Enhanced Vapour Sensing using Silicon Nanowire Devices Coated with Pt Nanoparticle Functionalized Porous Organic Frameworks

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Recently various porous organic frameworks (POFs, crystalline or amorphous materials) have been discovered, and used for a wide range of applications, including molecular separations and catalysis. Silicon nanowires (SiNWs) have been extensively studied for diverse applications, including transistors, solar cells, lithium ion batteries and sensors. Here we demonstrate the functionalization of SiNW surfaces with POFs and explore its effect on the electrical sensing properties of SiNW-based devices. The surface modification by POFs was easily achieved by polycondensation on amine-modified SiNWs. Platinum nanoparticles were formed in these POFs by impregnation with chloroplatinic acid followed by chemical reduction. The final hybrid system showed highly enhanced sensitivity for methanol vapour detection. We envisage that the integration of SiNWs with POF selector layers, loaded with different metal nanoparticles will open up new avenues, not only in chemical and biosensing, but also in separations and catalysis.

Introduction

Improved sensitivity and selectivity in the detection of gas-phase molecules for environmental monitoring, process control and safety, and medical diagnosis is of utmost importance.¹ One promising approach for the direct electrical detection of analytes is by using nanowires configured as field-effect transistors (FETs), which exhibit superior sensitivity as given by their high surface-to-volume ratio and the direct signal amplification by the transistor function.^{2, 3} Particularly silicon nanowire-based FETs (SiNW-FETs), pioneered by Lieber's group,⁴ have been studied for more than 15 years now and have attracted a great deal of interest, mainly for their controllable properties and compatibility with very-large-scale

integration (VLSI) processes and complementary metal–oxide–semiconductor (CMOS) technologies.^{5, 6} While most SiNW-FET studies focus on detection of analytes in aqueous solutions,^{7, 8} different gas-phase applications of electrical SiNW-based devices are attracting increasing interest.⁹ For instance, the research group of Haick published a number of systematic studies on the fundamentals and applications of functionalized SiNW-based FETs for the detection of volatile organic compounds (VOCs).^{10, 11} In addition, surface functionalization of SiNWs with Pd nanoparticles,¹² oligopeptides,¹³ diphenylchlorophosphate (DPCP) receptors,¹⁴ or 3-aminopropyltrimethoxysilane (APTES)¹⁵ allowed for the rapid detection of H₂, acetic acid vapours, DPCP and explosives, respectively. All these studies have shown the advantages of controlled surface modification of the SiNWs in tuning sensor selectivity.

A variety of porous materials,¹⁶ such as metal organic polyhedra (MOP),¹⁷ metal organic frameworks (MOFs)¹⁸ and covalent organic frameworks (COFs),¹⁹ have gained a lot of interest due to their exceptionally high specific surface areas, high specific gas storage and separation capabilities and their potential in catalysis and sensing applications,^{20, 21} and other electronic devices related to, e.g., resistance-switching memory,²² high-performance dielectrics,²³ and proton conductivity.²⁴ The chemical diversity of these porous materials allows for a fine-tuning of the chemical and physical properties by tailored synthesis.²⁵ In addition, the exposure of properly designed affinity sites on the porous materials enable further coupling of functional substrates, for instance to Au plasmonic substrates and to SiNWs platforms, expanding their

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application window significantly.^{20, 26} Along these lines, we developed and explored a unique hybrid construct: porous organic framework (POF)-decorated SiNWs for the investigation of chemical vapour sensing. POFs are extremely attractive as affinity layers as they are not only highly porous, but also highly stable due to the formation of covalent bonds rather than metal coordination bonds; some of the early reported MOF structures decompose gradually if environmental moisture is present.²⁷ In addition, post-synthesis strategies can be applied to POFs to further tune their physico-chemical properties. We report here on a surface modification strategy to yield POF-functionalized, SiNW-based devices, after which the electrical properties of the resulting hybrid construct were investigated upon changes in the environmental humidity and methanol vapours. Moreover, the post-synthesis functionalization of the POF-SiNW hybrid by the *in-situ* formation of Pt nanoparticles (PtNPs) results in advanced sensing properties of methanol vapours.

Results and discussion

The SiNW surface was functionalized with POFs via the polycondensation of melamine and terephthalaldehyde on the amine-modified SiNWs,²⁸ as illustrated in Fig. 1a, b. The POF-modified SiNWs together with the precipitated materials were harvested and cleaned for different characterizations.

The molecular details of the reactants and the effect of different solvents, temperature, reaction time and the use of catalyst on the products were examined by Fourier Transform Infrared spectroscopy (FTIR), as shown in Fig. S1. Only in the case of DMSO as the solvent, the precipitate in the reaction solution was found to be flocculent. Reactions at the other conditions gave granular products. For the products obtained in all solvents the FTIR spectra show vibrations around 1550 cm⁻¹ and 1480 cm⁻¹, which are attributed to the stretching vibration of the triazine ring,²⁹ indicating the successful incorporation of the melamine into the molecular network. However, vibrations around 1690 cm⁻¹ (C=O stretching) are absent only for the product synthesized in DMSO,

which proves that the highest conversion of functional groups initially present in the monomers was achieved in DMSO. Therefore, the reaction was optimized in this solvent. Moreover, the bands corresponding to imine bond vibration (*i.e.*, 1600 cm⁻¹) was absent in the FTIR spectra, indicating that the aldehyde group has reacted twice with an amino group from the melamine building block, forming a trisubstituted imine moiety. The high boiling point, combined with the high polarity of DMSO, contributes to the increased solubility of the initially formed polycondensated product via imine bonds, making subsequent condensations to a trisubstituted imine bonds possible as indicated by the structure in Fig. 1b.³⁰ In addition, considering the (in)stability of the Al electrodes on the SiNW chip during this reaction, we optimized the reaction time to 14 hours. Longer reaction times showed similar FTIR spectra of the product, as shown in Fig. S1b.

The porous structure of the obtained flaky POF material synthesized under optimized conditions was investigated by N₂ gas sorption at 77 K (Fig. 2a). At low relative pressures a rapid uptake of N₂ is observed, indicating the presence of micropores. At high relative pressures (*i.e.*, $P/P_0 > 0.8$) some hysteresis is observed, which is attributed to the presence of mesopores where some capillary condensation can take place. At high relative pressures (*i.e.*, $P/P_0 > 0.9$) a steep rise in adsorption was observed, which indicates the presence of even larger pores, likely due to inter-particle porosity.³⁰ The calculated Brunauer-Emmett-Teller (BET) specific surface area were found to be 620 m²/g and 640 m²/g for POFs synthesized for 14 hours and 72 hours, respectively. These values are lower than the one reported the first time for this material (1377 m²/g)²⁸, but very similar to more recently reported values for microporous organic polymer materials prepared via polycondensation (values ranging from 70 to 614 m²/g).³⁰⁻³² From the N₂ adsorption isotherms recorded at 77 K, the pore size distribution (PSD) was calculated with the use of Density Functional Theory (DFT), resulting in a pore diameter ranging from 1 to 55 nm (*i.e.*, micro- to mesopores; Fig. S2). Considering the presence of N atoms in the POF network and the likely favourable interaction with CO₂, CO₂ sorption isotherms were measured up to 1.2 bar at 273 K (Fig. 2b).

