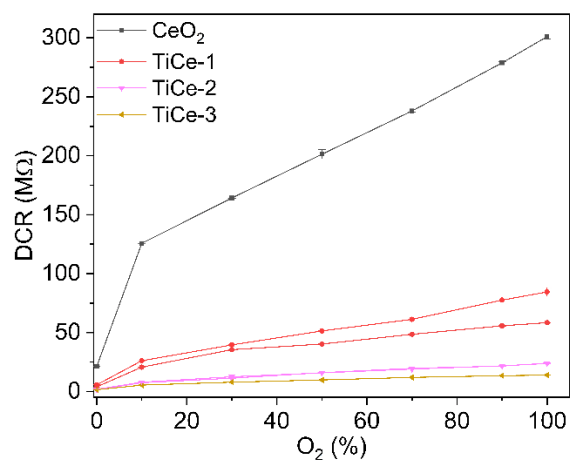


Figure S16. DC resistance of CeO₂ and mixed oxides when exposed to different volume concentrations of O₂ at a temperature of 310 °C.

Methods and Materials

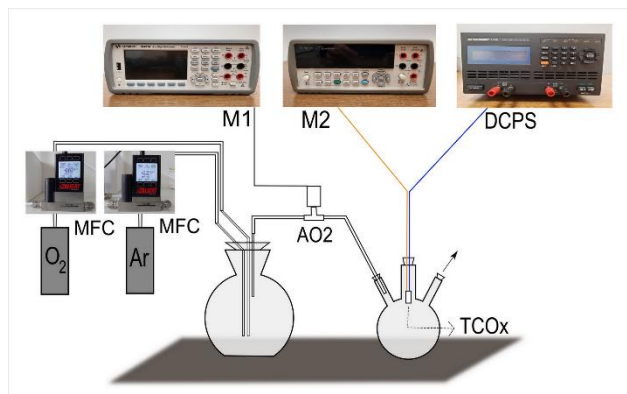


Figure S17. Schematic representation of the experimental setup for measuring the sensor response.

References

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