Electronic Supplementary Information for

Quasi-2D Co₃O₄ Nanoflakes as Efficient Gas Sensor *versus* Alcohol VOCs

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1. Setup applied for deposition of cobalt oxide gas-sensing layer.



Figure S1. Scheme of the setup used for the deposition of the cobalt oxide layer by electrochemical technique. The numbers indicate: 1 is the multielectroded chip wired at the multi-pin ceramic card (Siegert Co., Switzerland) whose Pt electrodes are employed as a working electrode, 2 is the electrochemical cell filled with the electrolyte, 3 is the graphite counter electrode, 4 is the Ag/AgCl_{sat} the reference electrode, 5 is the potentiostat, 6 is PC, 7 is a heating plate, 8 is the simplified electrical scheme of measurement in a three-electrode arrangement.

2. Experimental setup to study the chemiresistive response of the Co_3O_4 nanoflaked layer-based gas sensor.



Figure S2. The scheme of the experimental setup to study the chemiresistive response of the Co_3O_4 nanoflaked layer-based gas sensor. The numbers denote: 1 is an air compressor, 2 is a dry air generator (PG14L, Peak Scientific, UK), 3 is a gas generator (OVG-4, Owlstone, UK), 4 is a flow controller, 5 is a switching valve, 6 is a low-flow controller, 7 is a water bubbler, 8 is an opening switch, 9 is the chamber with an installed gas-sensor chip, 10 is the electronic measuring setup, 11 is a PC.

3. Field-effect transistor measurements.

The back gate resistance was measured simultaneously to be always at least two orders larger than the source-drain one. We have tested two similar sensors at room temperature conditions. The samples exhibited relatively a high source-drain resistance of an order of 1 GOhm with a clear response to the back gate voltage illustrated in Figure S3. The observed transconductance behavior depicts *p*-type of major charge carriers in the cobalt oxide layer confirmed by the inclination of this curve showing a greater slope in the region of negative back gate voltages. However, the limitations caused by room temperature conditions and device design do not allow us to calculate mobility and concentration values. The $I_{SD}(V_G)$ curves exhibit a mild hysteresis; the curve's slope does not depend on the source-drain voltage in the measured range of [10:40] V which allows one capturing the source-drain current at nA range.



Figure S3. The measurements of cobalt oxide layer transconductance in field-effect transistor (FET) geometry under room temperature. Source-drain current dependence on gate voltage for the sensor element under source-drain voltages to be in the range of [10:40] V (a) and 10 V (b) for sensor elements #1 and #3 correspondingly at the Co_3O_4 nanoflake-based multielectrode chip. Insert at (b) is the cartoon scheme of the measurements.

4. Electrochemical characterization of supporting electrolyte.

Current transient recorded in 0.2 M NaNO₃ supporting electrolyte shows an asymptotic decay over time to be linearized at Cottrell coordinates (Figure S1a, inset). The calculated diffusion coefficient seems to be rather small, though this value is effective due to complicated kinetics of the process. Cyclic voltammetry curves are given in Figure S1b to be taken in a few cycles. We can indicate two cathodic processes at -0.25 V and -1.0 V vs. Ag/AgCl_{sat.} correspondingly. The latter process could be also influenced by hydrogen evolution reaction which, in turn, favors a generation of the base.



Figure S4. Electrochemical characterization of supporting electrolyte, 0.2 M NaNO₃: a) current transient recorded at potential -1V vs. Ag/AgCl_{sat}; b) cyclic voltammetry results, 5 cycles are presented.

5. TEM characterization of single Co_3O_4 nanoflakes



Figure S5. TEM images for as-deposited (cobalt hydroxide) (a,b) and annealed (cobalt oxide) (c,d) samples.

6. XPS deconvolution results for the cobalt oxide layer

We have varied two parameters when we performed annealing of cobalt hydroxide in air, time of treatment and annealing temperature. The evaluated chemical composition is presented in Table S5.