Fig. 1 Schematic representation of (a) APTES grafting to the silanol-terminated surface of a SiNW, (b) the covalent modification process of the SiNW surface with melamine-terephthalaldehyde-based POFs, (c) the metalation of a POF-SiNW via an *in-situ* chemical reduction. Molecules 1-3: APTES, melamine, terephthalaldehyde, respectively.

Fig. 2 (a) N_2 sorption isotherm acquired at 77 K, (b) CO_2 sorption isotherm acquired at 273 K of the POF powder synthesized under optimized conditions, (c) SEM image of the bare SiNW, (d) SEM image of the SiNW decorated with POFs.

At 1 bar ($P/P_0 = 0.029$), the observed CO_2 uptake is 2.3 mmol/g, which is very similar to the high values of ~ 2.0 mmol/g and ~ 1.5 mmol/g as reported for the similar polymer networks (PI-1 and PI-2) rich in N atoms.³¹ The high value of CO_2 uptake here can be attributed to the high density of nitrogen in the POF structure originated from the melamine building blocks.

Similar surface modifications on silicon wafers were performed as model system for the SiNWs. These modified wafers were

investigated by X-ray photoelectron spectroscopy (XPS) and compared with the unmodified wafers. The relative atomic surface composition of Si, O, C and N is shown in Table S1. Upon modification with APTES, the N percentage increases from 0 to 2.5%, indicating the successful silanization. Meanwhile, ellipsometry measurements showed 0.7 nm as the optical thickness, indicating a monolayer of APTES formed on the Si wafer.³³

Fig. 3 Variation of drain-source current (I_{ds}) of bare SiNW and POF-modified SiNW with humidity at $V_g = -3$ V and $V_{ds} = 0.05$ V, (a) Real-time variation of I_{ds} after a step-wise increase of the relative humidity from 0 to 46%, (b) Increase of I_{ds} in time after the successive increase of RH from 0 to 60% (labels a-f refer to the injection of RH in 6.5, 13, 20, 33, 46 and 60%, respectively, while label g indicated the start of a pure N_2 flow). The inset shows the relative increase of I_{ds} as function of RH.

Fig. 4 TEM images after NaBH_4 reduction of POFs containing different amounts of H_2PtCl_6 , showing the formed Pt nanoparticles with different particle sizes. The molar ratios between H_2PtCl_6 and N atoms in the POFs are (a) 1 : 100, (b) 1 : 37, (c) 1 : 20, and (d) 1 : 4.

After the POF polycondensation and POF coupling to the APTES layer, the N percentage increases to a value of 31%. The observed N/C ratio is found to be very similar to the ratio observed in the pure POF powder (31%). Inspection of the SiNW before and after surface modification by using scanning electron microscopy (SEM) showed the presence of flaky POF material on the nanowire (Fig. 2d). Similar flaky POF structures were observed on the modified silicon wafers (Fig. S3).

Next, we have compared the electrical device response towards changes in humidity for POF-modified SiNWs and bare SiNWs using our home-built vapour sensing apparatus (Fig. S4).^{34,35} Both types of p-doped SiNWs were set in the depletion mode by the application of a back-gate potential of $V_g = -3$ V, and the varying drain-source current (I_{ds}) was registered under the conditions of a constant source-drain voltage (V_{ds}) set to 0.05 V. Step-wise increase of the relative humidity to RH = 46% shows for the bare SiNW a very slow increase of I_{ds} reaching more or less equilibrium after 2 h. The POF-modified SiNW showed a fast increase of I_{ds} and equilibration after *ca.* 3 min, which is around 40 times faster as compared to the unmodified sensor. The I_{ds} at equilibrium for the POF-modified SiNWs is about two times higher than for the bare SiNWs. In both

situations the I_{ds} increases, indicating an increase of the concentration of the majority charge carriers (here holes). This is understood as that the injection of water vapour results in partial deprotonation of surface silanol groups on the SiNW and changes the surface charge from neutral to negative, as $\text{Si-OH} \rightleftharpoons \text{Si-O}^- + \text{H}^+$, ($\text{p}K_a \sim 4$).³⁶ The resulting negatively charged Si-O^- on the surface will bend the SiNW valence band up, leading to more holes flowing through the p-doped SiNW channel, thus explaining the observed increase of I_{ds} . For the POF-modified SiNWs this effect is enhanced both in time and in overall drain-source current effect. This is attributed to the presence of the flaky POF structure with its high specific surface area and its richness in N atoms. The high specific surface area will contribute to a fast and increased uptake of water into the porous structure. The water ($\text{p}K_a \sim 15.7$)³⁷ taken up and the present secondary amines (the most basic nitrogen present in the system with a $\text{p}K_a$ of 11,³⁷ while the $\text{p}K_a$ of melamine is ~ 5)³⁸ in the POF will facilitate the formation of ammonium derivatives and hydroxyl groups, contributing to the partial deprotonation of the silanol groups on the surface. The POF-modified SiNWs were also investigated with varying RH between 6 and 60% and I_{ds} was found to increase with RH (Fig. 3b).

Fig. 5 Pt4f XPS region spectra of (a) metalation of POF powder, (b) metalation of POF powder after reduction, (c) metalation of POF-Si wafer, (d) metalation of POF-Si wafer after reduction.

The sensitivity response for humidity variation of the POF-modified SiNW sensor are found to be very high; within the concentration range studied, the signal increased by ~ 2 orders of magnitude, which is comparable to the values reported for humidity sensors using nanoporous polymer membranes³⁹ and graphene oxide.⁴⁰ In addition, the POF-modified sensor showed a satisfactory level of repeatability towards water vapour sensing, as it is demonstrated in Fig. S5.

Given the high CO₂ uptake of the POF powder, we tested the CO₂ sensing using POF-modified SiNWs. However, varying amounts of CO₂ in N₂ in the range of 0.5–5% at room temperature and 1 bar in the presence of water (and without water) did not show any sensor response. We speculate that in a dry state at room temperature, CO₂ may interact with POFs through physisorption. In such a case no ions are formed and therefore it hardly will affect the electrical properties of SiNWs. While primary/secondary amines, as well as triazine, can form carbamates with CO₂,^{41,42} we consider chemisorption to be unlikely, as the CO₂ isotherm in Fig. 2b shows hardly any adsorption-desorption hysteresis, suggesting a

completely reversible physical adsorption in our system. For a wet state, CO₂ reacted with water and carbonic acid was formed, however, an obvious change of pH was absent, therefore the water sensing dominates the outcome.

