Adjusting surface coverage of Pt nanocatalyst decoration for selectivity control in CMOS-integrated SnO$_2$ thin film gas sensors

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Section A: Experimental Details

Figure S1 Atomic force microscopy (AFM) characterisation of Pt nanoparticles deposited on a Si substrate. A topography scan is shown on the left, whereas an evaluation of the height distribution is presented on the right. Assuming quasi-spherical Pt nanoparticles, the deducted sizes are in good agreement with the TEM characterisation discussed in the main manuscript.

Figure S2 Sensor response S to CO (top row, a-d) and VOCs (bottom row, e-h) of pristine and Pt-decorated SnO₂ sensors (nanoparticle deposition times 10min, 20min, 30min) at three different relative humidity (rH) levels and operation temperatures of 200°C (empty bars) and 350°C (full bars).
**SUPPLEMENTAL INFORMATION**

Table S1 Literature comparison of microhotplate-based chemical sensors for CO and VOCs.

<table>
<thead>
<tr>
<th>Microhotplate Technology</th>
<th>Heating Efficiency [K/mW]</th>
<th>Sensing Material</th>
<th>Deposition Method</th>
<th>Target Gas / Lowest Conc.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEMS</td>
<td>8.6</td>
<td>CuO</td>
<td>Sputtering</td>
<td>CO / 100 ppm</td>
<td>[1]</td>
</tr>
<tr>
<td>MEMS</td>
<td>7.5</td>
<td>SnO₂</td>
<td>Inkjet printing</td>
<td>CO / 35 ppm</td>
<td>[2]</td>
</tr>
<tr>
<td>MEMS</td>
<td>30</td>
<td>ZnO</td>
<td>Sputtering</td>
<td>CO / &lt;1 ppm</td>
<td>[3]</td>
</tr>
<tr>
<td>CMOS-MEMS</td>
<td>20</td>
<td>PdO/PdO₂-SnO₂-Sb</td>
<td>Electrohydrodynamic jet printing</td>
<td>VOCs / 0.5 ppm</td>
<td>[4]</td>
</tr>
<tr>
<td>CMOS-MEMS</td>
<td>18</td>
<td>Pd-SnO₂, Pd-WO₃</td>
<td>Electrohydrodynamic jet printing</td>
<td>VOCs / 3 ppm</td>
<td>[5]</td>
</tr>
<tr>
<td>CMOS-MEMS</td>
<td>30</td>
<td>SnO₂-Pt</td>
<td>Spray pyrolysis + inert-gas condensation</td>
<td>CO / 0.5 ppm VOCs / 1 ppm</td>
<td>this work</td>
</tr>
</tbody>
</table>

Table S2 Literature comparison of SnO₂/Pt-based chemical sensors for CO and VOCs.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>0-3% mol.</td>
<td>Pt-doped SnO₂ flowerlike hierarchical structure</td>
<td>-</td>
<td>1-500 ppm isopropanol</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>0-5% mol.</td>
<td>SnO₂ microsphere / Pt nanoparticle composite</td>
<td>-</td>
<td>5-500 ppm methanol, ethanol, isopropanol, formaldehyde, acetone, xylene, n-butanol, toluene</td>
<td>-</td>
<td>[7]</td>
</tr>
<tr>
<td>0-2.5% mol.</td>
<td>Pt decorated SnO₂ nanoparticles</td>
<td>10-3000 ppm</td>
<td>500 ppm benzene, formaldehyde, toluene, xylene, acetone, butane, methane</td>
<td>~0.01-2</td>
<td>[8]</td>
</tr>
<tr>
<td>0-0.4% wt.</td>
<td>SnO₂ nanofibers functionalised by Pt nanoparticles</td>
<td>0.125-2.5 ppm</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>3.125% mol.</td>
<td>Pt nanoparticles decorated SnO₂ nanoneedles</td>
<td>1-4000 ppm</td>
<td>100 ppm acetylene, ethylene, ethane, methane</td>
<td>~5-10</td>
<td>[10]</td>
</tr>
<tr>
<td>0-2% mol.</td>
<td>Pt decorated polycrystalline SnO₂ nanosheet assembled microflowers</td>
<td>1-1000 ppm</td>
<td>1-1000 ppm benzene, acetone, toluene, methanol, formaldehyde, ethanol</td>
<td>~0.01-1</td>
<td>[11]</td>
</tr>
<tr>
<td>0.04-0.16% wt.</td>
<td>PtO₂ nanocatalysts-loaded SnO₂ multichannel nanofibers</td>
<td>1 ppm</td>
<td>0.4-5 ppm acetone, ethanol, formaldehyde, toluene</td>
<td>~0.1-1</td>
<td>[12]</td>
</tr>
<tr>
<td>0-9% wt.</td>
<td>Compact SnO₂ thin film with surface Pt nanoparticles</td>
<td>0.5-200 ppm</td>
<td>1-60 ppm mixture of acetylene, ethane, and propene</td>
<td>0.2-1.2</td>
<td>this work</td>
</tr>
</tbody>
</table>