| | Co2p (As-deposited) | | | | | | | | | | |
|-----------------------|---------------------|--------|--------|------|--------|--------|-------|-------|------------|--|--|
| Band | Pos | PosSep | B_FWHM | FWHM | Height | %Gauss | Area | %Area | ChiSquared | | |
| 1 - Co2p3/2 peak A | 780.50 | 0.00 | 2.40 | 2.40 | 5885 | 100 | 15055 | 30.29 | 54.02 | | |
| 2 - Co2p3/2 peak B | 782.61 | 2.11 | 2.83 | 2.83 | 2292 | 80 | 7565 | 15.22 | | | |
| 3- Co2p3/2 satellite | 785.90 | 5.39 | 5.13 | 5.13 | 1652 | 81 | 9855 | 19.83 | | | |
| 4 - Co2p1/2 peak A* | 795.98 | 15.48 | 3.08 | 3.08 | 2100 | 80 | 7527 | 15.15 | | | |
| 5- Co2p1/2 peak B* | 797.51 | 17.00 | 3.08 | 3.08 | 1154 | 100 | 3783 | 7.61 | | | |
| 6 - Co2p1/2 satellite | 802.55 | 22.05 | 4.72 | 4.72 | 1123 | 90 | 5913 | 11.90 | | | |

Table S1. XPS results for deconvolution of cobalt core-level spectrum at the as-deposited material

Table S2. XPS results for deconvolution of cobalt core-level spectrum at the material annealed at 300 °C for 4 h

| | Co2p (Annealed at 300 °C for 4 hours) | | | | | | | | | | |
|-----------------------|---------------------------------------|--------|--------|------|--------|--------|-------|-------|------------|--|--|
| Band | Pos | PosSep | B_FWHM | FWHM | Height | %Gauss | Area | %Area | ChiSquared | | |
| 1 - Co2p3/2 peak A | 780.08 | 0.00 | 2.55 | 2.55 | 10476 | 92 | 29529 | 45.42 | 52.74 | | |
| 2 - Co2p3/2 peak B | 782.61 | 2.53 | 3.08 | 3.08 | 3018 | 100 | 9894 | 15.22 | | | |
| 3- Co2p3/2 satellite | 788.83 | 8.75 | 4.62 | 4.62 | 997 | 100 | 4905 | 7.54 | | | |
| 4 - Co2p1/2 peak A* | 795.28 | 15.20 | 2.64 | 2.64 | 4310 | 80 | 13288 | 20.44 | | | |
| 5- Co2p1/2 peak B* | 797.51 | 17.43 | 2.79 | 2.79 | 1367 | 80 | 4452 | 6.85 | | | |
| 6 - Co2p1/2 satellite | 804.33 | 24.25 | 4.32 | 4.32 | 641 | 100 | 2943 | 4.53 | | | |

| Table S3. XPS results for deconvolution of oxygen core | e-level spectrum at as-deposited material |
|--|---|
|--|---|

| O 1s (As-deposited) | | | | | | | | | |
|---------------------|--------|--------|--------|------|--------|--------|-------|-------|------------|
| Band | Pos | PosSep | B_FWHM | FWHM | Height | %Gauss | Area | %Area | ChiSquared |
| 1 - low BE | 529.93 | 0.00 | 2.07 | 2.07 | 1256 | 100 | 2764 | 11.31 | 43.96 |
| 2 - higher BE | 531.27 | 1.34 | 1.90 | 1.90 | 10123 | 88 | 21686 | 88.69 | |

Table S4. XPS results for deconvolution of oxygen core-level spectrum at the material annealed at 300 °C for 4 h

| O 1s (Annealed at 300 °C for 4 hours) | | | | | | | | | |
|---------------------------------------|--------|--------|--------|------|--------|--------|-------|-------|------------|
| Band | Pos | PosSep | B_FWHM | FWHM | Height | %Gauss | Area | %Area | ChiSquared |
| 1 - low BE | 529.63 | 0.00 | 1.43 | 1.43 | 9468 | 80 | 15777 | 69.50 | 47.94 |
| 2 - higher BE | 531.26 | 1.64 | 1.90 | 1.90 | 3424 | 100 | 6925 | 30.50 | |

Table S5. The atomic concentration of Co, O, and C estimated out of XPS data for different temperature and time of annealing of the material in comparison with pristine samples

| sample | C 1s % | Co 2p % | O 1s % |
|-----------------------|--------|---------|--------|
| pristine/as-deposited | 8.5 | 23.1 | 68.5 |
| 25 min. 100°C | 40.7 | 11.3 | 48.0 |
| 50 min. 100°C | 39.8 | 11.2 | 49.1 |
| 250 min. 100°C | 37.0 | 12.1 | 50.9 |
| 25 min. 200°C | 32.7 | 18.7 | 48.6 |
| 50 min. 200°C | 33.6 | 18.0 | 48.5 |
| 250 min. 200°C | 31.6 | 19.9 | 48.6 |
| 25 min. 300°C | 31.7 | 18.2 | 50.0 |
| 50 min. 300°C | 31.2 | 19.1 | 49.8 |
| 250 min. 300°C | 27.8 | 20.0 | 52.2 |



