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Surface functionalization of ZnO:Ag columnar thin films with AgAu and AgPt bimetallic alloy nanoparticles as an efficient pathway for highly sensitive gas discrimination and early hazard detection in batteries

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For a fast and reliable monitoring of hazardous environments, the discrimination and detection of volatile organic compounds (VOCs) in the low ppm range is critically important, which requires the development of new chemical sensors. We report herein, a novel approach to tailor the selectivity of nanocomposite thin film sensors by investigating systematically the effect of surface decoration of Ag-doped ZnO (ZnO:Ag) columnar thin films. We have used AgPt and AgAu noble bimetallic alloy nanoparticles (NPs) to decorate the surfaces of ZnO:Ag and we have measured the resulting gas sensing properties towards VOC vapors and hydrogen gas. The gas response of the nanocomposite containing AgAu NPs to 100 ppm of ethanol, acetone, n-butanol, 2-propanol and methanol vapors was increased on average by a factor of 4 compared to the pristine ZnO:Ag columnar films. However, decoration with AgPt NPs led to a considerable reduction of the gas response to all VOC vapors and an increase of the response to H2 by roughly one order of magnitude, indicating a possible route to tailor the selectivity by surface decoration. As a result in this case, the reported NP-decorated ZnO:Ag thin film sensors should be suitable for the detection of H2 in Li-ion batteries, which is an early indication of the thermal runaway that leads to complete battery failure and possible explosion. To understand the impact of NP surface decoration on the gas sensing properties of ZnO:Ag thin films, we have employed density functional theory calculations with spin-Coulomb corrections and long-range dispersion interactions (DFT+U-D3(BJ)) to investigate the adsorption of various VOC molecules and hydrogen onto the Ag-doped and NP-decorated (10̅0) surface of zinc oxide ZnO. The calculated surface free energies indicate that AgAu/ZnO(10̅0) is the most favourable system for the detection of VOCs, which (benchmark in work function) is also the most reactive towards these vapors based on DFT calculations. Our calculated adsorption energies show that AgPt/ZnO(10̅0):Ag has the largest preference for H2 and the lowest preference for the organic adsorbates, which is in line with the high selectivity of AgPt/ZnO:Ag sensors towards the hydrogen-Zeeman molecule observed in our experiments.

Introduction

Nanocomposites that consist of noble metal nanoparticles (NPs) and micro- and nano-structures of semiconducting oxides, such as ZnO, SnO2 and CuO, have attracted significant attention and interest for their potentially highly sensitive detection of gases and VOC vapors, as well due to their excellent electronic, catalytic and optical properties. The surface decoration by NPs has shown to affect many sensor characteristics, including: (i) the sensitivity, enabling the detection of even trace amounts of gases; (ii) the selectivity towards certain gaseous species; (iii) the response and recovery times, which have been substantially reduced; and (iv) the acceptable stable operating temperatures, which have been shifted to values close to ambient conditions. Recently, highly sensitive and selective hydrogen gas nano-sensors have been described.
that are based on individual ZnO nanowires decorated by Pd NPs.\textsuperscript{4, 5} Guo et al. reported a remarkable enhancement of the gas sensing properties of ZnO nanorods by surface decoration with Au NPs, leading to fast response and recovery times, good selectivity and stable repeatability.\textsuperscript{4, 5} Majhi et al. have successfully prepared Au@ZnO core-shell NPs by a facile low-temperature solution route for highly selective H\textsubscript{2} gas detection, which was attributed to the chemical as well as catalytic effect of Au NPs.\textsuperscript{7}

However, recent results have demonstrated that bimetallic NPs have unique physico-chemical properties, superior to their monometallic counterparts, owing to the combination of their unique and the induced synergistic effects.\textsuperscript{4, 5, 8-10} Yong et al. have used density functional theory calculations to investigate the adsorption of CO\textsubscript{2}, H\textsubscript{2}O and NO on Ag-Au clusters for potential application as gas sensors and they found that adsorbates chemisorb on the surface of clusters with exothermic adsorption energies and finite charge transfer.\textsuperscript{10} Choi et al. decorated SnO\textsubscript{2} nanowire networks with bimetallic PdPt NPs, which led to fast response and recovery times during the detection of NO\textsubscript{2}.\textsuperscript{11} Fan et al. prepared ZnO loaded with PtAu bimetallic NPs, which showed high sensitivity to hydrogen down to the ppm-level, even at room temperature,\textsuperscript{12} whereas Hassan et al. decorated ZnO nanorods with PtPd bimetallic core-shell NPs for accelerated hydrogen gas detection.\textsuperscript{13}

Thus, it is crucially important to develop a technological approach which can control alloyed NP properties\textsuperscript{14} and to investigate the gas sensing performance of decorated nanocomposites comprising micro- and nanostructured semiconducting oxides and bimetallic NPs. The Ag-based alloys, such as AgPt and AgAu, are of particular interest due to the synergistic effect between the noble metal components, which makes them appealing for surface-enhanced Raman spectroscopy (SERS) as well as for applications in photocatalysis and sensing.\textsuperscript{4, 15-17} Ag-containing NPs have several advantages compared to other noble metals, e.g. harboring more active sites on their surface, which facilitates a more efficient electron transfer during the gas sensing applications.\textsuperscript{18} Ag-containing NPs are also more cost-effective in their preparation than their monometalic counterparts.\textsuperscript{12} Bimetallic AgAu NPs display a distinctive optical plasmon absorbance in the visible range\textsuperscript{19}. Their monometallic components have very similar lattice constants (4.09 Å for Ag and 4.08 Å for Au), allowing the preparation of different core-shell structures as well as alloys down to an average diameter of 4 – 5 nm,\textsuperscript{17} which are in high demand for device applications.

Despite the significant research potential, the effect\textsuperscript{20} of AgAu and AgPt NPs depositing the surface, surface decoration of semiconductor oxide micro- and nano-structures, especially single-wall nanotubes, has not received much attention. Therefore, in the present study, nanocomposites were prepared by the decoration of Ag-doped ZnO nanorod thin films (ZnO:Ag) with AgAu and AgPt NPs. Their gas sensing properties with regard to different VOCs and hydrogen gas were studied in detail. AgAu NP-decorated sensors showed a significant increase in sensitivity towards VOCs, whereas the AgPt-decorated sensors showed a change in the selectivity from VOCs to H\textsubscript{2} gas.

Furthermore, we can place the concept of noble metal alloy NP nanocomposite sensors in the context of early hazard detection in Li ion batteries (LIB). In this particular application scenario, the fast and reliable detection of H\textsubscript{2} gas is especially important for the operation of battery modules that contain a large number of cells in parallel. The electrolytes are composed of a lithium salt and aprotic organic solvents, typically organic carbonates or ether solvents, which can produce H\textsubscript{2} gas as a decomposition product.\textsuperscript{19-21} In this case, single battery cells inside a larger module experience degradation and a rise in internal temperature to a critical point, which is likely to have a catastrophic effect on the performance of adjacent cells. In addition, in events like the sudden penetration or puncturing of the battery, the commonly used organic carbonate electrolytes decompose and produce large quantities of H\textsubscript{2} gas, alongside a temperature increase of up to 200-250 °C. Thus, there is urgent demand for an immediate detection system with the potential for direct integration into the individual cells to avoid complete battery failure. In this study, the high sensitivity and fast response times of AgPt NP nanocomposite sensors is related to a potential application in this scenario.

The corresponding gas sensing mechanisms are proposed and supported by an extensive theoretical investigation. To uncover the origin of the unique gas sensing properties of the alloy NP-decorated ZnO:Ag thin films, first principles simulations were applied to study the sensing properties towards VOCs of the Ag-doped ZnO (1010) surface decorated with AgAu and AgPt clusters, whereas the metal ratios were chosen to reflect similar ratios as the experimentally obtained AgPt and AgAu NPs. The adsorption energies, electronic and structural implications of different scenarios have been investigated for the substitutional doping and adsorption of the alloy metal clusters onto the surface. Furthermore, the binding of ethanol, acetone, n-butanol, 2-propanol, methanol and molecular hydrogen on the ZnO:Ag as well as the Ag/Pt/ZnO:Ag and AgAu/ZnO:Ag modified surfaces are discussed to account for changes in selectivity and sensitivity. Whereas the sensitivity towards the VOC molecules was increased by the surfaces decorated with AgAu NPs, the Pt-based alloy NPs changed the nanocomposite’s selectivity to H\textsubscript{2} gas, in correspondence with the experiment.