To further explore the application of POF-modified SiNWs, we studied the post-synthesis functionalization of the porous layer through Pt metalation. This functionalization strategy started with impregnating the POF material with an aqueous chloroplatinic acid solution (H₂PtCl₆), followed by a reduction step using sodium borohydride (NaBH₄), as illustrated in Fig. 1c. The chloroplatinic acid protonates the nitrogen sites in the POF to ammonium groups having the negatively charged [HPTCl₆][−] as the counter ion. A suspension of POF in H₂PtCl₆ aqueous solution was shaken for different time intervals and the UV-vis absorption spectrum of the supernatant was recorded (Fig. S6a). A clear decrease of the H₂PtCl₆ absorption at 259 nm in time is observed, indicating the adsorption of the metal precursor in the POF precipitate. After the metalation, the POF changed colour from off-white to yellow (Fig. S6b). Subsequently, this material was treated with NaBH₄, and a clear

colour change from yellow to dark brown was observed for the POF material, indicating that the *in-situ* reduction to metallic Pt has taken place.

Next, the sample was inspected by transmission electron microscopy (TEM). Clear Pt nanoparticles of ca. 2 nm in diameter were observed, well dispersed over the flaky polymeric organic framework (Fig. 4b). In the TEM image recorded before the reduction step, no nanoparticles were observed and the images are similar to the untreated POFs (Fig. S7). Varying molar ratios of H_2PtCl_6 : N in POF have been investigated further: 1 : 100, 1 : 20, and finally 1 : 4 (Figures 4a, c, and d, respectively). Upon increasing Pt : N ratio the single particle diameter was found to increase to 3–4 nm (Fig. 4c) and for the highest ratios also the presence of agglomerates is observed (Fig. 4d). To get a better insight in the tomography of the hybrid materials, TEM images were taken from different tilted angles, from which a 3D representation was reconstructed (Supplementary Movie 1). From these results it can be seen that the formed Pt nanoparticles and agglomerates are found predominantly at the outer surface of the POF material and hardly inside the porous structure. This can be rationalized by a NaBH_4 reduction process that starts at the outside, resulting in the formation of Pt nanoparticles that block further entrance of the reducing agent into the porous structure. Table S2 summarizes the textural properties and CO_2 uptake of the metalized POFs with different molar ratios of H_2PtCl_6 : N in POF, nicely showing that the BET surface, micropore volume and CO_2 uptake reduction for increasing amounts of PtNPs.

To verify the metalation of POF and further *in-situ* reduction taken place on POF-modified Si substrate, XPS analysis was conducted. Figure 5a (powder sample) and 5c (modified Si wafer) show high-resolution region spectra of Pt 4f of the metalation of the products before the reduction. Both spectra show two main peaks at 73.2 eV and 76.8 eV, corresponding to $\text{Pt } 4f_{7/2}$ and $4f_{5/2}$ of PtCl_4^{2-} species, respectively.⁴³ After the NaBH_4 reduction, two peaks at 71.5 eV and 74.7 eV, corresponding to Pt^0 $4f_{7/2}$ and $4f_{5/2}$,

5d), which indicates the anchored Pt species are predominantly in the metallic state.

The method for the successful POFs impregnation with H_2PtCl_6 and the subsequent chemical reduction to metallic Pt nanoparticles has also been applied to POF-decorated SiNWs, to see whether this would have an effect on the affinity properties of the sensor coating. We first investigated the electrical behaviour of PtNP@POF-functionalised SiNWs to varying methanol vapour concentrations in the range of 1200 to 6400 ppm. Under the same depletion-mode conditions as described before the change of I_{ds} was monitored. Increasing the methanol vapour concentration results in an increase of I_{ds} (Fig. 6a). From the comparison with the response observed for the bare SiNW (which showed hardly any response) and the POF-SiNW (response increase of ca. 150 %; Fig. 6b), the enhanced effect of the Pt nanoparticles on the methanol response becomes very clear (increase of response of ca. 1350%). The gradually enhanced sensing resulting from these devices can be interpreted as follows.

In more detail, for the bare SiNW the injection of methanol vapour with the indicated concentration was not sufficient to affect the silanol dissociation; a similar performance has been reported by others.⁴⁴ For the POF-SiNW the injection of methanol showed an increase in response. As explained earlier for water, we attribute this to a pre-concentration effect. Although methanol is a slightly weaker acid than water ($\text{p}K_a \sim 16$ vs. 15.7)³⁷ it can protonate the secondary amines of the POFs as well, leaving the methoxide ions to dissociate the silanol groups, inducing a (more) negative surface charge, increasing the current of the p-type SiNW. For the PtNP@POF-SiNWs, the observed enhanced response toward methanol vapour, indicates an even higher methanol pre-concentration due to the presence of PtNPs. The observed increase in response upon the incorporation of Pt(0) NPs in the POF is directly related to an enhanced dissociation of the surface silanol groups of the SiNW, which may be explained by an increased amount of base (here methoxide ions) present in the system.

respectively, are much more prominent in the spectra (Figs. 5b and

Fig. 6 (a) Increase of I_{ds} in time after the successive increase of the methanol vapour concentration from 1200 to 6400 ppm of PtNP@POF-SiNW devices (labels a-e represent the moment of the injection of methanol vapour concentration at 1200, 2500, 3800, 5100, and 6400 ppm, and f is the pure N_2 flow) at $V_g = -3$ V and $V_{ds} = 0.05$ V. The inset shows the relative increase of I_{ds} ($\Delta I/I_0$) as function of the methanol

vapour concentration. (b) Normalized response upon exposure to 3000 ppm of methanol vapour for bare SiNW, POF-SiNW and PtNP@POF-SiNW sensors.

This is only possible by an increased basicity of the Pt(0)NP@POF compared to the pure POF, which can be attributed to an increased basicity of the secondary nitrogens present in the POF. This could be, *e.g.*, due to a net charge transfer from Pt(0) to these nitrogens, comparable to charge transfers reported in other Pt-N interactions.^{45, 46} Also, the enhancement could be the result of the improved sensitivity of the device due to the capacitive coupling of the gate potential via these PtNPs to the SiNW.⁴⁷ This implies that the potential of the PtNPs follows the back-gate potential, which contributes to the accumulation of holes in the SiNW channel near the PtNP sites. Similar results have been observed for PdNP-decorated SiNWs and SiNW biosensors.⁴⁷⁻⁴⁹

Lastly, cross-reactivity of the PtNP@POF-SiNW devices to other structurally related VOCs was also investigated (Fig. S8). The results clearly show the highest response for methanol vapour, over ethanol, isopropanol and acetaldehyde vapours. This trend follows the one of the dielectrical constants ($\epsilon_r = 33, 24.5, 21.1, 16.5$, for these analytes, respectively);³⁷ the higher ϵ_r the higher the polarity and the more favourable to the dissociation of $\text{Si-O}\cdots\text{H-B}^-$ ion pair (where B^- stands for the base) to Si-O^- and HB.