7. Study of Co_3O_4 nanoflake layer's impedance at varied a.c. frequencies

Figure S6. Nyquist plot for three Co_3O_4 nanoflake-based sensors at the multielectrode chip with material deposited for 75 s.

| Table S6. | Fitted | parameters | of an | equivalent | circuit | for Co ₃ C | 4 nanoflak | e-based | sensors | with | material |
|-----------|----------|------------|-------|------------|---------|-----------------------|------------|---------|---------|------|----------|
| deposited | l for 75 | s. | | | | | | | | | |

| | R1, Ohm | err, % | C1, F | err, % | R2, Ohm | err, % | CPE-T | err, % | CPE-P | err, % |
|-----------|---------|--------|----------|--------|---------|--------|----------|--------|-------|--------|
| #1, 0.1 V | 92286 | 1.41 | 2.37E-11 | 1.31 | 89243 | 1.75 | 1.49E-09 | 10.47 | 0.83 | 1.34 |
| #1, 5 V | 90322 | 2.56 | 2.39E-11 | 2.3 | 50004 | 4.62 | 8.74E-10 | 20.45 | 0.87 | 2.02 |
| #2, 0.1 V | 151240 | 2.4 | 2.58E-11 | 2.12 | 154340 | 2.53 | 9.37E-10 | 14.84 | 0.84 | 1.66 |
| #2, 5 V | 140770 | 3.04 | 2.63E-11 | 2.51 | 126530 | 3.38 | 5.25E-10 | 16.33 | 0.88 | 1.61 |
| #3, 0.1 V | 147400 | 2.01 | 2.54E-11 | 1.74 | 101270 | 2.99 | 1.05E-09 | 16.07 | 0.85 | 1.69 |
| #3, 5 V | 143010 | 2.52 | 2.57E-11 | 2.04 | 82516 | 4.26 | 8.24E-10 | 20.28 | 0.87 | 1.85 |
| #4, 0.1 V | 119690 | 1.5 | 2.60E-11 | 1.35 | 95076 | 2.05 | 1.02E-09 | 11.01 | 0.86 | 1.28 |
| #4, 5 V | 113790 | 2.64 | 2.62E-11 | 2.21 | 70387 | 4.26 | 6.19E-10 | 18.04 | 0.89 | 1.76 |



8. Estimation of the detection limit for Co_3O_4 nanoflake-based sensor to alcohol VOCs

Figure S7. The estimation of the detection limit for Co_3O_4 nanoflake-based sensor to alcohol VOCs, methanol, ethanol, isopropanol, and butanol. The extension follows the empirical Freundlich isotherm.

9. Performance of the same Co_3O_4 nanoflake-based sensor towards butanol with the one-year break at dry and humidified air.



Figure S8. The Co_3O_4 -nanoflake based sensor's response to butanol vapors after one year keeping at a shelf in dry air and humid-enriched, 30 rel. %, air.

10. The response of the Co₃O₄ nanoflake-based sensor towards humidity vapors



Figure S9. The Co_3O_4 -nanoflake based sensor's response to humidity vapors added to air: a) the R(t) transient upon exposure to H_2O vapors, 100-10000 ppm concentrations; b) the dependence of the chemiresistive response on the vapor concentration.

10. Literature review in the field of cobalt oxide gas sensors.

We have reviewed the literature devoted to cobalt oxide-based sensors. The results are presented in Table S7. To properly compare various data, we plot a sensitivity coefficient as a ratio of response in percent to the vapor concentration at *ppm* for methanol, ethanol, isopropanol, and butanol vapors (Figure S10).



Figure S10. Comparison of sensitivity coefficient of cobalt oxide-based gas sensors upon exposure to methanol (a), ethanol (b), isopropanol (c) and butanol (d).