Experimental

Sample synthesis

Ag-doped ZnO nanostuctured column thin films (ZnO:Ag) with a nominal thickness of 1.5 µm were deposited on glass substrates by a simple and inexpensive synthesis method from chemical solutions (SCS). Details of the SCS method used to create the doped ZnO columnar films were presented in previous works.\textsuperscript{21-24} The Ag doping content in the prepared samples was adjusted to 0.95 wt\%, which was confirmed in an earlier investigation by energy-dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS).\textsuperscript{24} All samples were thermally annealed at 650 °C for 2 h in air after deposition.

The alloy NPs were deposited onto the ZnO:Ag columnar thin films and Si wafer pieces (for reference measurements, Si-Mat, 10x10 mm\textsuperscript{2}) using a custom-built high vacuum deposition system
with an in-house Haberland type Gas Aggregation Source (GAS). For the generation of the AgAu and AgPt bimetallic alloy NPs, customized silver targets (Kurt J. Lesker, 99.99 %, 50.8 mm diameter) were used, with a drilled trench and a fitted Au wire (Alfa Aesar, 1.0 mm diameter, 99.95%) or Pt wire (Alfa Aesar, 1.0mm diameter, 99.95%), respectively. The deposition of alloy NPs by applying the target geometry methodology has been characterized in detail in an earlier work.29 A photograph depicting both targets in the geometry used is given in Figure 1a), while the whole PVV setup is sketched in Figure 1b). The respective target is mounted onto a DC planar magnetron source (Thin Film Consulting, IONIX-2UHV). Prior to deposition, the HV deposition system was evacuated to at least 10⁻⁴ Pa using a turbo molecular pump (Pfeiffer Vacuum, TMU 262) and a dry scroll pump (Agilent Technologies, SH-110). For sputtering, an Ar flow of 48 sccm, purity 99.999% was supplied at the gas inlet near the target (gas regulating valve: Pfeiffer, EVR116 with a hot ion cathode IR M 285 attached), resulting in a pressure of typically 136 Pa inside the GAS. For sputtering, a DC power of 40 W was supplied by the power source (Advanced Energy, MDX 500). Prior to every deposition, the target was cleaned and the NP growth was conditioned with a closed shutter for the time (at least 30 s) required to reach stable deposition conditions.

Sample characterization

Transmission Electron Microscopy (TEM) was used to investigate the nanostructure of the NP-decorated ZnO thin films using a Tecnai F30 G2 microscope (field emission gun, 300 kV) equipped with an in-house Haberland type Gas Aggregation Source (GAS). The C-1s line of adventitious carbon at roughly 285.0 eV was used for chemical composition of the deposited NPs and nanocomposites. X-ray photoelectron spectroscopy (XPS, Omicron NanoTech GmbH, Al-anode, 240W) was applied to investigate the chemical composition of the deposited NPs and nanocomposites. The C-1s line of adventitious carbon at roughly 285.0 eV was used for charge referencing of all recorded spectra. The software CasaXPS (version 2.3.16) was used to quantify the composition of the AgAu and AgPt alloy NPs. Micro-Raman studies were performed at room temperature with a WITec alpha 300 RA system in backscattering configuration. The Nd:YAG laser power at the laser position was less than 4 mW.34

Calculation details

Density functional theory (DFT) simulations were carried out using the Vienna ab-initio simulation package (VASP).35-38 All calculations were performed using the Vienna ab-initio simulation package (VASP). The valence electronic states were expanded via a plane-wave basis set with a kinetic energy cut-off of 400 eV. The projector augmented wave (PAW) method39 was used to describe the interactions between the core (Au: Pt: Xe) 4f⁴⁷; Ag: Kr; Zn: Ar; O: C: He) and the valence electrons. For the H atoms, the electron was treated as valence. The method of Grimme with Becke-Johnson damping (D3: (BJ))40 was applied to improve the description of the long-range dispersion forces. The simulations were carried out using the Perdew, Burke, and Ernzerhof (PBE)41 exchange-correlation functional within the generalised gradient approximation (GGA). An effective Uₜₐ value of 6.0 eV42 was applied to the strongly correlated and localised Zn 3d electrons to enhance the description of their on-site Coulomb interactions.43 However, no Hubbard Hamiltonian was employed for either the transition metal dopant or clusters states, as they are already delocalised given their low concentration44 and metallic properties, respectively. The structures were optimised using the conjugate-gradients technique and were considered converged when the forces on all atoms were less than 0.01 eV Å⁻¹. All calculations were spin-polarised to describe properly the unpaired electrons produced upon Zn(II) substitution by Ag(I).

The calculations of the insulating surfaces and isolated molecules were carried out sampling only the Γ point in the reciprocal space. However, the metallic phases were modelled using a Γ-centred Monkhorst-Pack mesh45 with a maximum separation of 0.17 Å between k-points. The partial occupancies for the surfaces and isolated molecules were determined using the Gaussian smearing method,46 with a width set at 0.05 eV. For the geometry optimisation of the metallic phases, the partial occupancies were simulated using the Methfessel-Paxton scheme order 1 with a smearing width of 0.10 eV. However, the tetrahedron method with Bloch corrections was used for the static calculations of the metallic phases to simulate the magnetic and electronic properties and to obtain accurate total energies. These criteria allowed convergence of the total energy within 10⁻⁴ eV per atom.

Results and discussion

Morphological, structural and micro-Raman characterizations

SEM micrographs of pristine ZnO-Ag columnar thin films, as well as of nanocomposites decorated with AgAu and AgPt bimetallic alloy NPs, are depicted in Figure 2. The morphology of a typical pristine ZnO-Ag thin film after heat treatment at 650 °C for 2 h (Figure 2a) and 2b) consists of closely packed and partially interconnected granites. The diameter of these granites varies between 50 and 400 nm. SEM micrographs of ZnO-Ag columnar thin films, which were decorated with AgPt NPs, are displayed in Figures 2c and 2d. The bimetallic AgPt NPs have a diameter ranging between 5 and 15 nm and are well distributed on the surface of the ZnO-Ag columnar thin film, without formation of percolating paths. However, due to the stochastic character of the deposition method, occasional agglomeration of small numbers of NPs are observed (see Figure 2d).

The SEM micrographs of ZnO-Ag thin films decorated by AgAu NPs are shown in Figures 2e and 2f. In this case, the deposited NPs exhibit...
typical NP diameters between 3 nm and 18 nm (see Figure 2f). In both cases, for both AgPt and AgAu alloy NPs, the mean diameter is considerably smaller than the grain diameter of the ZnO:Ag thin film. The observed diameters, as well as the sparse deposition with occasional agglomerations, agrees well with a typical NP deposition via GAS well below the percolation threshold.\(^2\)

Moreover, TEM experiments were conducted to investigate the nanostructure and verify the presence of alloy NPs. For example, Figure 3a depicts an overview image of an AgAu/ZnO:Ag nanocomposite. The electron diffraction (ED) pattern, recorded at the top of the displayed AgAu/ZnO:Ag grain, provides information that the doped columnar grains grow as single crystals along the c-axis of the Wurtzite-type structure. Furthermore, the ED pattern exhibits weaker diffraction intensities distributed on rings with d-spacings corresponding to ZnO. The appearance of these rings is attributed to polycrystalline ZnO, which is partially adhered to the surface. High resolution TEM micrographs (see Figure 3b) show the presence of NPs with diameters in the range of 5-20 nm, which is in good agreement with the observations from the SEM micrographs of Figure 2f. These NPs seem to be loosely bound to the ZnO surface and do not show a systematic intergrowth structure. The Fourier transform of the matrix verifies the presence of a single crystalline ZnO (zone axis [100]) phase. Due to the similar crystal structures of Ag and Au, the composition of the NPs could not be distinguished between the pure metals or alloy (zone axis [110]). To verify the presence of AgAu NPs (or AgPt NPs), the nanocomposite was investigated by EDX elemental mapping (see Figure 3c or Figure 52, respectively). The EDX elemental map (Figure 3c) clearly shows that the locations of the high Ag signal and the high Au signal overlap, which indicates the presence of AgAu alloy NPs. For Ag and Pt in the AgPt/ZnO:Ag nanocomposite (Figure 52), a similar trend is observed. It is reported that Ag and Pt form a miscibility gap ranging roughly from 13\(^{\%}\) to 98\(^{\%}\) with respect to Pt content.\(^4\),\(^5\)

