Supporting Information

**High Performance Oxygen Sensor by Multilayer Oxides with High Interfacial Conductivity**

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**Materials and Methods:**

**Preparation for porous Pt thin film electrodes**

To investigate the dependence of porosity of Pt films on the film thickness, porous Pt thin film was deposited on quartz using DC reactive magnetron sputtering at room temperature with different sputtering times from 5 min to 60 min. The sputtering chamber was evacuated to a background pressure below $10^{-6}$ mTorr before the deposition. Working gases of Ar and O$_2$ were introduced into the chamber at Ar/O$_2$ ratio of 1:4 and working pressure was 10 mTorr and sputtering power was 75 W. The as-deposited Pt thin films were annealed at 600 °C for 1 h and quenched in cool air.

**Preparation for SNDC/AO-based microbars**

SNDC multilayers were deposited on alumina substrates using RF magnetron sputtering. Before the deposition, the sputtering chamber was evacuated to a background pressure below $10^{-5}$ mTorr. The working gas is Ar and O$_2$ mixture with the ratio of 4:1 and pressure of 5 mTorr. Layers were sputtered sequentially with sputtering power of 200 W and 150 W for SNDC and AO, respectively, and layer thickness was tuned by changing deposition time. Two calcined SNDC/AO multilayer samples were co-calcined using glass powders at 850°C (slightly higher than melting point of glass) for 30 min. To limit movement of multilayers when glass powders were melt during co-calcination process, glass powders were sandwiched by two multilayers and filled in a chalk bar mold. After heat-treatment, chalk bar and glass outside microbar can be entirely removed by polishing. Subsequently, the microbar was transferred to an alumina holder with heterointerfaces perpendicularly aligned on the through-hole in alumina holder. Apertures between microbar and alumina holder were filled by inorganic seal gel and was dried in furnace at 80 °C for 12 h and 120 °C for 24 h, and the microbar can be fixed and sealed on the holder.
Preparation for YSZ-based microbars

8 mol.% Y$_2$O$_3$-doped ZrO$_2$ powders were prepared by sol-gel method and the synthesized YSZ powders were ground and sieved. Dry pressing and cold isotactic pressing at 200 MPa was applied to prepare green bodies which were then sintered at 1400°C for 4 h. The as-calcined YSZ pellet was fabricated into YSZ plate with thickness of 100 μm, width of 1 mm and length of 10 mm. The surfaces (1 mm×10 mm) of an YSZ plate and two alumina strips (thickness of 0.5 mm, width of 1 mm and length of 10 mm) were co-calcined, face-to-face, by high-temperature seal glass using the aforementioned method. However, in this case YSZ plate was sandwiched by two blank alumina strips.

Calculation of ionic conductivity

The electrical conductivities of microbars were calculated by eqn. S1:

$$\sigma_{\text{tot}} = \frac{L}{RNdb} \quad (\text{S1})$$

where $R$ is the resistance derived from impedance spectrum, $b$ is the width of electrodes and $L$ is the separation between two electrodes. The $L/b/d$ for YSZ-based microbar and SNDC/AO-based microbar is 0.8 mm/8 mm/100 μm and 0.6 mm/8 mm/4 μm, respectively.
Supplementary Figures

**Figure S1.** SEM images for Pt thin film deposited on quartz substrate in (a) pure Ar gas and in gas mixture of Ar and O$_2$ with flow rate ratio of 1:4 for (b) 60 min, (c) 45 min, (d) 30 min, (e) 15 min and (f) 5 min. (g) Low magnification and (h) high magnification SEM images for the Pt thin film deposited at sides of SNDC/AO multilayer in gas mixture of Ar and O$_2$ with flow rate ratio of 1:4 for 5 min. Scale bar: 5 μm.

**Figure S2.** (a) XRD patterns and (b) XPS spectra for Pt thin films deposited at the side of SNDC/AO multilayer microbar both before and after the decomposition process at 600 °C.
Figure S3. The Ce3d XPS spectrum of SNDC/AO multilayer microbar.

Figure S4. Typical impedance spectra measured at 150 °C and 200 °C for SNDC/AO-based micro-oxygen sensors.
**Figure S5.** The Arrhenius plots of conductivity for SNDC/AO multilayer microbar with $N=14$ as well as for YSZ bulk material.

**Figure S6.** Impedance spectra for SNDC/AO-based micro-oxygen sensors measured under dry air and humid air at 150 °C.
Figure S7. $P_{O_2}$ dependence of electrical conductivities for SNDC/AO multilayer microbar with different layer numbers measured at (a) 450 °C and (b) 500 °C.

Figure S8. The determination of response time ($t_{res}$) and recovery time ($t_{rec}$) for SNDC/AO-based micro-oxygen sensors measured at 500 °C.
Figure S9. Schematic view of the sensitivity testing configuration for micro-oxygen sensors.