Ref. Method, annealing Operation Analyte Sensitivity Sensitivity **Recalculated to** Year LoD Notes temperature (°C) Temperature calculation (min concentration) $(R_{\rm g} - R_{\rm air}) \times 100\% / R_{\rm air}$ (optimal), °C method or $(R_{b}-R_{g}) \times 100\%/R_{g}$, %/ppm Precipitation from cobalt up to 60%/ 1000 ppm n/a 2001 | sl 225 isobutane $(R_{\rm g} - R_{\rm air}) \times$ 0.06 100%/ R_{air} nitrate solution, 800 °C $\Delta R/R_0$ CH_4 4.5/3000 ppm 2003 s2 Reactive electron beam 240 0.15 n/a evaporation of cobalt on 21.7/100 ppm H_2 21.7 "pure" and surface-oxidized silicon wafers respectively 23.6/ 50 ppm CO 47.2 followed by an additional NO_2 -13.1/ 1 ppm 92.9 thermal treatment, 600 °C NH₃ 31/ 50 ppm 62 Reactive radio frequency 2005 s3 200 NO_2 n/a 26%/200 ppb n/a n/a sputtering 40%/ 20 ppm 400 acetone 25%/1 ppm 450 ethanol 22%/ 5 ppm 400 benzene 9%/ 1 ppm 400 ethyl acetate 400 CO the lowest concentration reported - 10 ppm n/a, possibly co-precipitation CO R_g/R_a 3.8/1000 ppm n/a 2006 s4 80 0.28 and hydrothermal methods

Table S7. Literature review on cobalt oxide synthesis and sensing performance (analyte, sensitivity, LoD)

| | | using cobalt nitrate precursor | 100 | H ₂ | | 3/ 1000 ppm | 0.2 | | |
|------|----|--|-----|--|---|--|------------------|-----|--|
| | | | 90 | CH ₄ | | 1.3/ 1000 ppm | 0.3 | | |
| 2006 | s5 | Two-step method: cobalt acetate reacts with ethylene glycol (EG) in the presence of poly(vinyl pyrrolidone) (PVP) to produce cobalt oxide precursor, and then the precursor is calcinated to produce Co_3O_4 , 500 °C | 300 | CO ethanol | R _g /R _a | ca. 1.9/1000 ppm | 0.0009 | n/a | |
| 2009 | s6 | Obtained at 300 °C from the CoCO ₃ submicrometer crystals after thermal transformation in laboratory air | 300 | ethanol CO | R _g /R _a | ca. 2.6/1 ppm ca. 1.4/10 ppb | 160 4000 | n/a | |
| 2009 | s7 | Template replication method and immobilization using dielectrophoresis process, using SBA-15, cobalt nitrate, 450 °C | 200 | СО | $(R_{\rm g} - R_{\rm air}) \times$ 100%/ $R_{\rm air}$ | 4.3%/10 ppm | 0.43 | n/a | |
| 2009 | s8 | Pulsed laser deposition | 400 | CO NO ₂ CH ₄ | R/R ₀ | ca. 1.2/20 ppm ca. 0.9/5 ppm ca. 1.05/20 ppm | 1 2.2 0.25 | n/a | |
| 2009 | s9 | Hydrothermal, using SBA-15, SBA-40b, SBA-100b and cobalt | 200 | со | $[(R_{\rm g} - R_{\rm air})/R_{\rm air}]$ $\times 100\%$ | ca. 10%/ 10 ppm | 1 | n/a | |

| | | nitrate | | | | | | | |
|------|-----|--|-----|-----------------|--|------------------|------|------------------|--|
| 2009 | s10 | Surfactant-assisted (SDBS) | 100 | toluene | R _g /R _a | 3.1/ 10 ppm | 21 | n/a | |
| | | | | acetone | | ca. 2.6/ 10 ppm | 16 | • | |
| | | | | ethanol | | ca. 1.5/ 10 ppm | 5 | • | |
| | | | | gasoline | - | ca.1.8/ 10 ppm | 8 | - | |
| | | | | propanol | - | ca. 1.75/ 10 ppm | 7.5 | - | |
| | | | | butanol | - | ca. 1.75/ 10 ppm | 7.5 | - | |
| 2010 | s11 | Chemical Vapor Deposition | 200 | ethanol | relative | ca. 0.5/100 ppm | 0.5 | n/a | |
| | | atmospheres at 500 °C. | | H ₂ | resistance variation upon exposure to the target gases | ca. 0.6/1000 ppm | 0.6 | | |
| 2012 | s12 | Modified template 2 step method, using SBA-15 and cobalt nitrate | 350 | ethanol | | 5.1/300 ppm | n/a | n/a | |
| 2014 | s13 | Thermal decomposition of cobalt nitrate at ZnO-PVP | 220 | нсон | R _g /R _a | 1.05/50 ppb | 100 | 5 ppb/ 50 ppb | |
| | | etching of ZnO. | | NO ₂ | - | ca. 1.02/100 ppb | 20 | | |
| | | | | СО | - | ca. 1.03/100 ppb | 30 | - | |
| | | | | CO ₂ | | ca. 1.01/100 ppm | 0.01 | - | |
| | | | | ethanol | | 1.1/100 ppb | 100 | - | |
| 2014 | s14 | Synthesized by sacrificial CNTs through SPMIC method using | 300 | acetone | R _g /R _a | low | | n/a | |