However, phase separation could not be identified within the measuring limits of the microscope used (Figure 52). Considering that Pt content is about 12\(^{\%}\) (see XPS studies below), it is reasonable to assume that a solid solution has formed.\(^6\)

Figure 51 shows the Raman spectra of the AgAu- and AgPt-decorated ZnO:Ag columnar films. For all samples, the two dominant peaks were observed at ~100 cm\(^{-1}\) and ~438 cm\(^{-1}\), which are attributed to the E\(_{2g}\) (low) and E\(_{2g}\) (high) modes of the wurtzite structure of ZnO, respectively. Other peaks with lower intensities were observed at ~337, ~380, ~576 and ~584 cm\(^{-1}\), which are attributed to E\(_{1g}\) (high), E\(_{1g}\) (low), A\(_{1g}\) (TO), E\(_{1g}\) (TO), A\(_{1g}\) (LO) and E\(_{1g}\) (LO) modes, respectively.\(^7\),\(^8\)

**XPS studies**

The ZnO:Ag nanocolonar thin film (as a reference layer), as well as the nanocomposites decorated with the AgPt and AgAu alloy NPs, were investigated by XPS. Figure 4a shows the overview spectra of the nanocomposites (AgAu: red line, AgPt: blue line) and the reference layer [magenta, bottom line]. Based on the characteristic peaks of these spectra, the elemental composition of these samples is determined. The elements Zn, O, C and Au are detected in all spectra. The position of the line C-1s in Figure 4b, which was used for charge referencing, indicates atmospheric surface contamination from organic compounds, such as carbohydrates. The prominent signal of Zn and O is attributed to the ZnO base layer. The comparison of the O-1s high resolution spectra (Figure 4b) indicates a similar peak position and shape for the investigated nanocomposites as well as for the pristine substrate. Ag is detected in all three samples, but the corresponding signal is rather weak, especially for the ZnO:Ag base layer, which is attributed to the low doping concentration of Ag. A comparison of high resolution spectra of the Ag-3d, Au-4d and Pt-4d lines can be found in Figure 53. The signal is stronger in the case of the AgAu NPs and AgPt NPs decorated nanocomposites, but due to the intentionally low surface coverage of NP, the signal is still weak for a precise quantification.\(^9\)

For further investigation of the deposited NPs, the reference spectra of AgPt and AgAu alloy NPs (deposited on silicon wafer pieces) are compared in Figure 4c and 4d. The overview spectra in Figure 4c indicates the presence of Si, Cr, O, C, Ag and Au or Pt for the AgAu and AgPt NPs, respectively. To quantify the composition of the alloy NPs, a detailed binding energy scan of the Ag-3d, Au-4d and Pt-4d lines from 382 eV to 333 eV is shown in Figure 4d. Additional peaks with an offset to lower binding energies (by roughly 30 eV) occur in the spectra, due to the use of a non-monochromated X-ray source. In case of the AgAu NPs, the offset peak from Ag-3d\(_{5/2}\) overlaps with the Au-4d\(_{5/2}\) line. Accordingly, the Au-4f line was used for the quantification of Au, which was estimated at 52\^{\%}\), in the AgPt NPs. For the AgPt NPs, the relevant Ag-3d and Pt-4d lines are well separated and correspond to a Pt content of roughly 12\(^{\%}\). Considering the lower sputtering rate of Pt compared to Au (roughly 0.57 of Au) and the difference in target design (three Au wires for AgAu and one Pt wire for AgPt), the difference in concentration of Ag in the AgPt and AgAu NPs is expected.\(^10\),\(^11\) The estimated composition of AgPt and AgAu NPs is presented in Table S1 in the Supporting Information.

**Gas sensing properties**

Figure 5a shows the gas response of the pristine ZnO:Ag, AgPt/ZnO:Ag and as well as AgAu/ZnO:Ag nanocomposites to hydrogen gas (H\(_2\)) and different VOCs vapors, including such as ethanol, acetone, n-butanol, 2-propanol and methanol, at an operating temperature of 250 °C. In a typical gas sensing experiment, the thin film sensor was exposed to a concentration of 100 ppm of each VOC or H\(_2\). However, in the case of the ZnO:Ag and AgAu/ZnO:Ag columnar films, an H\(_2\) concentration of 1000 ppm was used to underline the low sensitivity of these sensors towards H\(_2\). A considerable increase of the response to VOC vapors was observed for the ZnO:Ag columnar films that were decorated with AgAu NPs.

The gas response of the ZnO:Ag columnar films to 1000 ppm of hydrogen and 100 ppm of ethanol, acetone, n-butanol, 2-propanol and methanol is ~2.1, ~3.1, ~16.5, ~41, ~52.5 and ~31, respectively, while for AgAu/ZnO:Ag it is ~2, ~8, ~25, ~39, ~130.5, ~156.5 and ~140, respectively. Compared to the pristine ZnO:Ag thin film, the gas response of AgAu/ZnO:Ag to ethanol, acetone, n-butanol, 2-propanol and methanol was increased by factor of ~2.8, ~4, ~3.2, ~3 and ~4.5, respectively. The gas response values are also

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considerably higher compared to those obtained for monometallic Ag NP-decorated ZnO:Ag columnar films synthesized by the same method,14 proving the higher efficiency of bimetallic NP decoration. The low gas response to hydrogen gas is characteristic for all samples, with the exception of the AgPt/ZnO:Ag columnar films. AgPt-bimetallic decoration of the AgPt alloy NPs leads to a decrease in response in all of the VOCs tested, by a factor of 2, it enhances the sensitivity to 100 ppm of H2 gas by a factor 40. This is a large change compared to the almost no response to H2 gas in the case of the reference and the AgAu-decorated sample sets, which indicates the possibility of tailoring the selectivity of ZnO:Ag thin film sensors by surface decoration with bimetallic NPs of different alloy systems. In addition to contemporary approaches, e.g., the incorporating molecular sieve, the versatility of gas to produce a variety of metal, metal alloy and metal oxide NPs opens up a highly interesting research field for further improvements in sensor selectivity.

Figures 5b and 5c show the dependence of the gas response to H2 gas and different VOC vapors on the operating temperature for the AgPt/ZnO:Ag and AgAu/ZnO:Ag nanocomposites, respectively. In both cases, the optimal operating temperature is 250 – 300 °C. At operating temperatures lower than 200 °C no gas response higher than 1.5 was observed, and this temperature regime was therefore not investigated in detail any further.

The dynamic response of the AgPt/ZnO:Ag columnar films to 100 ppm of H2 gas at different operating temperatures (200 – 350 °C) is presented in Figure 6a. The calculated values for the associated response and recovery times are presented in Figure 6b. The response times are confined to a small range (11 – 20 s), while the recovery times decrease from 36 s to 10 s when the operating temperature rises from 200 to 350 °C.

The dependence of the H2 gas response (S(H2)) to its concentration at 250 and 300 °C is presented in Figure 6c. A power law relationship is observed (S(H2) ∝ p(H2)β), where β is the slope of log S(H2) vs. log p(H2),13 β ≈ 0.85 at both 250 and 300 °C. The theoretical detection limits calculated for the H2 gas (criterion for gas detection: Irepid > 1.2 S2) were ~1 and ~0.6 ppm at 250 and 300 °C, respectively.

The dynamic responses of the AgAu/ZnO:Ag columnar films to 100 ppm of VOC vapors at their optimal operating temperatures of 250 °C are presented in Figure 6d. All samples show fast signal recovery to the initial electrical baseline after evacuation of the vapors from the test chamber, which is essential for the reliability of sensors and their practical applications. The calculated response and recovery times versus the operating temperature are presented in Table 1 and Figure 6c. The recovery times for all samples are comparable to one of the best results reported for functionalized/decorated ZnO samples (see Table 2).

Table 2 shows other results for high performance VOC vapors sensors based on ZnO micro- and nano-structures functionalized/decorated with monometallic and bimetallic noble metals (Ag, Au, Ag, Pt). This table clearly demonstrates that our results are equivalent or superior in comparison to the performances reported for highly sensitive VOC sensors, although there are several reports of H2 response values much higher than for our AgPt/ZnO:Ag columnar films. However, the remarkable point of our materials in this case is the possibility of change the selectivity from VOC vapors to H2 gas, which opens the opportunity for the fabrication of highly selective gas sensors. In addition, the platinum content in the bimetallic AgPt NPs, which in this work was determined to be roughly 17%, results in a more cost-effective approach to tailor the sensor selectivity compared to the use of the pure material.

