A unique nanocrystalline, mesoporous PdO–SnO2 film exhibiting high sensitivity and selectivity to hydrogen gas at room temperature has been developed.

SnO2-based gas sensors work by monitoring changes in electrical resistance that result mainly from reduction/oxidation of the crystal surface by the target gas. To-date elevated temperatures1–6 or UV light7 are required to achieve rapid adsorption/desorption and oxidation/reduction kinetics needed for a practical, rapid, and sensitive H2 detector. Very recently, nanocrystalline SnO2-based sensors showed room temperature sensitivity towards ethanol and carbon monoxide, but poor sensitivity for hydrogen gas,8,9 whereas indium oxide doped SnO2 films deposited on microelectromechanical systems device showed an appreciable (but slow) response to H2 gas at room temperature.10 Here we are reporting a surfactant-templated unique nanocrystalline, mesoporous PdO–SnO2 film exhibiting very high sensitivity and selectivity to hydrogen gas at room temperature. As hydrogen is currently used in many different sectors of technology and is expected to be the fuel of the future, a H2-selective sensor material active at room temperature is of considerable immediate interest.11

Synthesis of mesoporous SnO2 powders using cationic6 or nonionic poly(ethylene oxide) based12 surfactants has been recently reported. However, these methods are incapable of producing high quality films of SnO2 or Pd-doped SnO2, and to-date there are no reports of nanocrystalline mesoporous SnO2 films having high surface area and room temperature gas sensitivity. We are reporting here a surfactant-directed assembly approach to form high surface area mesoporous Pd-doped SnO2 films exhibiting an interconnected nanocrystalline structure and high sensitivity for H2 gas at room temperature. We prepared uniform 8 mol% PdO–SnO2 (nominal composition) films on glass or Si-wafer substrates using the block copolymer surfactant Pluronic P123 (PEO20PPO70PEO20) as a structure directing agent,12 and tin (IV) tert-butoxide and Pd acetate as tin and palladium sources respectively (see experimental section in ESI†). To elucidate the role of nanostructuring, we also prepared films of identical composition without the surfactant. A main goal of our synthetic procedure was to incorporate Pd in SnO2 as PdO, because, in this form, it is known to suppress grain growth in bulk sol–gel systems13 and to increase both their on-set resistance value and sensitivity towards H2.2,3 In addition, PdO acts as an electron acceptor, trapping charge from the SnO2 conduction band. This trapped charge, along with that of ionosorbed oxygen, induces stronger depletion of electrons from the Sn oxide surface causing greater increases in resistance.3 Films prepared with (molar ratio P123/Sn = 0.024) and without surfactant are designated SnPd and SnPd0, respectively. The thickness of SnPd film measured by ellipsometry and FE-SEM is about 230 nm. The FTIR spectrum of the SnPd films dried at 100 °C showed C–H stretching vibrations associated with the surfactant. However, the spectrum of the corresponding air-annealed (400 °C/6 h) films showed complete removal of organics, having bands attributed solely to Sn–O (and possibly overlapped Pd–O) vibrations.14 As prepared SnPd films exhibited a broad low angle XRD peak (see Fig. S1 in ESI†) centered at 2θ = 1.57° (d = 5.62 nm), consistent with a worm-like micellar mesophase, whereas, as expected, the corresponding SnPd0 films showed no low angle X-ray diffraction. Upon calcination at 400 °C in air, SnPd0 films crystallized, causing the low angle XRD peak to shift only slightly to lower 2θ (larger d-spacing), reflective of the minor coarsening accompanying dimensionally-constrained framework crystallization. TEM imaging of calcined SnPd0 films (Fig. 1) revealed a sponge-like morphology composed of uniform ~5 nm diameter grains (Fig. 1a), which is also confirmed by FE-SEM shown in the inset of Fig. 1a (top left). Energy dispersive X-ray scattering (Fig. 1b) confirmed the presence of Pd, Sn and O in the film. Selected area electron diffraction (SAED) patterns (inset of Fig. 1a) are indexed as the tetragonal structure (cassiterite), typical for SnO2. The high-resolution electron micrograph (Fig. 1c) shows coalesced, almost spherical nanocrystalline grains with average diameters of 4–5 nm. Importantly, we could not locate any distinct PdO nanoparticles in FE-SEM or TEM investigations of the calcined films, and XPS analysis of the unspattered film surface shows a Pd 3d5/2 core level at 337.5 eV corresponding to the PdO2 ion.15 These results imply that either a PdO–SnO2 solid solutions formed,16 or that PdO exists as extremely uniformly dispersed nanoparticles, but we could not distinguish between the two by wide-angle XRD.17