| | | Co(NO ₃) ₂ precursor, 650 °C | | toluene formaldehyde ammonia | - | low low 1.1/ 10 ppm | 1 | | |
|------|-----|---|-----|--|--------------------------------|--|--|-----|---|
| 2014 | s15 | Synthesized via a facile template-free hydrothermal method and subsequent thermal decomposition | 200 | ethanol | R _g /R _a | ca. 3.3/ 5 ppm | 46 | n/a | |
| 2014 | s16 | Ethylene glycol (EG)-mediated solvothermal method followed by calcination | 180 | ethanol | R _g /R _a | 2/5 ppm | 20 | n/a | |
| 2014 | s17 | Fluoride anion-assisted hydrothermal and controlled annealing route, 350 °C | 100 | H ₂ CO | R _g /R _a | 1.05/10 ppm ca. 3.5/10 ppm | 0.5 25 | n/a | F-doped |
| 2015 | s18 | Thermal decomposition of cobalt nitrate by nanocasting, using KIT-6 silica as a structure matrix with further removal of silica matrix by sodium hydroxide, 300 °C | 200 | СО | R _g /R _a | ca. 1.2/1 ppm | 20 | n/a | |
| 2015 | s19 | Purchased or prepared by the solvothermal reaction of stock solutions and subsequent heat treatment (powders, hollow spheres, hollow hierarchical nanostructures), 400 °C | 250 | p-xylene ethanol p-xylene (275) toluene (275) formaldehyde (275) | R _g /R _a | ca. 170/5 ppm ca. 100/5 ppm ca. 100/ 5 ppm ca. 70/5 ppm ca. 10/5 ppm | 3380 1980 1980 1980 1380 180 | n/a | in comparison with Pt- modified hierarchical cobalt oxide nanostruct ures |

| | | | | benzene (275) ethanol (275) ammonia (275) hydrogen (275) | | ca. 7/5 ppm ca. 21/5 ppm ca. 4/5 ppm ca. 1/5 ppm | 120 400 60 - | | |
|------|-----|--|------------|---|--------------------------------|---|--|-----|---|
| 2016 | s20 | Commercial powder. A ceramic paste of the sensing material powder was prepared by mixing an organic dispersant consisting of 10 wt % ethyl cellulose and 90 wt % terpineol. The weight ratio of the sensing material powder to the organic dispersant was 1:16. The sensor was baked at 400 °C | 100 200 | NO H ₂ | R _g /R _a | 1.11/ 50 ppb 1.27/ 25 ppm | 220 | n/a | in comparison with Ag, Au, Pt modified powders |
| 2016 | s21 | Solvothermal process using poly(vinylpyrrolidone) to control morphology, 500 °C | 170 | ethanol xylene ether acetone methanol ethylbenzene toluene benzene | R _g /R _a | 2/10 ppm (13.4/ 50 ppm) ca. 1.1/ 50 ppm ca. 2/ 50 ppm ca. 6/ 50 ppm ca. 5/ 50 ppm ca. 2/ 50 ppm ca. 1.5/ 50 ppm ca. 1.5/ 50 ppm | 10 (25) 0.2 2 10 8 2 1 - | n/a | |