The dependence of the gas response on the concentration of VOC vapors for the AgAu/ZnO:Ag columnar films is presented in Figure 6d. For ethanol, acetonitrile, n-butanol, 2-propanol, and methanol the β value is 0.87, 0.88, 0.83, 0.82, and 0.78, respectively, which indicates the estimated theoretical detection limit for ethanol, acetonitrile, n-butanol, 2-propanol, and methanol are ~1, 0.8, 0.5, 0.4, 0.3 and 0.2 ppm, respectively.

Alloy NP-decorated thin film gas sensors as candidate materials for monitoring thermal runaway in Li-ion Batteries

From the gas sensing studies, it can be concluded that the surface decoration of the ZnO:Ag columnar films with AgAu NPs increases the selectivity to VOC vapors, while the surface decoration using AgPt NPs changes the response and leads to high selectivity to hydrogen gas. Thus, the selectivity of the ZnO:Ag films can be easily tuned using bimetallic NPs of different composition for surface decoration of the columns, which is of significant interest for gas sensor applications. In view of the versatility in tailoring the sensor's selectivity, and taking into account its fast response and recovery times, the alloy NP-decorated ZnO:Ag thin film sensors are highly promising materials for early hazard detection in LIBs, where many of the decomposition products, especially from the electrolyte solvents, are extremely flammable. In 14-16 Hazard detection in LIBs is especially demanding, as thermal runaway in a single functioning cell can rapidly destroy the whole device and other neighboring devices, leading to a complete failure of all individual cells. For critical applications, e.g., in the automotive sector, each cell should be equipped with a fast and robust hazard detection system in order to prevent fire spreading to other cells.

In the case of thermal runaway, the LIB heats to over 200 °C and produces large amounts of H2 gas. Applying the alloy NP/ZnO:Ag thin film sensors in close vicinity of each battery cell would allow the identification of failing units as the H2 gas produced can be detected. However, the thermal runaway provides the appropriate operating temperature for the sensor. Accordingly, the sensitivity of the AgPt/ZnO:Ag sensor towards H2 would be enhanced, whereas the temperature is raised, making this decorated surface an excellent material for the detection of thermal runaway in LIBs. In contrast, the AgAu/ZnO:Ag sensor has a significantly lower response towards H2 gas and is therefore an effective material to rule out sensor malfunction.

Thus, the integration of alloy NP/ZnO:Ag thin film sensors into individual battery cells is a potential pathway to achieve a cost-effective and fast detection method of the early stages of thermal runaway, and to avoid the deterioration of other cells connected in parallel.
Gas sensing mechanism for bimetallic alloy NP-decorated films

The gas sensing mechanism of the decorated columnar films can be explained by the electronic and chemical sensitization effects, i.e. the formation of nano-Schottky barriers at the interface between ZnO:Ag and the AgPt and AgAu alloy NPs, as well as the catalytic properties of the bimetallic NPs. Given that the diameter of the ZnO:Ag grains is larger than its Debye length, the nano-Schottky barriers formed at the Au/ZnO:Ag and Pt/ZnO:Ag interface have a low impact on the improvement of the gas sensing properties. Moreover, since the AgPt and AgAu NP-decorated ZnO:Ag columnar films exhibit very different sensing properties, it can be concluded that the chemical sensitization effect, i.e. the catalytic properties of the NPs, has a dominant effect. Choi et al. demonstrated that surface decoration of CuO NWs with different types of NPs, by modification of the conduction channel width, does not change the selectivity of the material. Therefore, the key parameter that explains the selectivity change by surface decoration with AgPt NPs are the excellent catalytic properties of Pt with respect to hydrogen. A number of studies have demonstrated that the addition of Pt NPs to different nano- and micro-structures of metal oxides can greatly enhance the response to H2 gas. The Pt NPs may provide more active sites than any other noble metal for the adsorption and catalytic dissociation of oxygen species and H2 molecules. During the sensing process, the spillover and oxidation of hydrogen molecules by the adsorbed oxygen species (see Eq. (1)) located near the AgPt bimetallic NPs leads to a high response to H2 gas. Taking into account the low concentration of roughly 12% of Pt in our bimetallic AgPt NPs, the strong shift of selectivity towards H2 gas is even more remarkable.

\[ 2O_{ads} + 2H_2 \rightarrow 2H_2O + 2e^- \]  

Liu et al. also observed that the addition of Pt NPs to SnO2 leads to a considerable decrease in the response to VOC vapors, while the addition of Au NPs leads to the opposite effect. These findings also support the large effect of the chemical sensitization on the gas sensing properties and the selectivity of the AgPt/ZnO:Ag columnar films to H2 gas. Another mechanism which can explain the high selectivity of the AgPt/ZnO:Ag samples is the formation of PThs species at the relatively high operating temperatures of 250 – 300 °C. Under these conditions, the number of hydrogen atoms per Pt atom increases, and the metal becomes a superior catalyst for hydride formation. In the case of the AgAu/ZnO:Ag columnar films, the greatly enhanced sensing properties towards VOCs can be explained by the excellent catalytic properties of the Au component of the NPs toward the dissociation of oxygen and VOC molecules. The Au NPs will provide more active sites for the adsorption of oxygen species than the pristine surface of ZnO. Many studies have demonstrated that the addition of Au NPs to nano- and micro-structures of metal oxides leads to an enhancement in the overall response and selectivity to VOC vapors. The proposed reaction for the oxidation of the VOC molecules by the adsorbed oxygen species can be described as follows:

\[ CH_3COCH_3(acetone) + 5O^+ \rightarrow 3CO_2 + 3H_2O + 6e^- \]  \( (2) \)
\[ CH_3OH(ethanol) + 6O^+ \rightarrow 2CO_2 + 3H_2O + 6e^- \]  \( (3) \)
\[ CH_2=CH_2(methylene) + O^+ \rightarrow HCHO + H_2O + e^- \]  \( (4) \)
\[ CH_2=CH(OH)(2-propenol) + O^+ \rightarrow (CH_2)CO(acetone) + H_2O + e^- \]  \( (5) \)
\[ VOC + nO^+ \rightarrow nCO_2 + nhH_2O + ne^- \]  \( (7) \)

Calculated properties

The DFT calculations have been performed to gain insight into the physio-chemical properties of the gas molecules (CH3OH, CH3COCH3, CH3CHO, CH3CH2OH, C2H4H2O, CH3OH and H2O) adsorbed on the Ag-doped ZnO(1010) surface decorated with Ag, Au, and AgPt clusters. The aim of these calculations is to support experiment and explain the experimentally observed enhanced sensitivity and the change in selectivity reported for the systems studied.

Terminations A and B of the ZnO(1010) surface were modelled using slabs with an area of 98.574 Å2 and containing 96 atoms distributed in 8 atomic layers, see Figure 7a. A vacuum gap of 20 Å along the direction perpendicular to the surface is added to separate each slab from its periodic image. More details regarding the stacking of the layers, and a description of the surface terminations and the number of layers with the atoms frozen at their bulk positions can be found elsewhere. The substitutional doping of the ZnO(1010) surface by Ag and its effect on the surface structure, energies, as well as on the electronic and magnetic properties are examined. One Zn atom is replaced in order to model the lowest Ag content value of 2.73 at%. Unfortunately I could not notice it before. 2-propenol does not have any CH2 groups. It is CH3-CH=CH2 n-butanol has the highest number of CH2 groups CH3-CH2-CH2-CH3.

\[
\text{Molecules by the adsorbed oxygen species can be described as follows:} \]

\[
\text{CH}_3 COCH_3 (acetone) + 5O^+ \rightarrow 3CO_2 + 3H_2O + 6e^- \]
\[
\text{CH}_3 OH (ethanol) + 6O^+ \rightarrow 2CO_2 + 3H_2O + 6e^- \]
\[
\text{CH}_2=CH_2 (methylene) + O^+ \rightarrow HCHO + H_2O + e^- \]
\[
\text{CH}_2=CH(OH) (2-propenol) + O^+ \rightarrow (CH_2)CO (acetone) + H_2O + e^- \]
\[
\text{VOC + nO^+ \rightarrow nCO}_2 + nhH_2O + ne^- \]

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where the face-centred cubic (fcc) Ag and hexagonal close-packed (hcp) Zn were modelled using the one- and two-atom primitive unit cells, respectively.