Surface acoustic wave-based nitrogen sorption analyses (at 77 K)18 along with refractive index measurements were used to understand the influence of the templating procedure on thin film porosity (as opposed to the porosity of related mesoporous powders). Fig. 2a plots the nitrogen adsorption-desorption
isotherms of the films prepared with and without surfactant. The SnPd_{0} film prepared without surfactant has a low pore volume and surface area of 14.4 m^{2} g^{-1} or 49.5 m^{2} cm^{-3}, compared to 143.5 m^{2} g^{-1} or 493 m^{2} cm^{-3} for the surfactant templated film SnPd_{S}. The pore size distribution of SnPd_{S} is quite narrow, and the mean pore diameter, about 6.2 nm, is comparable to the nanocrystal diameter (Fig. 2b). The SnPd_{0} film has a higher refractive index than the SnPd_{S} film, 1.69 compared to 1.30, due to its much lower porosity. The measured surface area of the SnPd_{S} film is quite high taking into account the high densities of the component oxides comprising the crystalline skeleton (6.95 and 8.3 g cm^{-3} for SnO_{2} and PdO, respectively), and comparable to reports of mesoporous SnO_{2} powders prepared using surfactant templating.^{12,19} There are no reports of corresponding nanocrystalline/high surface area PdO/SnO_{2} films except for the case where trimethylsilyl termination of the surface hydroxyl groups was employed to avoid surface condensation reactions and, at high temperature, form silica nanoparticles that pin grain boundaries and suppress grain growth.^{19} In our case, confinement within the nanodomains, established by the templating procedure, presumably serves to foster particle coalescence but limits 3D grain growth, allowing the formation of a highly porous, high surface area, doped oxide.

Motivated by the high surface area and uniform incorporation of PdO within the SnPd_{S} framework, gas sensing properties were measured at room temperature (21 ± 1 °C).^{20} The sensor film has an initial resistance value of about 100–110 MΩ in air. Fig. 3a shows the decrease of the electrical resistance of the SnPd_{S} film in...
response to pure CH$_4$ (1), 0.5% vol. CO-in-N$_2$ (2), 0.5% vol. H$_2$-in-N$_2$ (3) and humidified (R.H. = 50%) 0.5% vol. H$_2$-in-N$_2$ (4). The data indicate that the speed and magnitude of the response towards H$_2$ is much larger than the response to other reducing gases such as CO and CH$_4$. Also, the presence of H$_2$O vapor in the surrounding atmosphere does not appear to interfere with the response towards H$_2$.

Fig. 3b shows the sensor’s response towards increasing concentrations of hydrogen gas (0.05, 0.1, 0.2, 0.5, 1 and 2% vol.) in air. This response to different levels of H$_2$ in air is appreciably fast, especially as we approach the explosion limit of 4% vol. H$_2$-in-air. Fig. 3c shows reversible changes in resistance when the surrounding atmosphere is cycled between pure air and 0.05% vol. H$_2$-in-air, suggesting that the sensor responds very quickly to both the introduction as well as the removal of small amounts of H$_2$ gas in air. We have also tested the response to oxygen introduced in a hydrogen process stream by cycling the surrounding gas between the gas mixtures 3.5% H$_2$-balance N$_2$ and 3.5% H$_2$-10% O$_2$-balance N$_2$. In this situation (Fig. 3d), the sensor’s resistivity changes can alternately be utilized as an alarm to signify the undesirable presence of O$_2$ (or its removal) in a reducing process gas stream.

