Supporting Information

Detection of Exhaled Volatile Organic Compounds Improved by Hollow Nanocages of Layered Double Hydroxide on Ag Nanowires
Xuezhi Qiao, Xiangyu Chen, Chuanhui Huang, Ailin Li, Xiao Li, Zhili Lu, and Tie Wang*

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Supporting Information
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Section A. Materials and characterizations

Materials
Silver nitrate (AgNO$_3$), argentic chloride (AgCl), polyvinylpyrrolidone (PVP, MW=55,000), ethane glycol (EG), cobaltous nitrate (Co(NO$_3$)$_2$·6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), 2-methylimidazole, $p$-aminothiophenol ($p$-ATP), were purchased from Aladdin (China). All of the other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. Water used in the experiments was Nanopure water made using a Barnstead Nanopure Diamond system.

Characterizations
Crystallographic information of the samples was collected using powder XRD (D/MAX 2500; Rigaku, Tokyo, Japan) and HRTEM (JEM-2100F; JEOL, Tokyo, Japan). Transmission electron microscopy (TEM; JEM-1011; JEOL) images and selected area electron diffraction (SAED; JEM-1011; JEOL) patterns were obtained to determine the crystallinity and crystal structure of the samples. Surface morphologies of the samples were obtained using scanning electron microscopy (SEM; S-4800; Hitachi, Tokyo, Japan). Energy-dispersive X-ray elemental maps of the samples were obtained using HRTEM (JEM-2100F; JEOL). The Raman spectra were recorded using a LabRAM HR Evolution confocal Raman system (wavelengths: 532 and 785 nm; Horiba, Lille, France). Typically, the incident laser power was attenuated to 1 mW and the spectral data acquisition time was 10 s, to obtain a SERS spectrum with a 100× objective. Confocal microscopy images were acquired using a laser scanning microscope (LSM 510; Zeiss, Oberkochen, Germany) and processed using LSM 5 software (ver. 4.2; wavelength, 405 nm; Zeiss). The XPS spectra were recorded (SKL-12; Leybold-Heraeus, Shenyang, China). The specific surface area and pore diameter measurements were carried out by N$_2$ adsorption using a Quadrasorb SI-MP apparatus (Quantachrome, Boynton Beach, FL, USA) at 77 K.
Section B. Experimental section

Synthesis of PVP-capped Ag nanowire (Ag nanowire)
The Ag nanowires were synthesized using the polyol process as previously reported.[1] Briefly, 0.334 g of polyvinylpyrrolidone (PVP) was added to 17 ml of ethylene glycol and heated to 170°C. Next, 25 mg of finely ground AgCl was added for nucleation of the Ag seeds. After 2 min, 3 ml ethylene glycol containing 110 mg of AgNO3 was added over 5 min and the mixture was allowed to react for a further 30 min at 170°C. The nanowires were washed with methanol twice and the nanowires were redispersed in 20 ml methanol. The Ag nanowires were approximately 60.2 ± 10.1 nm in diameter and 5.8 ± 2.5 µm in length. Ag nanowires with diameters of 510 ± 100 nm and lengths of 15.5 ± 8.7 were synthesized using Ag nanowires as Ag seeds for further growth.

Synthesis of Ag nanowire @ZIF-67 (Ag@ZIF-67)
First, 10 mg of PVP capped Ag nanowire and 4.0 mmol of 2-methylimidazole were individually dissolved in 20.0 mL of methanol via ultrasonication for 30 min. After a homogeneous mixture was formed, 1.0 mmol of Co(NO3)2·6H2O was dissolved in 20.0 mL of methanol and then rapidly poured into the former solution under magnetic stirring and further stirring for 2 h. The precipitate was collected by centrifugation (5,000 rpm, 5 min).

Synthesis of Ag nanowire @Co-Ni LDH (Ag@LDH)
First, 50 mg of the prepared Ag@ZIF-67 and 50 mg of Ni(NO3)2·6H2O were dissolved in 20.0 mL anhydrous ethanol, followed by a solvothermal treatment at 80 °C for 1 h. The laurel green Ag nanowire Co-Ni LDH product was collected after centrifugation (5,000 rpm, 5 min).