Conclusions

In this study, POFs have been successfully covalently coupled to APTES-modified SiNWs. The observed increased sensitivity for water vapour detection, compared to the unmodified SiNW, is attributed to the enhanced water affinity by the high surface area of POFs, resulting in an increased surface silanol dissociation and concomitant increase of majority charge carriers (holes) and therefore an increase of the I_{ds} . Post-synthesis modification of the POFs results in the formation of well-dispersed and size-controlled PtNPs. The presence of the PtNPs in the POF contributes to the observed enhanced sensitivity for the detection of methanol vapour, likely as a consequence of the pre-concentration of methanol vapour and the capacitive coupling of the gate potential via the PtNPs to the SiNW. Here the introduced POF-SiNW platform is expected to become a challenging system for other post-synthesis modification with a range of different metal nanoparticles. Such systems might find utilization not only in chemical and (bio)sensing, but also in gas separations and catalysis.

Conflicts of interest

There are no conflicts to declare.

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TOC

Silicon nanowires functionalized with metalized porous organic frameworks exhibit superior sensing properties for methanol vapour detection.

Supporting information

to

Enhanced Vapor Sensing using Silicon Nanowire Devices Coated with Pt Nanoparticle Functionalized Porous Organic Frameworks

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Experimental Section

Surface Functionalization: The silicon wafers and SiNW chips were cleaned by sonication in acetone for 2 min, followed by a rinsing step with ethanol and Milli-Q water, and then dried by a N_2 gas flow. Next, the devices were cleaned/oxidized with air plasma for 2 min (Harrick PDC-002 at a pressure of ~ 0.2 mbar and an RF coil power of 29.6 W). To obtain an amino-terminated surface, the cleaned devices subsequently submerged in a 1 vol % solution of 3-amino propyl triethoxysilane (APTES) in ethanol (95%) at room temperature for half an hour. Afterwards, the devices were removed from the silane solution and were rinsed under flows of ethanol and then baked at 150 °C for 5 mins.¹ The POF-modified surface was prepared using optimized conditions, the APTES-modified SiNW chip and Si wafer were immersed a DMSO solution (30 ml) containing melamine (0.313 g / 2.5 mmol) and terephthaldehyde (0.5 g / 3.75 mmol), the solution was then heated at 180 °C for 14 hours. Afterwards, the devices were rinsed with acetone, THF and CH_2Cl_2 for several times and dried using a N_2 gas flow. The POF-SiNW devices and pieces of Si wafer were stored under an atmosphere of N_2 until further analysis or post-treatment. To obtain PtNP@POF-SiNW, the POF-SiNW device was treated with H_2PtCl_6 , followed by a reduction step using $NaBH_4$. The ratio of H_2PtCl_6 to N atoms in the POF was 1: 37.

Gas sorption analysis: The POF surface area and pore size distributions were measured by N_2 adsorption and desorption at 77 K in a Quantachrome Autosorb-6B setup. The surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.10, where P_0 was 765 mmHg. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT) pore model for carbon slit, as these were found to give the best fit. Samples were degassed at 393 K for 16 h under N_2 flow before analysis. CO_2 isotherms at 273 K were measured using a Tristar II 3020 (Micromeritics), and P_0 was 26039 mmHg. Prior to the measurements, the samples were degassed at 393 K under N_2 flow for at least 16 h.

X-ray Photoelectron Spectroscopy: XPS measurements were performed on a K-alpha Thermo Fisher Scientific spectrometer using a monochromatic Al $K\alpha$ X-ray source. The measurements were performed at ambient temperature and chamber pressure of about 10^{-8} mbar. The spot size was 400 μm . A flood gun was used for charge compensation. All the spectra measured were corrected by setting the reference binding energy of carbon (C1s) at 284.8 eV. The spectra were analyzed using the Thermo Advantage software package.

Ellipsometry: The ellipsometry measurements were carried out on a commercial imaging nulling-ellipsometer (EP3 Nanoscope, Accurion). The light source was a He-Ne laser with a wavelength of 658 nm. Measurements were performed for three different spots on each specimen. The following refractive indices were used in a three-layer model of substrate-organic-layer air: $n_{SiO_2} = 1.46$, $n_{air} = 1$, $n_{APTES} = 1.6$.²

Sensor Fabrication and Characterization: The surface-modified SiNW chips were wire-bonded using conductive glue and Al wires (25 μm in diameter) to the chip holder, and then placed in a home-built gas cell for vapor sensing.^{3, 4} For SiNW FET measurements, a standard Keithley

4200 semiconductor characterization system equipped with three source–measurement units was used for the electrical characterization of the SiNW device during the exposure to different vapors and vapor conditions.

Other measurements: Fourier transform infrared (FTIR) spectra were collected with a Nicolet 8700 spectrometer, using the KBr pellet method. Surfaces of the Si wafer and SiNW were analyzed with FEI Nova NanoSEM™ scanning electron microscopes (SEM). UV-vis measurements were performed on a Shimadzu spectrophotometer at room temperature. Transmission electron microscopy (TEM) images and tomography were obtained with a JEOL JEM1400 plus & JEM3200 FSC. Tomographic construction was performed using IMOD.⁵

Additional Data

Fig. S1: FTIR spectra; Fig. S2: Pore distribution; Fig. S3: SEM image; Fig. S4: Sensing set-up; Fig. S5: Semi-log relation between signal change vs. concentration and reproducibility; Fig. S6: UV-vis spectra; Fig. S7: TEM image; Table S1: Surface elemental composition; Table S2: Comparison of S_{BET} , micropore volume and CO_2 uptake.

Fig. 1 FTIR spectra of the product prepared in (a) different solvents and with/without catalyst, (b) a DMSO solution with different reaction times.

Fig. S2 Pore size distribution of the POF product, predicted from the data of N₂ sorption using a DFT method.

Fig. S3. SEM image of a POF-modified Si wafer.

Fig. 4 Vapor sensing set-up, PV: pressure valve, V: manual valve, MFC: mass flow controller, TWV: three-way valve.

Fig. 5 (a) Semi-log relation between the normalized signal increase and the different RH, (b) Repeatability of POF-modified SiNW device (yellow 46% RH, blue 38% RH, green 30% RH).

