Electronic Supplementary Material (ESI) for Nanoscale.

Electronic supplementary information

to

Enhanced vapour 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 unless stated otherwise.

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): XPS measurements were performed on a K-alpha Thermo Fisher Scientific spectrometer using a monochromatic Al Kα 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 Avantage 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: $n_{SiO2} = 1.46$, $n_{air}=1$, $n_{APTES} =1.6$.[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; Fig. S8: Sensor responses to different vapours; Table S1: Surface elemental composition; Table S2: Comparison of S_{BET}, micropore volume and CO_2 uptake.

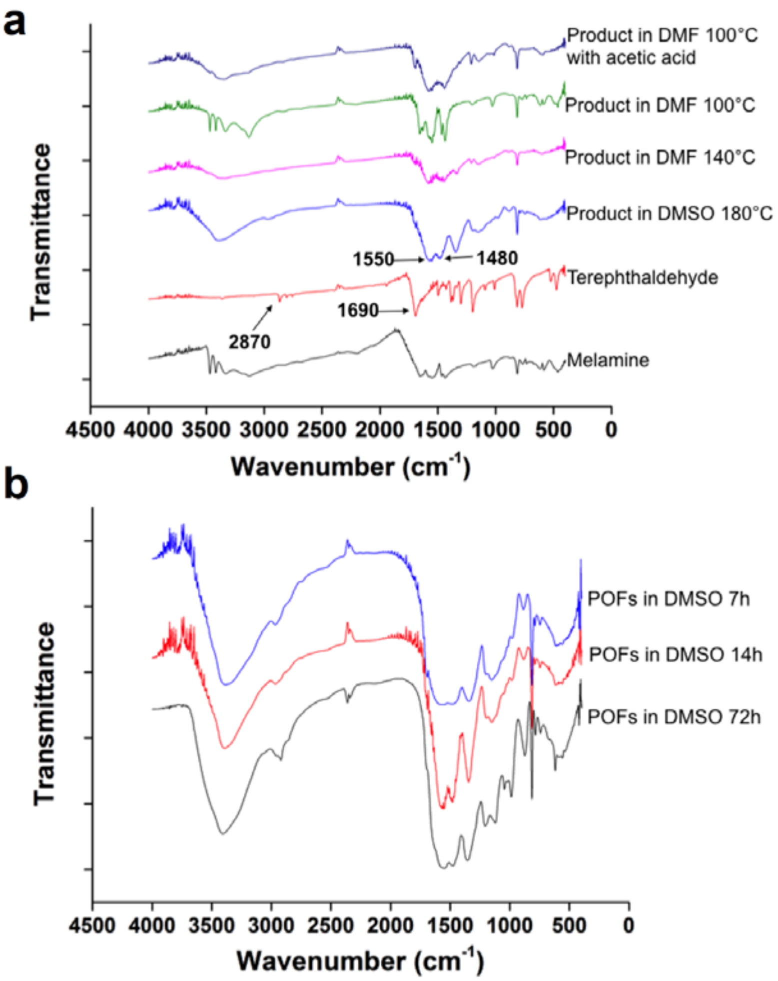

Fig. S1 FTIR spectra of the product prepared in (a) different solvents and with/without catalyst, (b) a DMSO solution with different reaction times.