Synthesis of p-ATP modified SERS substrates
The freshly prepared Ag nanowires, Ag@ZIF-67 and Ag@LDH were dispersed in 5 mL 10^{-5} M p-ATP ethanol solution and magnetically stirred for 1 h. The products were collected by centrifugation (5,000 rpm, 5 min), washed three times with ethanol and self-assembled on silicon wafer.

Fluorescence adsorption experiment
The freshly prepared Ag nanowires, Ag@ZIF-67 and Ag@LDH, were dropped on cover glass and placed inside a sealed chamber (5 cm radius by 6 cm height), where a 25 µL droplet of 84 µM ethanol solution of phthalaldehyde was used for detection. The sealed chamber was heated to 50°C to form the gaseous environment of the fluorescent probe. The cover glasses were kept at this temperature for 60 min for subsequent fluorescence detection.

SERS measurements
The SERS substrates were constructed by self-assembly of Ag nanowires, Ag@ZIF-67 or Ag@LDH. The substrates were placed inside a homemade chamber and incubated together with analytes of different concentrations at 60°C for 10 min. SERS measurements and Raman mapping were performed using a LabRAM HR Evolution confocal Raman system (wavelength, 785 nm; Horiba) with an acquisition time of 10 s and laser power of 0.5 mW.

Data analysis
PCA and HCA were performed using SPSS software (ver. 18.0; SPSS Inc., Chicago, IL, USA) for grouping spectral data based on the degree of resemblance. Both PCA and HCA were preceded by preprocessing done using Labspec 5 software (Horiba; standard values: 4 degrees, 9 dimensions), including smoothing; baseline subtraction (function: polynomial type, 8 degrees) and normalization (at 1,070 cm^{-1}). All spectra were analyzed in the 970–700 cm^{-1} range. The logarithmic data transformation produces the greatest Raman intensity, turning plausible multiplicative models into mathematically attractive additive models and rendering outliers less extreme. When there are zero values in the data, it is intuitive to use log10 (y + 1). A dendrogram was generated from the four PC scores by using Ward’s clustering algorithm and the squared Euclidean distance.
Section C. Computational section

Finite element method (FEM) simulations

The FEM environment of COMSOL Multiphysics (ver. 5.3; COMSOL) was used to test the proposed explanation for the gas molecule flow, adsorption and reaction of NWs, Ag@ZIF-67 and Ag@LDH.

Surface Reactions

Analyte molecules (A) can adsorb and desorb from surface sites (S) on the nanowire surfaces according to

\[ A + S \rightleftharpoons AS \]  

The adsorbed analyte (AS) can transform into a quenched state (QS) that does not contribute to the sensor signal. The quenching reaction is reversible: \( AS \rightleftharpoons QS \).

The rate of adsorption is

\[ r_{\text{ads}} = k_{\text{ads}} \cdot c_A \]  

where \( c_A \) is the concentration of A in the stream. The desorption rate is linear in the concentration of surface-adsorbed species, \( c_{AS} \):

\[ r_{\text{des}} = k_{\text{des}} \cdot c_{AS} \]  

The rate of the reversible quenching reaction is given by

\[ r_{\text{quench}} = -k_1 \cdot c_{AS} + k_2 \cdot c_{QS} \]  

Mass transport in the analyte stream

The equations in the Transport of Diluted Species interface describe the transport of the species, A, in the analyte stream according to

\[ \frac{\partial c_A}{\partial t} + \nabla \cdot (D_A \nabla c_A) + u \cdot \nabla c_A = 0 \]  

Here, \( D_A \) denotes the diffusion coefficient (SI unit: m\(^2\)/s), \( c_P \) denotes the species concentration (SI unit: mol/m\(^3\)), and \( u \) is the velocity vector (SI unit: m/s).

The injected sample concentration is input by the user and the default value is 100 mol/m\(^3\) over 2.5 m/s. Due to diffusive spreading just before the inlet section, a smooth pulse enters the sensor, which is described by a Gaussian distribution at the flow cell inlet with a maximum concentration of 80 mol/m\(^3\) (at default input settings) and a standard deviation of 2.