Fig. S6 (a) UV-vis measurements of 0.07 mM H_2PtCl_6 in water and the aqueous supernatant in the presence of POFs at different time intervals of contacting, showing the decrease of H_2PtCl_6 concentration and indicating the POF affinity for H_2PtCl_6 , (b) Sediments of three aqueous suspensions: POFs, metalation products and metalation products after *in-situ* reduction of the Pt^{4+} .

Fig. S7 TEM images of (a) pure POF powder, (b) impregnated POF with Pt^{4+} , (c) impregnated products after *in-situ* reduction using NaBH_4 as reductant.

Fig. S8 Response of a PtNP@POF-SiNW toward acetaldehyde (4000 ppm), isopropanol (3000 ppm), ethanol (3000 ppm), and methanol vapour (3000 ppm).

Table S1. Surface elemental information of different samples as obtained by XPS (values are rounded to integers).

Sample	Si (at.%)	O (at.%)	C (at.%)	N (at.%)
Bare Si wafer	54	36	10	0
APTES-modified Si wafer	45	32	19	4
POF-modified Si wafer	2	9	58	31
POF powder	0	9	59	31

Table S2. Comparison of the BET surface, micropore volume and CO₂ uptake between pure POFs and the metalation product (PtNP@POF) (- = not measured).

	Pure POF	100:1	20:1	4:1
BET surface (m ² /g)	609.9	271.9	207.6	54.5
Micropore volume (cm ³ /g)	0.102	0.047	0.0412	0.009
CO ₂ uptake (cm ³ /g) at 1 bar	55	46	39	-

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Enhanced Vapour Sensing using Silicon Nanowire Devices Coated with Pt Nanoparticle Functionalized Porous Organic Frameworks

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Recently various porous organic frameworks (POFs, crystalline or amorphous materials) have been discovered, and used for a wide range of applications, including molecular separations and catalysis. Silicon nanowires (SiNWs) have been extensively studied for diverse applications, including transistors, solar cells, lithium ion batteries and sensors. Here we demonstrate the **covalent attachment/functionalization of POFs onto SiNW surfaces with POFs** and explore **the-its** effect on the electrical sensing properties of SiNW-based devices. The surface modification by POFs was easily achieved by polycondensation on amine-modified SiNWs. Platinum nanoparticles were formed in these POFs by impregnation with chloroplatinic acid followed by chemical reduction. The final hybrid system showed highly enhanced sensitivity for methanol vapour detection. We envisage that the integration of SiNWs with POF selector layers, loaded with different metal nanoparticles will open up new avenues, not only in chemical and biosensing, but also in separations and catalysis.

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Introduction

Improved sensitivity and selectivity in the detection of gas-phase molecules for environmental monitoring, process control and safety, and medical diagnosis is of utmost importance.¹ One promising approach for the direct electrical detection of analytes is by using nanowires configured as field-effect transistors (FETs), which exhibit superior sensitivity as given by their high surface-to-volume ratio and the direct signal amplification by the transistor function.^{2, 3} Particularly silicon nanowire-based FETs (SiNW-FETs), pioneered by Lieber's group,⁴ have been studied for more than 15 years now and have attracted a great deal of interest, mainly for their controllable properties and compatibility with very-large-scale

integration (VLSI) processes and complementary metal–oxide–semiconductor (CMOS) technologies.^{5, 6} While most SiNW-FET studies focus on detection of analytes in aqueous solutions,^{7, 8} different gas-phase applications of electrical SiNW-based devices are attracting increasing interest.⁹ For instance, the research group of Haick published a number of systematic studies on the fundamentals and applications of functionalized SiNW-based FETs for the detection of volatile organic compounds (VOCs).^{10, 11} In addition, surface functionalization of SiNWs with Pd nanoparticles,¹² oligopeptides,¹³ diphenylchlorophosphate (DPCP) receptors,¹⁴ or 3-aminopropyltrimethoxysilane (APTES)¹⁵ allowed for the rapid detection of H₂, acetic acid vapours, DPCP and explosives, respectively. All these studies have shown the advantages of controlled surface modification of the SiNWs in tuning sensor selectivity.

A variety of porous materials,¹⁶ such as metal organic polyhedra (MOP),¹⁷ metal organic frameworks (MOFs)¹⁸ and covalent organic frameworks (COFs),¹⁹ have gained a lot of interest due to their exceptionally high specific surface areas, high specific gas storage and separation capabilities and their potential in catalysis and sensing applications.^{20, 21} **and other electronic devices related to, e.g., resistance-switching memory,²² high-performance dielectrics,²³ and proton conductivity.²⁴** The chemical diversity of these porous materials allows for a fine-tuning of the chemical and physical properties by tailored synthesis.²⁵ In addition, the exposure of properly designed affinity sites on the porous materials enable further coupling of functional substrates, for instance to Au plasmonic substrates and to SiNWs platforms, expanding their

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[†]Electronic Supplementary Information (ESI) available: Surface functionalization; gas sorption analysis; X-ray photoelectron spectroscopy; ellipsometry; sensor fabrication and characterization; other measurements and results; the tomography of hybrid materials PtNP@POFs (TEM images were taken from different tilted angles) in MPG format. See DOI: 10.1039/x0xx00000x

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ARTICLE

Journal Name

application window significantly.^{20, 26} Along these lines, we developed and explored a unique hybrid construct: porous organic framework (POF)-decorated SiNWs for the investigation of chemical vapour sensing. POFs are extremely attractive as affinity layers as they are not only highly porous, but also highly stable due to the formation of covalent bonds rather than metal coordination bonds; some of the early reported MOF structures decompose gradually if environmental moisture is present.²⁷ In addition, post-synthesis strategies can be applied to POFs to further tune their physico-chemical properties. We report here on a surface modification strategy to ~~covalently bind yield POFs-functionalized~~, ~~to~~ SiNW-based devices, after which the electrical properties of the resulting hybrid construct were investigated upon changes in the environmental humidity and methanol vapours. Moreover, the post-synthesis functionalization of the POF-SiNW hybrid by the *in-situ* formation of Pt nanoparticles (PtNPs) results in advanced sensing properties of methanol vapours.

Results and discussion

~~POFs were covalently grafted onto the~~ SiNW surface ~~was functionalized with POFs~~ via the polycondensation of melamine and terephthalaldehyde on the amine-modified SiNWs,²⁸ as illustrated in Fig. 1a, b. The POF-modified SiNWs together with the precipitated materials were harvested and cleaned for different characterizations.