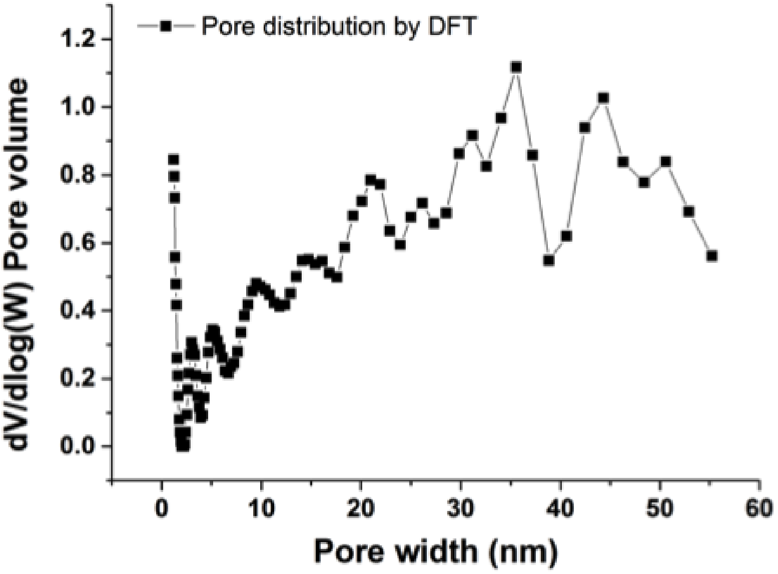

Fig. S2 Pore size distribution of the POF product, predicted from the data of N_2 sorption using a DFT method.

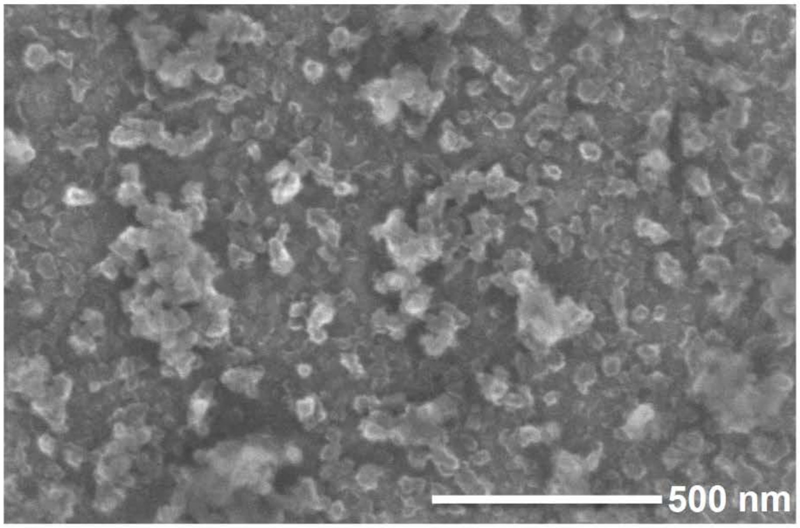

Fig. S3 SEM image of a POF-modified Si wafer.

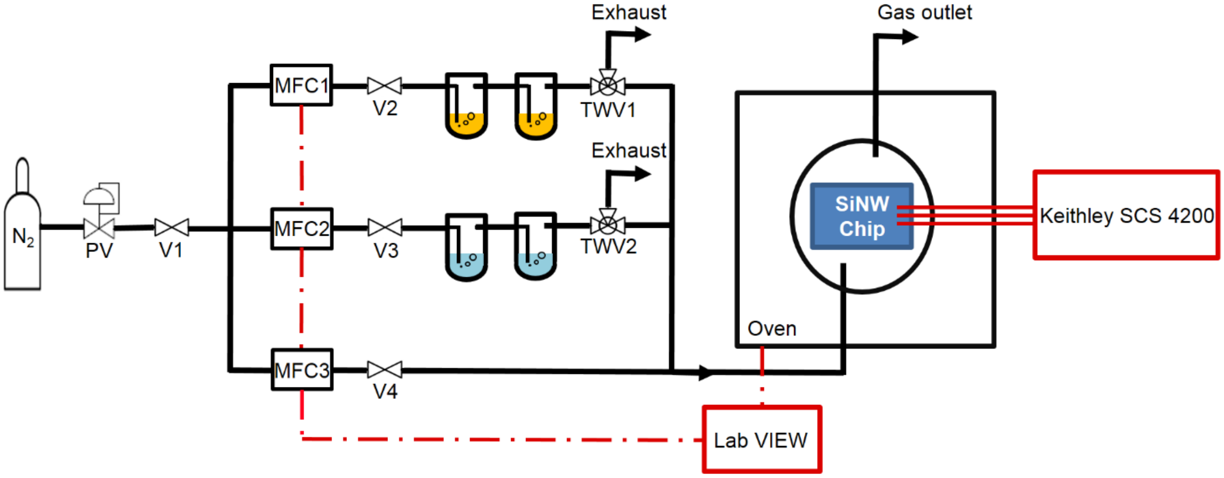

Fig. S4 Vapor sensing set-up, PV: pressure valve, V: manual valve, MFC: mass flow controller, TWV: three-way valve.