The surface free energy (σ) of the partially decorated material has been estimated using,

$$\sigma = \gamma + \frac{E_{\text{total}} - E_{\text{pris}} - E_{\text{dop}} + E_{\text{vac}}}{A} \tag{9}$$

where γ is the surface energy for the relaxed pristine ZnO (1010) surface, \(E_{\text{total}}\) is the energy of the Ag-doped ZnO(1010) surface, \(E_{\text{pris}}\) is the energy of the pristine ZnO(1010) surface, \(E_{\text{dop}}\) is the energy of one atom in the bulk of fcc Ag and \(E_{\text{vac}}\) is the energy of one atom in the bulk of hcp Zn. The values for the relaxed pristine ZnO(1010) surface were taken from previous work,32 and Table S2 shows the close agreement between the experimental and simulated lattice parameters for Ag and Zn.

Table 3 displays the surface free energies for the Ag-doped systems, indicating that only termination A is slightly stabilised by 14-18 meV Å\(^{-2}\) with respect to its pristine parent structure. However, substitutional doping of termination B, and in particular of its 3-fold Zn site, lead to the most thermodynamically stable doped surfaces, although they are less favourable than the pristine parent plane.

The simulations suggest that in both terminations, the most exposed undercoordinated cation positions is ~5 meV Å\(^{-2}\) more favourable than the substitution of the 4-fold sites. It was found that large in-plane displacements of approximately 1 Å for the atoms within the topmost layer account for the exothermic enthalpy during the insertion of Ag in termination A. Moreover, minor concomitant shifts of 0.15 Å towards the bulk are also observed for the sub-surface plane of Zn atoms and the surface layer of counter-ions. These horizontal and vertical atomic shifts are only allowed in the doped termination A due to the large interlayer spacing of 1.848 Å between the surface and sub-surface planes.44 In contrast, the densest topmost layers of termination B experience negligible displacements, with the exception of the O atoms surrounding the 3- and 4-fold Ag dopants, which move by 0.43 and 0.45 Å, respectively.

The Bader charge analysis34,35 shows that Zn ions draw 58-60% of the electrons required to become neutral atoms from the Ag atoms, in agreement with their different charges in the pristine and doped surfaces, respectively. However, the largest electronic transfer is 68% for the doping of the 3-fold position of termination B in doped, which is also the most stable surface of this study. We found different nodal compensation mechanisms for the electronic deficit caused by the replacement of the Zn atoms leaving both in the two terminations of the ZnO(1010) surface. In contrast termination A, the 3-fold Zn ions provide an excess of electrons, which also reduces the exposed oxygen atoms by a further 0.1 e, thereby increasing the ionic character of the topmost surface layer.

In contrast termination B, the scenario for the charge compensation of Zn only involves the oxidation of its neighbouring oxygen atoms, as illustrated in Figure 7b. The charge density difference schemes were constructed by subtracting the sum of the electron charge densities of the clean surface and isolated dopant, with identical structure as in the doped form, from the electron density of the total system obtained from static static calculations. The simulation of the doped terminations A and B suggests that most atoms remain non-magnetic, following the process represented in equation (9). However, the Ag introduced alongside the 3-fold oxygen ions that directly coordinate the dopant atoms become slightly magnetic, ca 0.3 μB per atom. From the small magnetic moment calculated for the dopant, an electronic distribution of \(\frac{e}{2} t^2 r^2\) has been inferred, corresponding to Ag\(^{+}\) ions in a pseudo-tetrahedral crystal field of oxygen atoms.

The electronic properties of the doped surfaces were further investigated by measuring the work function (φ) in order to gauge their reactivity as reducing agents.36,37 The work function is the energy needed to remove an electron from the Fermi level (\(E_F\)) of the surface into the electrostatic potential of the vacuum (\(\Phi\)), calculated as \(\Phi = V_F - E_F\). Table 3 shows large reductions of over 50% in the work function values of all the doped surfaces with respect to their pristine counterparts, with between 2.61 and 2.64 eV for the doped 4-fold position in both terminations.

However, for further analysis, we focus on the 4-fold doped slab of termination B, which possesses the lowest surface energy and is therefore likely to be the prominent plane exposed in the crystal morphology of ZnO.

Impregnation with AgAu, and AgPt was also explored as means to add decoration to the doped ZnO(1010) surface and reduce the detection limit of VOCs. Clusters composed of 10 atoms were chosen, as this is the smallest size to produce a close analogue to the experimental Ag content, i.e. 48% and 88% in AgAu and AgPt NPs, respectively (cf. Table S1). The initial geometries for both noble bimetallic nanoclusters were derived from the fcc crystal structure common to the three monometallic materials14,15 and the secondary Au or Pt element was placed at random crystallographic positions. Table S2 illustrates the excellent agreement between the experimental and simulated lattice parameters for monometallic Au and Pt. Three different positions for the adsorption of the bimetallic clusters were chosen, i.e. (i) above, (ii) close to, and (iii) far away from the Ag dopant. Term \(-\left(\text{E}_{\text{clus}} + \text{E}_{\text{dop}}\right)\)/\(A\) was added to equation (9), to evaluate the surface free energy of the fully decorated material; where \(X\) represents either fcc Au or Pt; \(E_F\) is the energy of one such atom in the bulk; \(x\) and \(y\) are the number of Ag and X atoms, respectively, in the cluster; \(E_{\text{clus}}\) becomes \(E_{\text{clus}+\text{dop}}\), which is the energy of the Ag-doped ZnO(1010) surface decorated with the NPs, while the remaining variables keep their previous definition.

The simulations suggest that the addition of the bimetallic cluster increases the surface free energy with respect to the doped surface, particularly for the Pt-based particles, see Table 4. The most thermodynamically favourable adsorption position depends on the nature of the cluster, as AgAu is likely to sit far from the Ag dopant, while AgPt prefers a closer position.

The stability of the clusters on the surface was calculated using the adsorption energy (\(E_{\text{ads}}\).
The lack of correlation between the adsorption energies of Ag₉Pt and their surface free energies can be explained based on the random position that Pt can adopt within the cluster during geometry optimisation. The positive values calculated for all the adsorption energies, which are largest for Ag₉Au₉, indicate that although these are thermodynamically unfavourable processes, the impregnated NPs lead to the most stable adsorption position of the Au- and Pt-based NPs, respectively. The lowest adsorption energy values of 5.32 and 2.95 eV were calculated for the most stable adsorption position of the Au- and Pt-based NPs, respectively.

The incorporation of both nanoclusters slightly raises the work function of the fully decorated surfaces with respect to the doped system. The lowest work function is predicted for the facet containing the Ag₉Pt NP in the most favourable adsorption position. However, the largest value for this type of thermodynamic work was calculated for the surface decorated using the Ag₉Au₉ cluster in the most stable binding site. The small magnetic moments of the Ag dopant vanish after adsorption of the nanoclusters in any of the positions considered. Most of the adsorbed clusters are non-magnetic, but the simulations reveal a small mean value of 0.04 μB for each atom within the Ag₉Au₉ particles sited above and close to the dopant. Large positive charges of 1.4 e⁻, 1.37 e⁻ and 1.38 e⁻ are located on the Ag atom of the cluster, while the secondary Au and Pt metals are reduced by about 0.7 and 0.4 e⁻, in agreement with their respective electronegativities. The net charge balance results in all noble bimetallic particles upon adsorption losing ~0.0 e⁻ to the Zn atoms underneath and the O ions near the dopant.

The adsorption of the single molecules onto the doped and NP-decorated ZnO(10̅10) surfaces was also studied and it was found that all these processes release energy, see Table 5. The molecules were introduced in several orientations at 1.5 Å from the surface and were subsequently allowed to relax to their equilibrium adsorption geometries. The calculated adsorption energies on the Ag-doped surface are roughly ~1.5 to ~1.7 eV for all the alcohols, which subtly depends directly on their molar mass. However, the strength of binding is approximately 0.5 eV less favourable for CH₃OH than for the alcohols, suggesting different chemical nature of their carbonyl and hydroxyl functional groups. The simulations suggest that the non-polar H₂ molecule has the overall lowest adsorption energy at ~1.0 eV. The introduction of the Ag₉Pt nanocluster reduces the energetic preference of the alcohols and ketone for the decorated surface by approximately 1.0 and 0.5 eV, respectively, compared to the doped system. The largest energy released at Eads = −1.387 eV was found for the adsorption of H₂ on the Ag₉Pt/ZnO:Ag surface, indicating a change in selectivity in agreement with our experiments. The impregnation with Ag₉Au₉ NPs leads to larger adsorption energies and enhanced sensitivity towards the VOCs with respect to the Ag₉Pt/ZnO:Ag surface. Remarkably, the decreasing order of binding strength for the organic molecules is Eads(CH₃COOH) ≈ Eads(2-C₃H₇OH) > Eads(CH₃OH) > Eads(n-C₃H₇OH) > Eads(CH₄OH), showing no dependence on the type of functional group. The binding energy of ~0.070 eV for H₂ on Ag₉Au₉/ZnO:Ag is the lowest calculated in this study, which explains the lack of selectivity found in our experiments for this molecule.