| 2016 | s22 | Nanocasting method with ordered mesoporous silica as a hard template (KIT-6, SBA- 15), Co(NO ₃) ₂ ·6H ₂ O, 400 °C | 175-200 | ethanol NO2 H2 formaldehyde acetone toluene methane | R _g /R _a or R _a /R _g | 7/ 100 ppm (concentration dependence is not discussed and hard to consider) ca. 1.5/100 ppm - (ca. 1/100 ppm) ca. 2.5/100 ppm ca. 2.9/100 ppm ca. 2.4/100 ppm ca. 2/ 100 ppm | 6 0.5 - 1.5 1.9 1.4 1 | n/a | |
|------|-----|---|-------------------|---|--|--|--|---------------------|--|
| 2016 | s23 | Transferring cobalt-solution- dipped polystyrene mono- layers onto sensor substrates and subsequent removal of the PS template by heat treatment, 400 °C | 200 250 275 | ethanol xylene toluene (200) benzene (200) HCHO (200) CO (200) | (R _g -R _a)/R _a | 112.9/5 ppm, ca. 70/0.25 ppm ca. 20.7/5 ppm, 1/0.25 ppm ca. 37/5 ppm ca. 25/5 ppm ca. 5/5 ppm ca. 4/5 ppm | 2258, 28000 414, 400 740 500 100 80 | sub-ppb 0.05 ppm | the exact value of LoD for ethanol is not indicated |
| 2016 | s24 | Hydrothermal route using cobalt nitrate and NH₄F, 350 °C | RT | NH ₃ H ₂ S CO | R _g /R _a | ca. 1.2/0.2 ppm, 9.5/100 ppm 2.0/100 ppm 1.4/100 ppm | 100, 8.5 1 0.4 | 0.2 ppm | |

| | | | | H ₂ | | 1.2/100 ppm | 0.2 | | |
|------|-----|---|-----|----------------------------------|--------------------------------|---------------------------|-----------|---------|--|
| | | | | C ₂ H ₅ OH | | 1.5/100 ppm | 0.5 | | |
| 2017 | s25 | Chemical bath deposition, | 200 | NO ₂ | $(R_{\rm g} - R_{\rm air})$ | 16%/100 ppm | 0.16 | n/a | |
| | | ammonium fluoride. 400 °C | | Cl ₂ | - ^ 100%/ N _{air} | 22%/100 ppm | 0.22 | | |
| | | | | H ₂ S | - | 340%/100 ppm, 68%/5 | 3.4, 13.6 | | |
| | | | | | - | | | | |
| | | | | NH ₃ | | 46%/100 ppm | 0.46 | | |
| | | | | CH₃OH | | 25%/100 ppm | 0.25 | | |
| | | | | C ₂ H ₅ OH | - | 18%/100 ppm | 0.18 | | |
| 2017 | s26 | Hydrothermal treatment and | 100 | ethanol | R _g /R _a | ca. 1.7/1 ppm, 10.4/ ~100 | 70, 9.4 | 0.2 ppm | |
| | | a post thermal annealing procedure of cobalt nitrate at carbon foam, 200, 250 and 350 °C | | | - | | | | |
| | | | | toluene | | ca. 1.1/~100 ppm | 0.1 | | |
| | | | | NO ₂ | | ca. 0.9/ about 10 ppm | -1 | | |
| | | | | NH ₃ | | ca. 1.05/ ~100 ppm | 0.05 | | |
| | | | | methanol | - | ca. 1.6/ ~100 ppm | 0.6 | | |
| | | | | formaldehyde | - | ca. 1.5/ ~100 ppm | 0.5 | | |
| | | | | ethylene glycol | - | ca. 4.9/ ~100 ppm | 3.9 | | |
| | | | | со | | ca. 1.06/ about 10 ppm | 0.6 | | |
| | | | | benzyl alcohol | | ca. 2.3/ ~100 ppm | 1.3 | | |
| | | | | acetone | | ca. 1.25/ ~100 ppm | 0.25 | | |
| 2017 | s27 | Post-thermal conversion of | 111 | acetone | R _g /R _a | 6.8/20 ppm, 16.5/ 100 | 29, 15.5 | n/a | |
| | | $(CO(NH_3)_6)COF_6 H_2O precursor$ | | | | | | | |