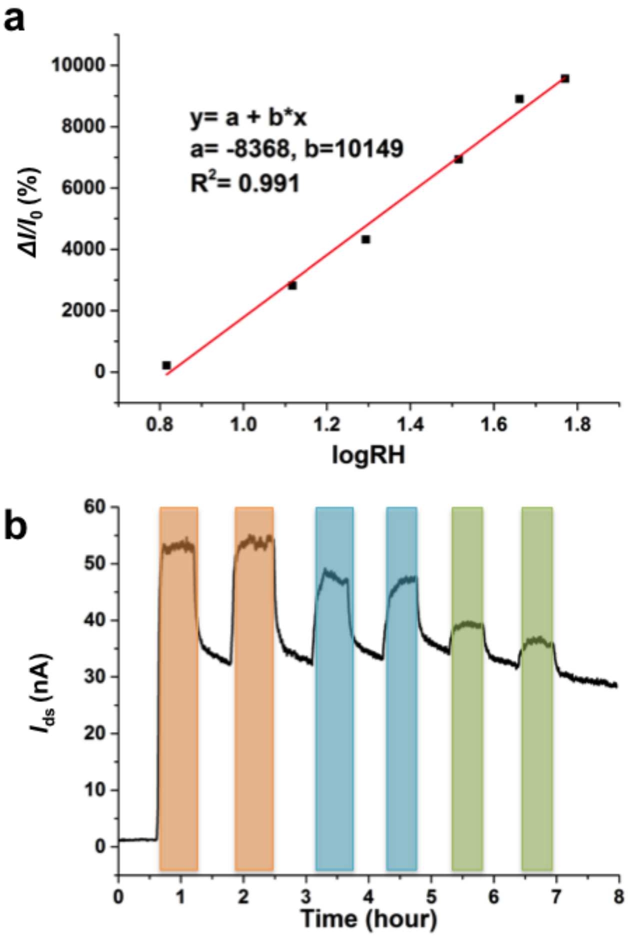

Fig. S5 (a) Semi-log relation between the normalized signal increase and the different RH values, (b) Repeatability of POF-modified SiNW device (yellow 46% RH, blue 38% RH, green 30% RH).