It was found that all the VOCs adsorb molecularly on the doped as well as on the NP-decorated ZnO(10̅10) surfaces, in line with previous reports. In contrast the doped surface, three adsorption positions relative to the Ag atom were tested, i.e. the molecules directly interacting with the defect, or as well as with its first and second nearest Zn neighbours. In the case of the VOCs, the preferred mode involves direct coordination between the adsorbate oxygen and the exposed Ag or Zn atom at around 2.15 and 2.00 Å, respectively. The hydroxy group of the alcohols forms a short hydrogen bond at the typical distance of 1.39 to 1.53 Å with a surface 3-fold oxygen atom, as shown in Figure 7c for n-CH₃OH. Other configurations are at least 0.108 eV less favourable than the most stable binding modes, as they involvecooperative dissociative adsorption or distorted hydrogen bonds. For example, CH₃OH can dissociate the hydroxy hydrogen, which is donated to the closest oxygen from the coordinated Ag adsorption site. Moreover, n-CH₃OH can form hydrogen bonds with the oxygen lying either closer or farther away from the coordinated Ag and Zn cation than in the most stable adsorption modes. The free rotation around the C-OH bond and weak dispersion forces allow the hydrocarbon fragment of the alcohols to orientate as close as possible to the surface atoms all the adsorption modes. Conversely, the flat ketone molecule stays adsorbed in a bent configuration, giving rise to the tetrahedral nature of the metallic coordination site and the trigonal geometry of the sp²-hybridised carbonyl oxygen. Unsurprisingly, the H₂ molecule has both minor exothermic molecular and moderately exothermic dissociative adsorption modes. This molecule appears tilted and hovering at 2.10 Å from any of the Zn sites and the closest 3-fold oxygen. H₂ also dissipates upon interaction with the AgO or OO pair sites. For the dissociative adsorption configurations, the hydrogen atoms sit at 1.63 Å from the Ag-dopant and at the usual O-H bond distance of 0.98 Å from the 3-fold oxygen.

The addition of Ag₉Pt changes the adsorption geometry of CH₃OH, which prefers to interact through its hydroxy H with the Pt atom at a distance of 2.30 Å, which increases by 0.38 Å for CH₃OH. However, the alcohols of higher molar mass, i.e. n-C₃H₇OH and 2-C₃H₇OH, instead coordinate to the Pt atom by their hydroxy O at an average distance of 2.37 Å. CH₃COOH binds the Pt atom at 2.20 Å, which is the smallest value reported for any VOC interacting with the Ag₉Pt/ZnO:Ag surface. Different behaviours were calculated for the hydrocarbon radical of the VOCs, which lies more parallel to the surface for the low mass alcohols and the ketone than for n-CH₃OH and 2-C₃H₇OH. H₂ interacts upon adsorption to the Pt site, with the H atoms separated by 2.16 Å, explaining the largest exothermic enthalpy for the interaction with the supported Ag₉Pt cluster, as shown in Figure 7d.

Shifting to the Ag₉Au₉ particle increases the number of interactions between the surface and the VOC molecules, justifying the larger adsorption energies with respect to the Ag₉Pt/ZnO:Ag surface. The DFT adsorption geometries indicate that 2-C₃H₇OH and CH₃OH form the dative H-bonds to Ag and H-Au bonds at 2.40 and 2.62 Å, respectively, see Figure 7e. Furthermore, n-CH₃OH and CH₃OH have similar adsorption configurations as the alcohols of...
intermediate molecular mass, but coordinate the Au atom at least 0.14 Å further away. CH₃COOH can only form the O-Ag interaction at 2.30 Å, which is the shortest for the bimetallic AgAu cluster, as displayed in Figure 7F. Finally, the H₂ molecule stays perpendicular to the surface and 2.52 Å from the Au atom, leading to the smallest adsorption energy calculated for this molecule in this study.

Bader charge analysis shows that all VOCs become positively charged upon adsorption on the doped surface, with the largest transfer of 0.09 e⁻ obtained for the Ag site, as shown in Table 5. Charge donations decrease around 50% after introducing the AgPt cluster and the negative values calculated for the low molecular mass alcohols confirm their adsorption geometry via the hydroxyl H. Electron transfers vanish for the molecules adsorbed on AgPt as well as on AgAu clusters with the exception of the negatively charged n-C₆H₄OH and CH₃OH, which sit furthest away from the cluster. H₂ suffers the largest charge withdrawal reported for adsorptions on the doped surface, but it is predicted that the H-Zn hydrogen gains −0.20 e⁻ while the hydroxyl H loses 0.64 e⁻. The reverse direction of electron transport for the interaction with the bimetallic nanoclusters was observed, as H₂ gains a small electronic charge and remains molecular.

Conclusions

In summary, the surface of ZnO:Ag nanostructured columnar grains was successfully decorated with AgPt and AgAu bimetallic alloy NPs using a custom-made high vacuum deposition system with an in-house Haberland type Gas Aggregation Source. Gas sensing measurements were carried out to reveal the response of the thin films to H₂ gas and various VOC vapors. The underlying gas sensing mechanisms for the AgPt as well as AgAu NP-decorated ZnO:Ag thin films was proposed and discussed in terms of the electronic and chemical sensitivity effect of the bimetallic alloy NPs.

The nanocomposites with AgAu NPs exhibit a highly improved response to VOC vapors compared to the pristine ZnO:Ag thin films and previously reported nanocomposites based on ZnO:Ag and Ag NPs. The gas response to 100 ppm of ethanol, acetone, n-butanol, 2-propanol and methanol vapors was increased by a factor of ~2.8, ~6, ~3.2, ~3 and ~4.5, respectively, compared to pristine ZnO:Ag thin films. In contrast, the nanocomposite decorated with the AgPt NPs shows a remarkable change in selectivity toward H₂ gas. While the response to all VOC vapors is considerably decreased once AgPt NPs are introduced on the surface of ZnO:Ag columnar films, the response to H₂ is increased by more than one order of magnitude.

The affinity of small molecules towards the doped and NP decorated ZnO(1010) surfaces was also investigated computationally. The doping with Ag atoms was modelled, where it was found that the most stable substitution occurs for the 3-fold Zn surface sites. Subsequently, AgPt and AgAu clusters prefer to bind the surface above and far away from the dopant atom, respectively. When studying the adsorption of CH₃OH, CH₂=CH₂, n-C₆H₄OH, 2-C₆H₅OH, CH₃COOH and H₂ on the doped surfaces and at the nanoclusters, it was also studied. It was found that the VOCs release the largest and smallest energies upon adsorption to the doped surfaces and AgPt cluster, respectively, in agreement with the enhanced selectivity of the former. The dissociative adsorption of H₂ on the AgPt/ZnO(1010):Ag surface causes has the largest calculated adsorption energy calculated for any of the NP decorated surfaces, supporting the change in selectivity reported for this system.

We have shown that the decoration of ZnO:Ag columnar thin films with bimetallic NPs of noble metals provides a viable route to tailor the sensitivity as well as selectivity of ZnO:Ag gas sensors. It was found that AgAu NPs lead to high sensitivity as well as fast response and recovery times for the detection of the types of VOCs studied. In addition, the possibility to change the selectivity of ZnO:Ag thin films by surface decoration with bimetallic NPs is a feasible, effective and flexible approach for the fabrication of highly selective sensors.

Considering the low concentration of about 12%Ag of Pt in the AgPt bimetallic alloy NPs, this sensor is a promising prototype of a cost effective H₂ gas sensor for early hazard detection in lithium ion batteries. Given the high versatility and adaptability of the thin film fabrication process, in combination with the application of alloy NPs for surface decoration, the approach presented in this work offers significant potential for gas sensing applications, for example for the early detection of thermal runaway in LIB.

Conflicts of interest

There are no conflicts to declare.