The adsorption and desorption of analyte at the active pillar surfaces give rise to a net flux at the corresponding boundaries:

\[ N_A = -r_{\text{ads}} + r_{\text{des}} \]  

The mass flux due to desorption is dependent on the local concentration of adsorbed surface species and is hence coupled to the equations in the surface reactions, described below.

Mass transport and reactions on the active surfaces

In this example, surface diffusion is ignored on the active surfaces. Therefore, using the reactions described by Equations 1-3, the balance equations for surface species A and Q are:

\[ \frac{d}{dt} c_{SA} = r_{\text{ads}} - r_{\text{des}} \]  

\[ \frac{d}{dt} c_{SQ} = r_{\text{quench}} \]  

The rate of adsorption depends on the concentration of species P in the analyte stream and therefore the equations describing the surface reactions (above) are coupled to that of the free analyte flow (Equation 4).

Fluid flow

The flow regime is laminar in the cell.

The calculated flow field serves as input to Equation 4, to describe the convective mass transport.
Figure S1. High magnification SEM images of nanocomposite, (a) Ag nanowire, (b) Ag@ZIF-67, (C) Ag@LDH.
Figure S2. XRD pattern of Ag nanowire, Ag@ZIF-67 and Ag@LDH.
Figure S3. (a) XPS spectra of Ag nanowire, Ag@ZIF and Ag@Ni-Co LDH. High-resolution XPS spectra of Ag nanowire Ag@ZIF-67 and Ag@LDH: (b) Ag 3d, (c) Co 2p and (d) Ni 2p.
Figure S4. Raman spectrum of Ni-Co LDH. The Raman peaks at 462 and 532 cm\(^{-1}\) correspond to Ni-OH/Co-OH, Ni-O/Co-O (\(A_g\)) stretching modes. The peaks at 615 and 681 cm\(^{-1}\) correspond to the \(F_{2g}(1)\) and \(A_{1g}\) models of Co(OH)\(_2\), respectively.
Figure S5. Schematic illustration of the strategy used to detect aldehydes.
Figure S6. SERS spectra of p-ethylbenzaldehyde at different concentrations (range from $10^{-8}$ to $10^{-4}$ (v/v)) collected on different SERS-active substrates: (a) Ag, (b) Ag@ZIF-67, (c) Ag@LDH.
Figure S7. TEM of (a) Ag wires, initially 7.3 ± 1.6 µm in length and 400 ± 100 nm in diameter. (b) Ag@ZIF. (c) Ag@LDH.
Figure S8. Interaction between gaseous molecules and substrates. (a) Elastic collision (i) of gaseous and bare nanowires. (b) Gaseous molecules combine (i) with nanowires through pore guidance. (ii) Elastic collision (i) of gaseous and nanowire-combined molecules in the nanopore. (iii) Conformational inversion of gaseous molecules. (iv) Inelastic collision of gaseous molecules with the nanopore and molecules trapped in the pore with depletion of kinetic energy. (c) Gaseous molecules combine (i) with nanowires within the hollow structure. (ii) Elastic collision (i) of gaseous molecules with combined molecules in the nanocage and recombination with nanowires. (iii) Conformational changes of gaseous molecules with conformational inversion. (iv) Inelastic collision of gaseous molecules with the nanocage and molecules dropping down to the substrate with depletion of kinetic energy.
Figure S9. Repeatability of microarrays SERS sensors. The average SERS intensity (Avg) and relative standard deviation (RSD) of 50 spots.