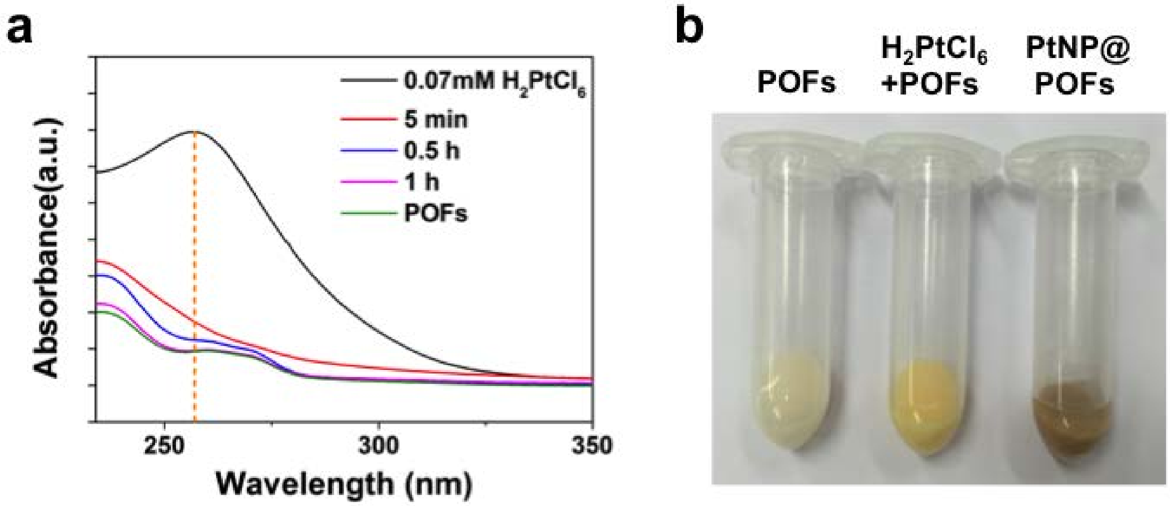

Fig. S6 (a) UV-vis measurements of 0.07 mM H_2PtCl_6 in water and the aqueous supernatant in the presence of POFs at different time intervals of contacting, showing the decrease of H_2PtCl_6 concentration and indicating the POF affinity for H_2PtCl_6, (b) Sediments of three aqueous suspensions: POFs,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

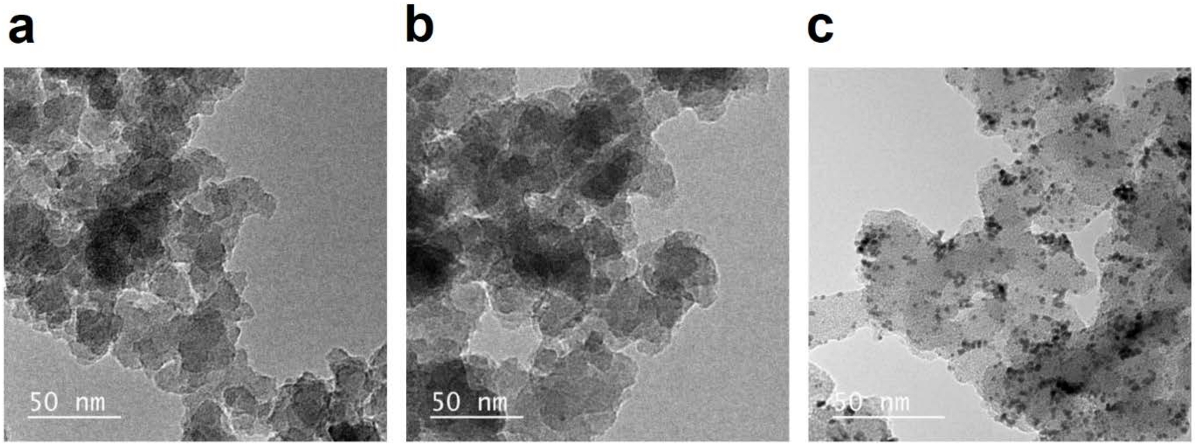

Fig. S7 TEM images of (a) pure POF powder, (b) impregnated POF with Pt^{4+}, (c) impregnated products after *in-situ* reduction using $NaBH_4$ as reductant.

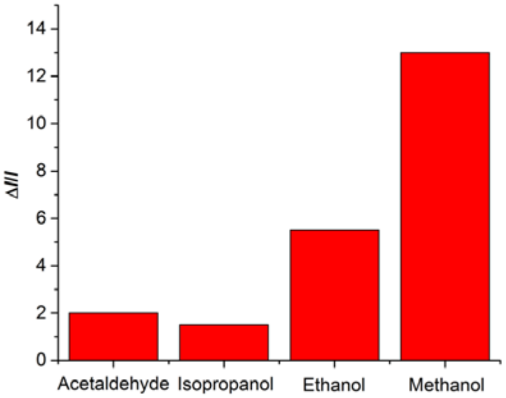

Fig. S8 Response of a PtNP@POF-SiNW toward acetaldehyde (4000 ppm), isopropanol (3000 ppm), ethanol (3000 ppm), and methanol vapour (3000 ppm).

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 CO_2 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	-

References

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