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Author Contributions

A.V., V.P., and O.L. synthesized the AgAu and AgPt bimetallic alloy NPs. V.P., A.V., M.I.T., M.H., H.C. and S.N. adapted technological approach for material synthesis and integration/fabrication of the sensors for early hazard detection in batteries. V.P. and O.L. carried out the measurement of sensing properties of sensors based on such structures and analyzed data. T.D., N.W. and L.K. performed TEM studies and analysis. V.P., V.S. and K.A. N.H. performed chemistry studies and final approval of the version of the manuscript. O.L., A.V., F.F., L.K., S.N. and R.A. conducted study conception and design and final approval of the version to be published. All authors reviewed the manuscript.

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Figure 1. (a) Photographic image of the AgAu (top half) and AgPt (bottom half) composite targets; (b) Schematic illustration of the custom-built HV deposition system for bimetallic alloy NP deposition.
Figure 2. SEM micrographs of ZnO:Ag columnar thin films after thermal annealing at 650 °C for 2 h: (a,b) pristine ZnO:Ag thin films; (c,d) ZnO:Ag thin films decorated by AgPt NPs; (e,f) ZnO:Ag thin films decorated by AgAu NPs.
Figure 3. (a) Overview TEM micrograph of a AgAu/ZnO:Ag nanocomposite: Electron diffraction pattern of the tip of the AgAu/ZnO:Ag nanostructure verify that these are single crystalline structures and exhibit a c-axis growth direction. (b) HRTEM of a AgAu NP attached to the surface of the AgAu/ZnO:Ag nanostructure and corresponding FFT. (c) EDX elemental mapping of the marked region indicates the presence of AgAu alloy NPs.
Figure 4. (a) Overview XPS spectra of ZnO:Ag columnar thin film (magenta line) and nanocomposites with AgAu (blue line) and AgPt (red line) bimetallic alloy NPs; (b) high resolution spectra of C-1s and O-1s lines; XPS spectra of AgAu alloy NP layers (blue line) and AgPt (red line) for overview (c); and detailed quantification of NP composition (d).
Figure 5. (a) Gas response to H\textsubscript{2} gas and different VOC vapors for ZnO:Ag, AgPt/ZnO:Ag and AgAu/ZnO:Ag columnar films at 250 °C operating temperature. The concentration of VOC vapors is 100 ppm. The concentration of H\textsubscript{2} gas is 100 ppm for the highly responsive AgPt/ZnO:Ag composite while it is 1000 ppm for the pristine ZnO:Ag thin film and AgAu/ZnO:Ag composite. Temperature dependence of the gas response for the AgPt/ZnO:Ag (b) and AgAu/ZnO:Ag (c) nanocomposite.

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Figure 6. (a) Dynamic response of a AgPt/ZnO:Ag nanocomposite sensor to 100 ppm of H$_2$ gas at different operating temperatures (200 – 350 °C). (b) The response and recovery times of a AgPt/ZnO:Ag nanocomposite sensor to 100 ppm of H$_2$ gas versus operating temperature. (c) The dependence of H$_2$ gas response to H$_2$ gas concentration for AgPt/ZnO:Ag at 250 and 300 °C. (d) Dynamic response of a AgAu/ZnO:Ag nanocomposite sensor to 100 ppm of VOC vapors and 1000 ppm of H$_2$ gas at 250 °C. (e) Response and recovery times of a AgAu/ZnO:Ag nanocomposite sensor versus operating temperature for different VOCs. (f) Dependence of gas response to the concentration of VOC vapours for AgAu/ZnO:Ag at 250 °C of operating temperature.
Figure 7. (a) Side view of the simulation slabs for terminations A and B of the ZnO(10\overline{1}0) surface. The 3- and 4-fold Zn positions that were doped with Ag are displayed within red circles, and the dashed lines represent the surface terminations. (b) Charge density flow (\rho) for the substitutional doping using Ag of the termination B of the ZnO(10\overline{1}0) surface. Electron density gain and depletion surfaces are in yellow and green, respectively. Isosurfaces display a value of \pm 0.002 e Å\(^{-3}\). (c) Molecular adsorption of n-C\(_4\)H\(_9\)OH on the termination B of the ZnO(10\overline{1}0):Ag surface. (d) Dissociative adsorption of H\(_2\) on the termination B of the AgPt/ZnO(10\overline{1}0):Ag surface. (e) Molecular adsorption of C\(_2\)H\(_5\)OH and (f) CH\(_3\)COCH\(_3\) on the termination B of the Ag\(_{Au}/ZnO(10\overline{1}0):Ag surface. Crystallographic directions are indicated for all panels.
Table 1. Overview over of the calculated response and recovery times to VOC vapors at different operating temperatures.

|                | Temperature, °C | 200 | 250 | 300 | 350 |
|----------------|-----------------|-----|-----|-----|-----|
| **ZnO:Ag**     | Ethanol         |     |     |     |     |
| Resp. time (s) | 62              | 49  | 22  | 18  |
| Rec. time (s)  | 16              | 9   | 3   | 2   |
| **Acetone**    |                 |     |     |     |     |
| Resp. time (s) | 114             | 65  | 41  | 18  |
| Rec. time (s)  | 47              | 11  | 3   | 2   |
| **n-Butanol**  |                 |     |     |     |     |
| Resp. time (s) | 88              | 105 | 43  | 38  |
| Rec. time (s)  | 22              | 10  | 4   | 3   |
| **2-Propanol** |                 |     |     |     |     |
| Resp. time (s) | 57              | 65  | 38  | 24  |
| Rec. time (s)  | 16              | 6   | 4   | 3   |
| **Methanol**   |                 |     |     |     |     |
| Resp. time (s) | 80              | 51  | 17  | 40  |
| Rec. time (s)  | 28              | 10  | 4   | 3   |
| **AgPt/ZnO:Ag**| Hydrogen        |     |     |     |     |
| Resp. time (s) | 15              | 11  | 14  | 20  |
| Rec. time (s)  | 36              | 20  | 15  | 10  |
| **Acetone**    |                 |     |     |     |     |
| Resp. time (s) | 78              | 21  | 29  | 20  |
| Rec. time (s)  | 36              | 11  | 5   | 3   |
| **n-Butanol**  |                 |     |     |     |     |
| Resp. time (s) | 61              | 6   | 28  | 8   |
| Rec. time (s)  | 29              | 7   | 5   | 3   |
| **2-Propanol** |                 |     |     |     |     |
| Resp. time (s) | 113             | 94  | 43  | 40  |
| Rec. time (s)  | 43              | 15  | 3   | 2   |
| **Methanol**   |                 |     |     |     |     |
| Resp. time (s) | 46              | 23  | 45  | 34  |
| Rec. time (s)  | 32              | 8   | 4   | 2   |
| **AgAu/ZnO:Ag**| Ethanol         |     |     |     |     |
| Resp. time (s) | 29              | 18  | 17  | 15  |
| Rec. time (s)  | 39              | 28  | 10  | 8   |
| **Acetone**    |                 |     |     |     |     |
| Resp. time (s) | 96              | 66  | 85  | 48  |
| Rec. time (s)  | 47              | 41  | 11  | 6   |
| **n-Butanol**  |                 |     |     |     |     |
| Resp. time (s) | 51              | 45  | 69  | 49  |
| Rec. time (s)  | 28              | 26  | 21  | 7   |
| **2-Propanol** |                 |     |     |     |     |
| Resp. time (s) | 59              | 25  | 73  | 38  |
| Rec. time (s)  | 33              | 23  | 14  | 6   |
| **Methanol**   |                 |     |     |     |     |
| Resp. time (s) | 98              | 29  | 50  | 15  |
| Rec. time (s)  | 35              | 22  | 12  | 6   |
Table 2. Comparison of the sensing properties for VOC and H₂ sensors based on metal oxides modified/decorated with different noble metals.