| | 1 | | | | | | | | |
|------|-----|--|--------------|--------------|------------------------------------|----------------------------------|----------|-----|-----------------------|
| | | after a fluorine-assisted | | | | ppm | | | |
| | | | | pentane | | 4.8/100 ppm | 3.8 | _ | |
| | | | | ammonia | | 5.6/100 ppm | 4.6 | - | |
| | | | | methanol | - | 6.1/100 ppm | 5.1 | - | |
| | | | | formaldehyde | - | 6.4/100 ppm | 5.4 | _ | |
| | | | | ethanol | - | 8.7/100 ppm | 7.7 | _ | |
| 2017 | s28 | Precipitation and subsequent | 120 | со | R _{CO} /R _{air} | ca. 5.1/6.7 ppm | 61.2 | n/a | different humidity |
| | | thermal decomposition of a carbonate precursor, 500 °C | 240 | - | | ca. 2.4/6.7 ppm | 20.9 | - | |
| 2017 | s29 | Solution-combustion synthesis, 350°C (and | 100 (25% RH) | acetone | R _g /R _a | 6.3/10 ppm (150 °C in humid air) | 53 | n/a | |
| | | annealing at 300 or 600 °C) | | ethane | _ | 3.7/250 ppm (125 °C in dry air) | 1.08 | | |
| | | | | СО | _ | 3.6/100 ppm (100 °C in dry air) | 2.6 | | |
| 2017 | s30 | Atomic layer deposition | 350 | ethanol | I _{air} /I _{gas} | ca. 1.25/5 ppm | 5 | n/a | |
| 2018 | s31 | Hydrothermal method using | 200 | ethanol | R _g /R _a | 12.6/50 ppm | 23.2 | n/a | |
| | | 500 °C | | methanol | | ca. 6.2/50 ppm | 10.4 | - | |
| | | | | ammonia | | ca. 4.3/50 ppm | 6.6 | _ | |
| | | | | acetone | | ca. 8.2/50 ppm | 14.4 | _ | |
| 2018 | s32 | Hydrothermal method, 300- 500 °C | 185 | ethanol | R _g /R _a | 2.5/1 ppm, ca. 140/100 ppm | 150, 139 | n/a | |
| | | | | acetone | | ca. 60/ 100 ppm | 59 | - | |

| | | | | methanol formaldehyde ammonia nitrogen dioxide | - | ca. 30/100 ppm ca. 55/100 ppm ca. 29/100 ppm ca.2/100 ppm | 29 54 28 1 | - | |
|------|--------------------|--|-----------------|---|--------------------------------|--|---------------------|---------|---|
| 2018 | s33 | Synthesized using cobalt nitrate precursor at | 200 | ethanol | R _g /R _a | ca. 1.2/4.3 ppb, ca. 2.5/4.3 ppm | 4651.2, 34.9 | 4.3 ppb | |
| | | methylimidazole. The | | H ₂ S | | ca. 1.3/4.3 ppm | 7.0 | | |
| | | templates are removed using the organic solvent | | NH ₃ | - | ca. 1.25/4.3 ppm | 5.8 | - | |
| | | methylbenzene, 300-450 °C. | | CH ₃ OCH ₃ | - | ca. 2.0/4.3 ppm | 23.3 | 1 | |
| | | | | НСНО | - | ca. 1.26/4.3 ppm | 6.0 | - | |
| | | | | NO ₂ | | 1.25/4.3 ppm | 5.8 | - | |
| | | | 170 | C ₂ H ₆ S | - | ca. 1.3/250 ppb, 3.15/125 ppm | 120, 1.72 | - | |
| | | | | CH ₄ S | - | ca. 1.7/125 ppm | 0.6 | - | |
| | | | | CH ₃ COCH ₃ | - | ca. 2.1/125 ppm | 0.9 | - | |
| | | | | H ₂ S | - | ca. 1.45/125 ppm | 0.36 | - | |
| | | | | НСНО | - | ca. 1.5/125 ppm | 0.4 | - | |
| | | | | NH ₃ | - | ca. 1.7/125 ppm | 0.6 | - | |
| 2019 | s34 | Oxygen plasma treatment of a | 200 | formaldehyde | $(R_{\rm g} - R_{\rm air})$ | 5%/50 ppb | 100 | 40 ppb | |
| | | (PVA) film followed by heat | | H ₂ | - × 100%/ R _{air} | ca. 12%/500 ppm | 0.024 | | 1 |
| | treatment, 500 °C. | | NH ₃ | - | ca. 2.5%/1 ppm | 2.5 | 1 | | |