The molecular details of the reactants and the effect of different solvents, temperature, reaction time and the use of catalyst on the products were examined by Fourier Transform Infrared spectroscopy (FTIR), as shown in Fig. S1. Only in the case of DMSO as the solvent, the precipitate in the reaction solution was found to be flocculent. Reactions at the other conditions gave granular products. For the products obtained in all solvents the FTIR spectra show vibrations around 1550 cm⁻¹ and 1480 cm⁻¹, which are attributed to the stretching vibration of the triazine ring,²⁹ indicating the successful incorporation of the melamine into the molecular network. However, vibrations around 1690 cm⁻¹ (C=O

stretching) are absent only for the product synthesized in DMSO, which proves that the highest conversion of functional groups initially present in the monomers was achieved in DMSO. Therefore, the reaction was optimized in this solvent. Moreover, the bands corresponding to imine bond vibration (*i.e.*, 1600 cm⁻¹) was absent in the FTIR spectra, indicating that the aldehyde group has reacted twice with an amino group from the melamine building block, forming a trisubstituted imine moiety. The high boiling point, combined with the high polarity of DMSO, contributes to the increased solubility of the initially formed polycondensated product via imine bonds, making subsequent condensations to a trisubstituted imine bonds possible as indicated by the structure in Fig. 1b.³⁰ In addition, considering the (in)stability of the Al electrodes on the SiNW chip during this reaction, we optimized the reaction time to 14 hours. Longer reaction times showed similar FTIR spectra of the product, as shown in Fig. S1b.

The porous structure of the obtained flaky POF material synthesized under optimized conditions was investigated by N₂ gas sorption at 77 K (Fig. 2a). At low relative pressures a rapid uptake of N₂ is observed, indicating the presence of micropores. At high relative pressures (*i.e.*, $P/P_0 > 0.8$) some hysteresis is observed, which is attributed to the presence of mesopores where some capillary condensation can take place. At high relative pressures (*i.e.*, $P/P_0 > 0.9$) a steep rise in adsorption was observed, which indicates the presence of even larger pores, likely due to inter-particle porosity.³⁰ The calculated Brunauer-Emmett-Teller (BET) specific surface area were found to be 620 m²/g and 640 m²/g for POFs synthesized for 14 hours and 72 hours, respectively. These values are lower than the one reported the first time for this material (1377 m²/g)²⁸, but very similar to more recently reported values for microporous organic polymer materials prepared via polycondensation (values ranging from 70 to 614 m²/g).³⁰⁻³² From the N₂ adsorption isotherms recorded at 77 K, the pore size distribution (PSD) was calculated with the use of Density Functional Theory (DFT), resulting in a pore diameter ranging from 1 to 55 nm (*i.e.*, micro- to mesopores; Fig. S2). Considering the presence of N atoms in the POF network and the likely ~~favorable~~ ~~favorable~~ interaction with CO₂, CO₂ sorption isotherms were measured up to 1.2 bar at 273 K (Fig. 2b).

Fig. 1 Schematic representation of (a) APTES grafting to the silanol-terminated surface of a SiNW, (b) the covalent modification process of the SiNW surface with melamine-terephthalaldehyde-based POFs, (c) the metalation of a POF-SiNW via an *in-situ* chemical reduction. Molecules 1-3: APTES, melamine, terephthalaldehyde, respectively.

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Journal Name

ARTICLE

Fig. 2 (a) N_2 sorption isotherm acquired at 77 K, (b) CO_2 sorption isotherm acquired at 273 K of the POF powder synthesized under optimized conditions, (c) SEM image of the bare SiNW, (d) SEM image of the SiNW decorated with POFs.

At 1 bar ($P/P_0 = 0.029$), the observed CO_2 uptake is 2.3 mmol/g, which is very similar to the high values of ~ 2.0 mmol/g and ~ 1.5 mmol/g as reported for the similar polymer networks (PI-1 and PI-2) rich in N atoms.³¹ The high value of CO_2 uptake here can be attributed to the high density of nitrogen in the POF structure originated from the melamine building blocks.

Similar surface modifications on silicon wafers were performed as model system for the SiNWs. These modified wafers were

investigated by X-ray photoelectron spectroscopy (XPS) and compared with the unmodified wafers. The relative atomic surface composition of Si, O, C and N is shown in Table S1. Upon modification with APTES, the N percentage increases from 0 to 2.5%, indicating the successful silanization. Meanwhile, ellipsometry measurements showed 0.7 nm as the optical thickness, indicating a monolayer of APTES formed on the Si wafer.³³

Fig. 3 Variation of drain-source current (I_{ds}) of bare SiNW and POF-modified SiNW with humidity at $V_g = -3$ V and $V_{ds} = 0.05$ V, (a) Real-time variation of I_{ds} after a step-wise increase of the relative humidity from 0 to 46%, (b) Increase of I_{ds} in time after the successive increase of RH from 0 to 60% (labels a-f refer to the injection of RH in 6.5, 13, 20, 33, 46 and 60%, respectively, while label g indicated the start of a pure N_2 flow). The inset shows the relative increase of I_{ds} as function of RH.

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ARTICLE

Journal Name

Fig. 4 TEM images after NaBH_4 reduction of POFs containing different amounts of H_2PtCl_6 , showing the formed Pt nanoparticles with different particle sizes. The molar ratios between H_2PtCl_6 and N atoms in the POFs are (a) 1 : 100, (b) 1 : 37, (c) 1 : 20, and (d) 1 : 4.

After the POF polycondensation and POF coupling to the APTES layer, the N percentage increases to a value of 31%. The observed N/C ratio is found to be very similar to the ratio observed in the pure POF powder (31%). Inspection of the SiNW before and after surface modification by using scanning electron microscopy (SEM) showed the presence of flaky POF material on the nanowire (Fig. 2d). Similar flaky POF structures were observed on the modified silicon wafers (Fig. S3).

Next, we have compared the electrical device response towards changes in humidity for POF-modified SiNWs and bare SiNWs using our home-built vapour sensing apparatus (Fig. S4).^{34,35} Both types of p-doped SiNWs were set in the depletion mode by the application of a back-gate potential of $V_g = -3$ V, and the varying drain-source current (I_{ds}) was registered under the conditions of a constant source-drain voltage (V_{ds}) set to 0.05 V. Step-wise increase of the relative humidity to RH = 46% shows for the bare SiNW a very slow increase of I_{ds} reaching more or less equilibrium after 2 h. The POF-modified SiNW showed a fast increase of I_{ds} and equilibration after ca. 3 min, which is around 40 times faster as compared to the unmodified sensor. The I_{ds} at equilibrium for the POF-modified SiNWs is about two times higher than for the bare SiNWs. In both

situations the I_{ds} increases, indicating an increase of the concentration of the majority charge carriers (here holes). This is understood as that the injection of water vapour results in partial deprotonation of surface silanol groups on the SiNW and changes the surface charge from neutral to negative, as $\text{Si-OH} \rightleftharpoons \text{Si-O}^- + \text{H}^+$, ($\text{p}K_a \sim 4$).³⁶ The resulting negatively charged Si-O^- on the surface will bend the SiNW valence band up, leading to more holes flowing through the p-doped SiNW channel, thus explaining the observed increase of I_{ds} . For the POF-modified SiNWs this effect is enhanced both in time and in overall drain-source current effect. This is attributed to the presence of the flaky POF structure with its high specific surface area and its richness in N atoms. The high specific surface area will contribute to a fast and increased uptake of water into the porous structure. The water ($\text{p}K_a \sim 15.7$)³⁷ taken up and the present ~~nitrogen-containing group~~ secondary amines (the most basic nitrogen present in the system with a $\text{p}K_a$ of 11,³⁷ while the $\text{p}K_a$ of melamine is ~ 5)³⁸ in the POF will facilitate the formation of ammonium derivatives and hydroxylide groups, contributing to the partial deprotonation of the silanol groups on the surface. The POF-modified SiNWs were also investigated with varying RH between 6 and 60% and I_{ds} was found to increase with RH (Fig. 3b).