Section B: Computational model for nanoparticle decoration

1. Methodology
A simple numerical 2D model was constructed to provide basic insight on the process of nanoparticle decoration by gas phase deposition. Discretising both area and time, a 100×100 tetragonal grid was created and its initially unoccupied sites were one-by-one gradually occupied at random; a process which can be visualised as black squares randomly replacing white squares in an initially totally white chessboard. This way, each black square corresponded to a nanoparticle (3 nm in diameter in the real world, or 3 nm in side length in the model) being deposited on a specific position of a flat, square substrate. By “specific position” it is meant that neither Ostwald [13] nor Smoluchowski [14] ripening was accounted for in our model; the “nanoparticles” remained in their landing positions. The evolution in the number of free sides was calculated (i.e., sides of black squares next to white squares; 4 for a single black square, 6 for two adjacent black squares, etc.), which in our rough approximation corresponded to the number of free facets of nanoparticles, i.e., the catalytically active sites for all processes related to the sensing mechanism. The mean distance between nearest-neighbouring “nanoparticles” was also calculated as a function of coverage. Finally, the classic Cluster Multiple Label Technique (CMLT) algorithm [15] was utilised to calculate the site percolation threshold of our 2D grid. This is a commonly used method where the critical percolation coverage is determined from the maximum of the reduced average cluster size

\[
I_{\text{av}}(C) = \frac{\sum_{m=1}^{m_{\text{max}}} i_m m^2 - m_{\text{max}}^2}{G}
\]

where \(m\) is the cluster size, \(m_{\text{max}}\) is the size of the largest cluster, \(i_m\) is the frequency of occurrence of a cluster of size \(m\), and \(G\) is the total number of “nanoparticles” (i.e., occupied sites) in the simulated grid. The meaning of the reduced average cluster size becomes clear if one considers that the maximum cluster size is deducted from the average cluster size; therefore, when all clusters connect into a large, dominating cluster, \(I_{\text{av}}\) drops to zero, thus revealing the critical concentration for site percolation. All presented values were averaged over >10 calculations each. Variations between individual calculations were negligible; as such, no error bars were included in the figures since their sizes would not be noticeable.

2. Results and Discussion
According to our numerical model (and given its inherent approximations in interpreting experimental data), the number of exposed, catalytically active nanoparticle facets increases monotonically within the range of surface coverages studied experimentally (up to ~9%), as indicated by the red curve of Fig. S3a. For the experimental levels of coverage, most nanoparticles remain isolated from their neighbours, with each newly-deposited nanoparticle adding 4 new facets at first; this number gradually decreases as the probability of adjacent landings increases with coverage. A peak is reached at ~50% coverage; after that the overall number of exposed facets decreases as the probability of a new nanoparticle landing next to another is >50%. This is indirectly supported through the blue curve, which depicts the mean nearest neighbour distances on our virtual substrate. At low coverages, these distances average ~3 edge lengths (approximately 10 nm) but drop fast to ~1.5 edge lengths at about 10% coverage. Although the model does not account for ripening, it is intuitively suggested that such short distances could readily facilitate coalescence upon deposition. The percolation threshold is also indicated by the black curve in Fig. S3a (also derived with higher accuracy in Fig. S4) at 60% surface coverage. Determining it is of essence because it allows to estimate the coverage levels necessary for electrical conduction via a network of coalesced nanoparticles instead of the SnO\(_2\) support, which would be the practical limit for our sensing methodology. Clearly, experimental coverage levels discussed here are far from percolation, and the conductive medium remains the SnO\(_2\) substrate. However, the short distances between neighbouring nanoparticles at high coverages may imply the presence of a near-percolating
network of carrier-depleted islands below the nanoparticles. Of course, we need to emphasise once more that our derivations are rough approximations which do not consider 3D effects, ripening, nanoparticle shape and/or size variations or coalescence; for the effect of the latter in modifying the expected percolation threshold, more discussion is presented in [16].

What is of particular interest is the dependence of nanoparticle aggregation on coverage (Fig. S3b). We counted the number of distinct nanoparticles (or nanoparticle aggregates, i.e., squares on our grid adjacent to each other either through their sides or through their corners; the rationale being that if two nanoparticles feel the presence of each other they would aggregate/coalesce, given the opportunity). The calculated areal density (in NP/μm²) is indicated by the black curve. As expected, with increasing coverage this curve deviates from the “maximum number of nanoparticles” blue line (which indicates only isolated single nanoparticles), reaching a maximum value at around 15% coverage. However, performing a similar survey to experimental nanoparticles such as those shown in the TEM micrographs of Fig. 3 (red curve), it is evident that the areal density of distinct nanoparticles already starts dropping at considerably lower coverages (~6-7%). A direct comparison of theoretical and experimental nanoparticle numbers is not of primary importance here, rather the changes of slopes of the curves with increasing area coverage. The experimental nanoparticle areal density can be higher than the theoretical limit (model considering quadratic nanoparticles) due to their quasi-circular shapes and their size distribution.

Figure S3 a) Number of free edges (red), mean nearest neighbour distance (blue), and reduced average cluster size (black) indicating the percolation threshold, as a function of coverage for a 100 × 100 tetragonal grid gradually occupied by theoretical “nanoparticles” (squares 3 nm in side length). Corresponding experimental areal coverages extend up to ~9%. In this regime, nanoparticles are mostly isolated and at nearest-neighbour distances
of ~5-10 nm. b) Number of distinct entities for theoretical (black) and experimental nanoparticles (red) obtained from surveys of equal areas of theoretical supports (right) and TEM micrographs (Fig. 3). Peaks at different coverage levels indicate more pronounced coalescence for the latter, due to their ability to migrate on the support (unlike their theoretical counterparts).

Fig. S4 Number of free edges (red), mean nearest neighbour distance (blue) for a 100 × 100 tetragonal grid gradually occupied by theoretical “nanoparticles” (squares 3 nm in side length), as a function of coverage. The reduced average cluster size (olive) was calculated on a 1000 × 1000 tetragonal grid with cyclic boundary conditions, to indicate the percolation threshold with better definition than with the 100 × 100 case shown in Fig. S3a. Nevertheless, the result is the same: 60% coverage. Corresponding experimental areal coverages extend up to ~9%. In this regime, nanoparticles are mostly isolated and at nearest-neighbour distances of ~5-10 nm.

References