Avg=223  RSD=7.8%
Figure S10. SERS spectra of typical aldehydes collected on microarrays SERS sensors. (a) formaldehyde, (b) oxalaldehyde, (c) glutaraldehyde, (d) benzaldehyde, (e) p-ethylbenzaldehyde, (f) salicylaldehyde, (g) p-nitrobenzaldehyde, (h) blank.
Figure S11. Hierarchical cluster analysis (HCA) of the dataset comprising different types of aldehydes.
Figure S12. SERS spectra of other anti-interference analyses collected on microarrays SERS sensors. (a) ethanol, (b) n-hexane, (c) hexene, (d) acetone, (e) H₂O, (f) NH₃, (g) CO₂, (h) H₂S, (i) ethyl acetate.
Figure S13. Selectivity of the SERS substrate for VOC detection and anti-interference analyses.
Figure S14. The detection of aldehyde in mixed mimetic exhalation. (a) SERS spectra of other potentially interfering lung cancer biomarkers, including hydrocarbons (n-hexane, n-octane, cyclohexane), alcohols (methyl alcohol, ethyl alcohol), ketones (acetone, butanone), organic acid (acetic acid), esters (ethyl acetate), aromatic compounds (methylbenzene), H2S, and NH3. The concentration of potentially interfering lung cancer biomarkers was 1 ppm. (b) SERS spectra of aldehydes (1 ppm) reacted with the substrate in the presence of other potentially interfering lung cancer biomarkers. (c) SERS spectra of aldehydes (10 ppm, 100ppb, 10ppb) reacted with the substrate in the presence of other potentially interfering lung cancer biomarkers. (d) Relationship between corresponding intensity and concentration in mixed mimetic exhalation.
Figure S15. The HCA dendrogram of the dataset of detection system of mixed mimetic exhalation.
Figure S16. The Raman spectra collected from Ag@LDH sensor at different time.
Figure S17. Detection of pixels in a microarray for the scanning of Raman signals. In total, 340 pixels were imaged in each circular well using a computer-controlled x–y translational stage.
SUPPORTING INFORMATION

Figure S18. Schematic diagram of conversion from Raman mapping images to barcode. First, reads the R, G, B values of the Raman mapping images. Second, the read RGB value is corresponding to the standard curve chromaticity diagram to obtain the corresponding concentration. Third, encodes the concentration directly into a barcode for electronic reading. The entire process can be automatically obtained by computer.
Figure S19. SERS mapping and barcode of the detection system of mixed mimetic exhalation. SERS mapping images acquired using peak intensity at 1623 cm\(^{-1}\) for circular wells of detection system of mixed mimetic exhalation. The corresponding barcode was acquired from the value of R, G, B of Raman mapping.
Table S1. Characteristic Raman peaks of different aldehydes after reaction with the modified SERS substrates.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>$\nu$</th>
<th>$\delta$</th>
<th>$\nu$</th>
<th>$\delta$</th>
<th>$\nu$</th>
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<td>formaldehyde</td>
<td>1031 cm$^{-1}$</td>
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<td>1196 cm$^{-1}$</td>
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<td>1344 cm$^{-1}$</td>
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<tr>
<td>oxalaldehyde</td>
<td>$\delta$CC(n-Pe)</td>
<td></td>
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<tr>
<td>glutaraaldehyde</td>
<td>$\delta$CC(n-Pe) *</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>benzaldehyde</td>
<td>1031 cm$^{-1}$</td>
<td>1172 cm$^{-1}$</td>
<td>1196 cm$^{-1}$</td>
<td>1258 cm$^{-1}$</td>
<td>1344 cm$^{-1}$</td>
</tr>
<tr>
<td>$p$-ethylbenzaldehyde</td>
<td>$\delta$CH(Ar)</td>
<td>$\delta$CH(Et)</td>
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<td></td>
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</tr>
<tr>
<td>salicylaldehyde</td>
<td>$\delta$CH(Ar)</td>
<td>$\delta$CH(Et)</td>
<td>$\nu$NO$_2$</td>
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<tr>
<td>$p$-nitrobenzaldehyde</td>
<td>$\delta$CH(Et)</td>
<td>$\nu$ring</td>
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</tbody>
</table>

$v$: denotes stretch;
$\delta$: denotes bend;
*: CH in-plane deformation
References


Author Contributions

T. W. conceived the idea and supervised the project. X. Q. and A. L designed and performed the experiments and collected the data. X. Q. carried out the data analysis. X. Q., X. C., C. H., A. L. and X. L. carried out the SERS substrate preparation and simulation calculation. X. Q. and T. W. cowrote the paper. All authors discussed the results and commented on the manuscript.