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Journal Name

ARTICLE

Fig. 5 Pt4f XPS region spectra of (a) metalation of POF powder, (b) metalation of POF powder after reduction, (c) metalation of POF-Si wafer, (d) metalation of POF-Si wafer after reduction.

The sensitivity response for humidity variation of the POF-modified SiNW sensor are found to be very high; within the concentration range studied, the signal increased by ~ 2 orders of magnitude, which is comparable to the values reported for humidity sensors using nanoporous polymer membranes³⁹ and graphene oxide.⁴⁰ In addition, the POF-modified sensor showed a satisfactory level of repeatability towards water vapour sensing, as it is demonstrated in Fig. S5.

Given the high CO_2 uptake of the POF powder, we tested the CO_2 sensing using POF-modified SiNWs. However, varying amounts of CO_2 in N_2 in the range of 0.5–5% at room temperature and 1 bar in the presence of water (and without water) did not show any sensor response. We speculate that in a dry state at room temperature, CO_2 may interact with POFs through physisorption. In such a case no ions are formed and therefore it hardly will affect the electrical properties of SiNWs. While primary/secondary amines, as well as triazine, can form carbamates with CO_2 ,^{41,42} we consider chemisorption to be unlikely, as the CO_2 isotherm in Fig. 2b shows hardly any adsorption-desorption hysteresis, suggesting a

completely reversible physical adsorption in our system. For a wet state, CO_2 reacted with water and carbonic acid was formed, however, an obvious change of pH was absent, therefore the water sensing dominates the outcome.

To further explore the application of POF-modified SiNWs, we studied the post-synthesis functionalization of the porous layer through Pt metalation. This functionalization strategy started with impregnating the POF material with an aqueous chloroplatinic acid solution (H_2PtCl_6), followed by a reduction step using sodium borohydride (NaBH_4), as illustrated in Fig. 1c. The chloroplatinic acid protonates the nitrogen sites in the POF to ammonium groups having the negatively charged $[\text{HPTCl}_6]^-$ as the counter ion. A suspension of POF in H_2PtCl_6 aqueous solution was shaken for different time intervals and the UV-vis absorption spectrum of the supernatant was recorded (Fig. S6a). A clear decrease of the H_2PtCl_6 absorption at 259 nm in time is observed, indicating the adsorption of the metal precursor in the POF precipitate. After the metalation, the POF changed colour from off-white to yellow (Fig. S6b). Subsequently, this material was treated with NaBH_4 , and a clear

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Journal Name

colour change from yellow to dark brown was observed for the POF material, indicating that the *in-situ* reduction to metallic Pt has taken place.

Next, the sample was inspected by transmission electron microscopy (TEM). Clear Pt nanoparticles of ca. 2 nm in diameter were observed, well dispersed over the flaky polymeric organic framework (Fig. 4b). In the TEM image recorded before the reduction step, no nanoparticles were observed and the images are similar to the untreated POFs (Fig. S7). Varying molar ratios of H_2PtCl_6 : N in POF have been investigated further: 1 : 100, 1 : 20, and finally 1 : 4 (Figures 4a, c, and d, respectively). Upon increasing Pt : N ratio the single particle diameter was found to increase to 3–4 nm (Fig. 4c) and for the highest ratios also the presence of agglomerates is observed (Fig. 4d). To get a better insight in the tomography of the hybrid materials, TEM images were taken from different tilted angles, from which a 3D representation was reconstructed (Supplementary Movie 1). From these results it can be seen that the formed Pt nanoparticles and agglomerates are found predominantly at the outer surface of the POF material and hardly inside the porous structure. This can be rationalized by a NaBH_4 reduction process that starts at the outside, resulting in the formation of Pt nanoparticles that block further entrance of the reducing agent into the porous structure. Table S2 summarizes the textural properties and CO_2 uptake of the metalized POFs with different molar ratios of H_2PtCl_6 : N in POF, nicely showing that the BET surface, micropore volume and CO_2 uptake reduction for increasing amounts of PtNPs.

To verify the metalation of POF and further *in-situ* reduction taken place on POF-modified Si substrate, XPS analysis was conducted. Figure 5a (powder sample) and 5c (modified Si wafer) show high-resolution region spectra of Pt 4f of the metalation of the products before the reduction. Both spectra show two main peaks at 73.2 eV and 76.8 eV, corresponding to $\text{Pt} 4f_{7/2}$ and $4f_{5/2}$ of PtCl_4^{2-} species, respectively.⁴³ After the NaBH_4 reduction, two peaks at 71.5 eV and 74.7 eV, corresponding to $\text{Pt}^0 4f_{7/2}$ and $4f_{5/2}$, respectively, are much more prominent in the spectra (Figs. 5b and 5d), which indicates the anchored Pt species are predominantly in

the metallic state.

The method for the successful POFs impregnation with H_2PtCl_6 and the subsequent chemical reduction to metallic Pt nanoparticles has also been applied to POF-decorated SiNWs, to see whether this would have an effect on the affinity properties of the sensor coating. We first investigated the electrical ~~behavior~~ behaviour of PtNP@POF-functionalized SiNWs to varying methanol vapour concentrations in the range of 1200 to 6400 ppm. Under the same depletion-mode conditions as described before the change of I_{ds} was monitored. Increasing the methanol vapour concentration results in an increase of I_{ds} (Fig. 6a). From the comparison with the response observed for the bare SiNW (which showed hardly any response) and the POF-SiNW (response increase of ca. 150 %; Fig. 6b), the enhanced effect of the Pt nanoparticles on the methanol response becomes very clear (increase of response of ca. 1350%). The gradually enhanced sensing resulting from these devices can be interpreted as follows.