The maximum gas sensitivity value $S$ (defined as the ratio of sensor resistance in air, $R_a$, to that in a sample gas, $R_s$) of our sensor film (SnPd$_4$) was found to be about 300, 5000, and 20 000 for 0.05, 0.5 and 2% vol. H$_2$-in-air, and 100 000 for 0.5% vol. H$_2$-in-N$_2$, respectively. These values are very high (~3–4 orders of magnitude) in comparison to previously reported sensors operating at high (200–400 °C) temperatures. Moreover, our sensor’s response to H$_2$ in air is also very fast for practical rapid detection of H$_2$. Beyond room temperature operation, another advantage of this sensor is that it is relatively insensitive to CO or CH$_4$, especially in the presence of O$_2$ (e.g. the sensor’s sensitivity towards 0.05% vol. H$_2$ in air is 300-fold larger than towards 0.05% vol. CO in air).

It has been reported that reduced grain size could enhance the sensitivity of SnO$_2$ towards reducing gases. The unusually high hydrogen sensitivity and rapid response of our films at room temperature presumably results from the high surface area, 3-D accessible sponge-like mesoporous structure, and uniform incorporation of PdO in the SnO$_2$ lattice. The surfaces of the interconnected nanosized single crystalline grains of PdO-SnO$_2$ allow rapid room temperature reduction of SnO$_2$ in response to H$_2$, causing a dramatic decrease of resistance values. When the film is exposed to air (oxygen), the reduced film surface reverts back to its original state. This surface reduction/oxidation process proceeds with no measurable changes in lattice spacing or nanostructure of the SnO$_2$. In the case of CO or CH$_4$, the film shows much weaker room temperature sensitivity, as a result of the weak interaction of CO gas with Pd$^{2+}$ and Sn$^{4+}$ ions at room temperature$^{13,14}$, and the much weaker reducing character of CH$_4$ gas. On the other hand, H$_2$O vapor only physisorbs on the SnO$_2$ surface at $T < 100$ °C with practically no$^{22}$ or very little effect on sensor’s electrical resistance.$^{23}$

In conclusion, we have demonstrated a synthesis approach that combines nanostructuring, molecular-level dispersion of a Pd catalyst, and homogenous film formation in a simple ‘one-pot’ process, leading to a unique material that overcomes existing barriers to rapid room temperature hydrogen detection by tin oxide. As an example, alternating between air and 0.5% vol. H$_2$ gas in N$_2$ changes the resistance reversibly and rapidly by a factor of about $10^3$ at room temperature. An additional advantage of this material is its relative insensitivity to other combustible gases such as CO or CH$_4$, or to ubiquitous H$_2$O vapour.

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Notes and references

17. If a Pd atom substitutes a Sn atom in the tetragonal SnO$_2$ lattice (space group P$4_3$mmm), there will be a 4% change in the lattice size, as a result of the shorter Pd–O bond distance (2.02 Å) compared to the Sn–O bond (2.10 Å). Overall there will be about 0.3% change in lattice size for 8 mol% substitution of Sn by Pd in the lattice. In this case, there will be only a 0.1° shift in the 20 angle of the most intense (110) reflection of tin oxide, which cannot be detected due to the broad peaks of our nanocrystalline thin film sensor. On the other hand, if PdO exists as discrete nanoparticles, it would be hard to detect it with wide-angle XRD since its most intense peaks, (101) and (002), coincide with the (101) peak of SnO$_2$.
20. The SnPd$_4$ film prepared without surfactant showed negligible response towards H$_2$ gas at room temperature.
Nanocrystalline mesoporous palladium activated tin oxide thin films as room-temperature hydrogen gas sensors†

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Electronic supplementary information (ESI)

Experimental:

All chemicals were used as received. Tin (IV) tert-butoxide (Sn(OBu')₄), palladium acetate (Pd(CH₃COO)₂) and solvents (n-propanol and i-butanol) were obtained from Aldrich, while the acetic acid was supplied by J.T. Baker. The surfactant Pluronic P123 was donated by BASF Corporation. Compressed gas mixtures of 0.5% vol. H₂-in-N₂, 0.5% vol. CO-in-N₂, forming gas (7% vol. H₂-in-N₂), N₂, CH₄ and compressed air were obtained from Matheson Tri-Gas.