| | | | | CO ₂ | | - | - | | |
|------|-----|---|-----|-----------------|--|------------------------------|-----------|-------|--|
| 2019 | s35 | Spray pyrolysis (cobalt acetate | RT | acetone | R _{analyte} /R _{air} | 235/50 ppm | 468 | 1 ppm | |
| | | different deposition | | ethanol | | ca. 5/50 ppm | 8 | | |
| | | temperatures, 473 to 773 K in steps of 100 K | | ammonia | - | ca. 4/50 ppm | 6 | | |
| | | | | xylene | - | ca. 1/50 ppm | - | | |
| | | | | toluene | - | ca. 2/50 ppm | 2 | | |
| | | | | acetaldehyde | - | ca. 30/50 ppm | 58 | | |
| 2019 | s36 | Porous Co ₃ O ₄ assembled from nanoparticles was acquired by | 100 | n-butanol | R _g /R _a | 21/100 ppm, ca. 3.5/5 ppm | 20, 50 | n/a | |
| | | heating Co-MOFs which were prepared using Co ²⁺ ions and 2-methylimidazole at room | | butanone | - | ca. 12.5/100 ppm | 11.5 | - | |
| | | | | isopropanol | | ca.11/100 ppm | 10 | | |
| | | | | xylene | - | ca. 7.5/100 ppm | 6.5 | | |
| | | | | ammonia | | ca. 2.4/100 ppm | 1.4 | | |
| | | | | methylbenzene | - | ca. 6.2/100 ppm | 5.2 | | |
| | | | | acetone | - | ca. 5.2/100 ppm | 4.2 | | |
| | | | | ethanol | - | ca. 13.5/100 ppm | 12.5 | | |
| 2019 | s37 | Sol–gel, using precursor Co(CH ₃ COO) ₂ .4H ₂ O, 600 °C | n/a | LPG | R _g /R _a | ca. 1.15/1000 ppm | 0.015 | n/a | |
| 2019 | s38 | Wet-chemical method, cobalt acetate, urea. 300 °C | 300 | ethanol | R _g /R _a | ca. 2/1 ppm, 20.3/100 ppm | 100, 19.3 | 1 ppm | |
| | | | | formaldehyde | | 3.2/100 ppm | 2.2 | | |

| | | | | acetone methane benzene ammonia | - | 4.8/100 ppm 1.4/100 ppm 2.1/100 ppm 2.5/100 ppm | 3.8 0.4 1.1 1.5 | - | |
|------|-----|---|-----|--|--|---|---|--------------------|--|
| 2020 | s39 | Electrospinning method using ethanol or N,N- dimethylformamide (DMF) solvents mixed with cobalt(II) nitrate and polyvinylpyrrolidone (PVP) applied for the electrospinning, 600 °C. | 100 | CO NO ₂ C ₂ H ₆ O H ₂ | R/R ₀ , R ₀ /R | 2.4/5 ppm ca0.8/5 ppm ca. 0.5/5 ppm ca. 0.1/5 ppm | 28 n/d n/d n/d | - | |
| 2020 | s40 | Co ₃ O ₄ microspheres are synthesized via amorphous- coordination polymers based self-template method, 500 °C. | 220 | xylene toluene benzene acetone ethanol formaldehyde | R _g /R _a | ca. 3/10 ppm ca. 2.9/100 ppm ca. 1.5/100 ppm ca. 3/100 ppm ca.2.9/100 ppm ca.2.8/100 ppm | 20 1.9 0.5 2 1.9 1.8 | 0.35 ppm - - | |
| 2020 | s41 | Combination of an h- $CoO \rightarrow \beta$ -Co(OH) ₂ phase transition followed by thermal oxidation led to the spontaneous deposition of Co_3O_4 on interdigitated electrodes, 500 °C. | 200 | acetone ethanol C ₆ H ₆ CH ₂ O | R _g /R _a , R _a /R _g | ca. 1.07/20 ppb, 12.4/1 ppm ca. 6/1 ppm ca. 5/1 ppm ca. 3/1 ppm | 350, 1240 500 400 200 | 13.8 ppb | |

| | | | | NH ₃ NO ₂ | | ca. 2/1 ppm ca. 2.1/1 ppm | 100 | - | |
|------|-----|---|-----|------------------------------------|--------------------------------|------------------------------|-----|-----|--|
| 2020 | s42 | Polyol approach using cobalt (II) acetylacetonate precursor and PVP, 500 °C | 170 | СО | l _g /l _a | 1.57/300 ppm | n/a | n/a | |

There are several reviews on Co₃O₄, i.e. by J.M. Xu and J.P. Cheng ⁴³ and by X. Wang et al. ⁴⁴

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