In more detail, for the bare SiNW the injection of methanol vapour with the indicated concentration was not sufficient to affect the silanol dissociation; a similar performance has been reported by others.⁴⁴ For the POF-SiNW the injection of methanol showed an small increase of in response. As explained earlier for water, we attribute this effect to a pre-concentration effect of methanol in the porous POF. Although methanol is a slightly weaker acid than water ($\text{p}K_a$ ~16 vs. 15.7)³⁷ and it can protonate the secondary amines of the POFs as well, leaving the methoxide ions contributes to the dissociate the ion of the silanol groups, inducing a (more) negative surface charge, increasing the current of the p-type SiNW. For the PtNP@POF-SiNWs, the observed enhanced response toward methanol vapour, indicates an even higher methanol pre-concentration due to the presence of PtNPs, and concomitant more negatively surface charge. The observed increase in response upon the incorporation of Pt(0) NPs in the POF is directly related to an enhanced dissociation of the surface silanol groups of the SiNW, which may be explained by an increased amount of base (here methoxide ions) present in the system.

Fig. 6 (a) Increase of I_{ds} in time after the successive increase of the methanol vapour concentration from 1200 to 6400 ppm of PtNP@POF-SiNW devices (labels a–e represent the moment of the injection of methanol vapour concentration at 1200, 2500, 3800, 5100, and 6400 ppm, and f is the pure N_2 flow) at $V_g = -3$ V and $V_{ds} = 0.05$ V. The inset shows the relative increase of I_{ds} ($\Delta I/I_0$) as function of the methanol

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Journal Name

ARTICLE

vapour concentration. (b) Normalized response upon exposure to 3000 ppm of methanol vapour for bare SiNW, POF-SiNW and PtNP@POF-SiNW sensors.

This is only possible by an increased basicity of the Pt(0)NP@POF compared to the pure POF, which can be attributed to an increased basicity of the secondary nitrogens present in the POF.⁷ This could be, e.g., due to a net charge transfer from Pt(0) to these nitrogens, comparable to charge transfers reported in other Pt-N interactions.^{45,46} Also, the enhancement could be the result of the improved sensitivity of the device due to the capacitive coupling of the gate potential via these PtNPs to the SiNW.⁴⁷ This implies that the potential of the PtNPs follows the back-gate potential, which contributes to the accumulation of holes in the SiNW channel near the PtNP sites. Similar results have been observed for PdNP-decorated SiNWs and SiNW biosensors.⁴⁷⁻⁴⁹

Lastly, cGross-reactivity of the PtNP@POF-SiNW devices to other structurally related VOCs was also investigated (Fig. S8). The results clearly show the highest response for methanol vapour, over ethanol, isopropanol and acetaldehyde vapours. This trend follows the one of the dielectrical constants ($\epsilon_r = 33, 24.5, 21.1, 16.5$, for these analytes, respectively);³⁷ the higher ϵ_r the higher the polarity and the more favourable to the dissociation of $\text{Si-O}\cdots\text{H-B}^+$ ion pair (where B^+ stands for the base) to Si-O^- and HB.

Conclusions

POFs formed by the polycondensation of melamine and terephthalaldehyde in DMSO as the solvent have been successfully covalently coupled to APTES-modified silicon nanowires. The observed increased sensitivity for water vapour detection, compared to the unmodified silicon nanowires, is attributed to the enhanced water affinity by the high surface area POF, resulting in an increased surface silanol dissociation and concomitant increase of majority charge carriers (holes) and therefore an increase of the drain source current (I_{ds}). Post-synthesis modification of the porous POF by chloroplatinic acid treatment and subsequent sodium borohydride reduction results in the formation of Pt^0 nanoparticles. The diameter of these nanoparticles was found to be 2–4 nm and depended on the loading density of chloroplatinic acid. The Pt^0 nanoparticles are found at the outer surface of the POF as deduced from 3D-TEM imaging. The presence of the Pt^0 nanoparticles in the POF contributes to the observed enhanced sensitivity for the detection of methanol vapour, likely as a consequence of the pre-concentration of methanol vapour and the capacitive coupling of the gate potential via the PtNPs to the SiNW.

With this study we have shown for the first time that POFs can be utilized successfully for the formation and dispersion of Pt^0 nanoparticles and that such an affinity layer can be bound covalently to the surface of SiNWs. These modified nanowires showed highly enhanced response towards methanol vapours. Here the introduced POF-SiNW platform is expected to become a challenging system for other post-synthesis modification with a range of different metal nanoparticles. Such systems might find utilization not only in chemical and bio-sensing, but also in gas separations and catalysis.

In this study, POFs have been successfully covalently coupled to APTES-modified SiNWs. The observed increased sensitivity for water vapour detection, compared to the unmodified SiNW, is attributed to the enhanced water affinity by the high surface area of POFs, resulting in an increased surface silanol dissociation and concomitant increase of majority charge carriers (holes) and therefore an increase of the I_{ds} . Post-synthesis modification of the POFs results in the formation of well-dispersed and size-controlled PtNPs. The presence of the PtNPs in the POF contributes to the observed enhanced sensitivity for the detection of methanol vapour, likely as a consequence of the pre-concentration of methanol vapour and the capacitive coupling of the gate potential via the PtNPs to the SiNW. Here the introduced POF-SiNW platform is expected to become a challenging system for other post-synthesis modification with a range of different metal nanoparticles. Such systems might find utilization not only in chemical and (bio)-sensing, but also in gas separations and catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Silicon nanowires functionalized with metalized porous organic frameworks exhibit superior sensing properties for methanol vapour detection.

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Enhanced Vapour Sensing using Silicon Nanowire Devices Coated with Pt Nanoparticle Functionalized Porous Organic Frameworks

Anping Cao,^{a,b} Meixia Shan,^a Laura Paltrinieri,^{a,c} Wiel Evers,^{a,d} Liangyong Chu,^a Lukasz Poltorak,^a Johan H. Klootwijk,^e Beatriz Seoane,^{a,f} Jorge Gascon,^{a,g} Ernst J. R. Sudhölter^a and Louis C. P. M. de Smet^{*a,c,h}

Statement of contributions

A.C. constructed the project idea with the help of M.S., E.J.R.S and L.C.P.M.d.S., and performed the (surface) chemistry, sensor fabrication and sensor measurements. M.S. measured the sorption and pore size properties of the POFs. Laura P. performed the XPS analysis. W.E. performed the TEM analysis. L.C. performed the SEM measurement. Lukasz P. contributed to design of the experiments and surface chemistry. J.H.K. designed the SiNW chips and supervised the device fabrication. J.G. and B.S. reviewed the manuscript and provided valuable comments. A.C., E.J.R.S and L.C.P.M.d.S. wrote the first draft of the manuscript. E.J.R.S and L.C.P.M.d.S. supervised the project. All authors contributed to and have approved the final manuscript.