Preparation of sols

2.43 mmol Sn(OBu')₄ was first dissolved in 12.3 mmol n-propanol. To this 0.0583 mmol surfactant dissolved in 16.4 mmol n-propanol was added with stirring. A mixture of 9.72 mmol acetic acid in 12.3 mmol n-propanol, followed by 14.2 mmol i-butanol was added to the above solution with stirring. The stirring was continued overnight (16 h). 0.211 mmol Pd(CH₃COO)₂ was dissolved in 22 mmol acetone and added to the above sol with stirring. The doped sol is then filtered through a 0.2 μm GHP Acrodisc® membrane.
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(Gelman Laboratory) prior to use for coating depositions. For comparison, a PdO-SnO₂ film without surfactant was also prepared. The nominal oxide molar ratio SnO₂:PdO = 92:8 was maintained in the sols. The total oxide (SnO₂ + PdO) equivalent content in the sols was about 5.8% wt. in all cases.

Preparation of films

Homogeneous films were deposited on plasma cleaned silicon wafers, Corning 7059, and silica glass substrates by spin-coating under ambient conditions (room temperature 21±1°C, relative humidity 5-10%), employing a spinning rate of 1,800 rpm. The films were stored in plastic boxes overnight and then dried at 100°C in air. The resulting dried films were then calcined for 6 h at 400°C in air.

Characterization

Refractive index and thickness measurements were made with a J.A. Wollam Co. M44 spectroscopic ellipsometer. All refractive index values (reported at a wavelength of 630.5 nm) and thickness measurements were made in triplicate and averaged. FTIR spectra were taken on a Bruker spectrometer (model Vector 22). XRD was recorded on a Siemens D-500 diffractometer, using a Cu Kα source. TEM was performed on a JEOL 2010 microscope, equipped with an energy dispersive X-ray scattering measurement (EDX) facility. High resolution SEM (FE-SEM) images were obtained in a Hitachi field-emission scanning electron microscope. X-ray photoelectron spectra (XPS) were obtained in a Kratos Axis Ultra XPS using a monochromatic Al Kα X-ray source.
Gas Sensing Measurements

For gas sensing measurements, the films were deposited on SAW substrates. The sensor film was sealed with copper O-ring inside a custom stainless steel holder, having appropriate electrical contacts with the two gold electrodes of the SAW device substrate, and equipped with inlets and outlets for gas flow. A mixture of air, 0.5% vol. H₂-in-N₂, 0.5% vol. CO-in-N₂, forming gas (7% vol. H₂—in-N₂), CH₄ and N₂ was flown over the sensor at a fixed total flow rate of 100 SCCM and Pₜot = 1 atm, adjusted with the aid of 2 mass flow controllers (Brooks Instr.). The gas relative humidity (R.H.) was controlled by flowing part of the gas through a bubbler filled with DI water. The film’s electrical response (resistance range of 30 MΩ and lower) to different gases was recorded with a Hewlett Packard 3478A digital multimeter connected with a computer for data acquisition using LabView software. All dynamic resistance measurements are therefore reported from 30 MΩ to lower values and the data points are collected in every 1 sec of interval. A Techtron® DT-20 multimeter was used to record film resistances manually above 30 MΩ.
Fig. S1. Low angle XRD of SnPd$_S$ films deposited on Corning 7059 glass substrates. The low angle XRD of the corresponding SnPd$_0$ film prepared without surfactant is also shown.
Fig. S2. The wide angle XRD of SnPd₈ films deposited on Corning 7059 glass substrates heated at 100 and 400 °C. The 400 °C film shows broad peaks corresponding to cassiterite SnO₂ structure. The SnO₂ (101) peak overlaps with broad amorphous peak arising from the glass substrate.