| Sensing material                          | VOCs conc. (ppm) | Gas response \((I_{\text{gas}}/I_{\text{air}})\) or \((R_{\text{air}}/R_{\text{gas}})\) | Operating temperature \((\degree\text{C})\) | Response time (s) | Recovery time (s) |
|-------------------------------------------|------------------|---------------------------------------------------------------------------------|---------------------------------|------------------|------------------|
| Ag-ZnO films [27]                         | EtOH 2000        | ~ 2                                                                              | 225                             | 5                | -                |
| Ag/ZnO nanorods [28]                      | EtOH 100         | 36.52                                                                            | 360                             | 50               | 28               |
| ZnO-Ag hybrids [19]                       | EtOH 100         | 101.8                                                                            | 370                             | ~ 15             | ~ 20             |
| Ag-ZnO nanorods [41]                      | EtOH 50          | 34.8                                                                             | 25                              | -                | -                |
|                                               | Acetone 50       |                                                                                  | 280                             | -                | -                |
|                                               | Methanol 50      |                                                                                  | 14.5                            | -                | -                |
| Ag-loaded ZnO [41]                        | EtOH 100         | ~ 75                                                                             | ~ 30                            | -                | -                |
|                                               | Acetone 100      |                                                                                  | ~ 68                            | 240              | -                |
|                                               | Methanol 100     |                                                                                  | ~ 55                            | -                | -                |
| Au-doped ZnO NWs [40]                     | EtOH 1000        | ~ 37                                                                             | 240                             | -                | -                |
| Au-ZnO NWs [4]                            | EtOH 100         | 33.6                                                                             | 380                             | 3                | 1                |
| Au/ZnO nanorods [41]                      | EtOH 100         | 89.5                                                                             | 300                             | 2                | 2                |
|                                               | EtOH 1000        | 32                                                                              | 300                             | -                | -                |
|                                               | Acetone 100      | 21                                                                              | 400                             | 2                | 2                |
|                                               | Acetone 100      | 32                                                                              | 400                             | 4                | 4                |
|                                               | EtOH 100         | 20                                                                              | 13                              | -                | -                |
|                                               | Acetone 100      | 16                                                                              | 300                             | -                | -                |
|                                               | Methanol 100     | 7                                                                               | -                               | -                | -                |
| Au/ZnO yolk-shell nanospheres [41]         | EtOH 100         | ~ 75                                                                             | 300                             | 75               | 600              |
|                                               | Acetone 100      | 37                                                                              | 300                             | 2                | 38               |
|                                               | Methanol 100     | ~ 22                                                                             | 320                             | -                | -                |
|                                               | Acetone 100      | 8.9                                                                              | 100                             | 10               | -                |
|                                               | Methanol 50      | ~ 75                                                                             | 300                             | 75               | 600              |
| Au@ZnO core-shell nanoparticles [3]        | EtOH 100         | ~ 63                                                                             | 300                             | 75               | 600              |
|                                               | Acetone 100      | ~ 22                                                                             | 320                             | -                | -                |
|                                               | Acetone 100      | 49.56                                                                            | -                               | -                | -                |
|                                               | Acetone 100      | 74.41                                                                            | 270                             | 5                | 3                |
| Pt/ZnO NWs [47]                            | EtOH 50          | 32.6                                                                             | 265                             | -                | -                |
| PtAu/ZnO nanorods [13]                     | H₂ 250           | ~ 160                                                                            | 130                             | -                | -                |
| PtPd/ZnO nanorods [14]                     | H₂ 10 000        | ~ 3                                                                              | 100                             | 5                | 76               |
| AgPt/ZnO-Ag columnar films (this work)     | H₂ 100           | 43                                                                               | 250                             | 11               | 20               |
|                                               | EtOH 100         | 70                                                                               | 300                             | 14               | 15               |
|                                               | Acetone 100      | 8.3                                                                              | 250                             | 7                | 12               |
|                                               | 2-propanol 100   | 14.3                                                                             | 250                             | 6                | 7                |
|                                               | n-butanol 100    | 16.2                                                                             | 250                             | 94               | 15               |
|                                               | Methanol 100     | 13                                                                               | 250                             | 23               | 8                |
|                                               | EtOH 100         | 85                                                                               | 18                              | 28               | -                |
|                                               | Acetone 100      | 99                                                                               | 66                              | 41               | -                |
|                                               | 2-propanol 100   | 156.5                                                                            | 250                             | 45               | 26               |
|                                               | n-butanol 100    | 130.5                                                                            | 250                             | 25               | 23               |
|                                               | Methanol 100     | 140                                                                              | 29                              | 22               | -                |

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Table 3. Calculated surface energies after relaxation ($\gamma_r$) for terminations A and B of the pristine ZnO(1010) surface. The surface free energies ($\sigma$) are also reported for both terminations of the Ag-doped ZnO(1010) surface. The work function ($\Phi$) values are indicated for the pristine and doped surfaces.

| Termination | Doping site | $\gamma_r/\sigma$ (meV Å$^{-2}$) | $\Phi$ (eV) |
|-------------|-------------|---------------------------------|-------------|
| A           | pristine    | 190                             | 5.40        |
|             | 3-fold      | 172                             | 2.50        |
|             | 4-fold      | 176                             | 2.61        |
| B           | pristine    | 84                              | 5.80        |
|             | 3-fold      | 125                             | 2.84        |
|             | 4-fold      | 130                             | 2.64        |

Table 4. Calculated surface free energy ($\sigma$) and work function ($\Phi$) for the Ag-doped ZnO(1010) surface decorated with the Ag$_5$Au$_5$ and Ag$_9$Pt clusters. The adsorption energy ($E_{ads}$) for the NPs on the Ag-doped ZnO(1010) surface is reported. The relative position of the NP with respect to the Ag-dopant is also indicated. The doping was carried out in the 3-fold position of termination B.

| Cluster | Position | $\sigma$ (meV Å$^{-2}$) | $E_{ads}$ (eV) | $\Phi$ (eV) |
|---------|----------|--------------------------|----------------|-------------|
| Ag$_5$Au$_5$ | above   | 181                       | 5.54           | 3.01        |
|          | close    | 184                       | 5.88           | 3.10        |
|          | far      | 179                       | 5.32           | 3.12        |
| Ag$_9$Pt | above    | 192                       | 6.63           | 2.95        |
|          | close    | 209                       | 8.30           | 2.95        |
|          | far      | 194                       | 6.79           | 3.15        |
Table 5. Adsorption energies (E_{ads}) and charge transfers (Δq) for the CH₃CH₂OH, CH₃COCH₃, n-C₄H₉OH, 2-C₃H₇OH, CH₃OH and H₂ molecules on the Ag-doped ZnO(101̅0) surface and following decoration with the Ag₅Au₅ and Ag₉Pt clusters. The relative position of the adsorbate with respect to the dopant is also indicated. The doping was carried out in the 3-fold position of termination B.

| Molecule | Position | ZnO(101̅0)-Ag | Ag₅Pt | Ag₉Pt | CH₃CH₂OH  | CH₃COCH₃ | n-C₄H₉OH  | 2-C₃H₇OH  | CH₃OH  | H₂ |
|----------|----------|----------------|-------|-------|-----------|-----------|-----------|-----------|---------|----|
|          |          | E_{ads} (eV)   | Δq (e⁻) |       | E_{ads} (eV) | Δq (e⁻) | E_{ads} (eV) | Δq (e⁻) | E_{ads} (eV) | Δq (e⁻) |
| CH₃CH₂OH | defect   | -1.527         | 0.09  | -0.590| -0.04     | -0.762   | 0.00       |          |         |    |
|          | close    | -1.486         | 0.02  | -0.590| -0.04     | -0.762   | 0.00       |          |         |    |
|          | far      | -1.602         | 0.03  | -0.590| -0.04     | -0.762   | 0.00       |          |         |    |
| CH₃COCH₃ | defect   | -1.122         | 0.07  | -0.663| 0.02      | -0.798   | 0.00       |          |         |    |
|          | close    | -1.021         | 0.04  | -0.663| 0.02      | -0.798   | 0.00       |          |         |    |
| n-C₄H₉OH | defect   | -1.027         | 0.04  | -0.663| 0.02      | -0.798   | 0.00       |          |         |    |
|          | close    | -1.122         | 0.07  | -0.663| 0.02      | -0.798   | 0.00       |          |         |    |
| 2-C₃H₇OH | defect   | -1.316         | 0.09  | -0.555| 0.05      | -0.798   | 0.00       |          |         |    |
|          | close    | -1.530         | 0.03  | -0.555| 0.05      | -0.798   | 0.00       |          |         |    |
| CH₃OH    | defect   | -1.649         | 0.08  | -0.453| -0.07     | -0.528   | -0.02      |          |         |    |
|          | close    | -1.421         | 0.02  | -0.453| -0.07     | -0.528   | -0.02      |          |         |    |
| H₂       | defect   | -1.046         | 0.44  | -1.387| -0.07     | -0.070   | -0.02      |          |         |    |
|          | close    | -0.268         | 0.02  | -1.387| -0.07     | -0.070   | -0.02      |          |         |    |
|          | far      | -0.291         | 0.03  | -1.387| -0.07     | -0.070   | -0.02      |          |         |    |