

Electronic Supplementary Information

Environmental formaldehyde sensing at room temperature by smartphone-assisted and wearable plasmonic nanohybrids

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Supplementary Discussion

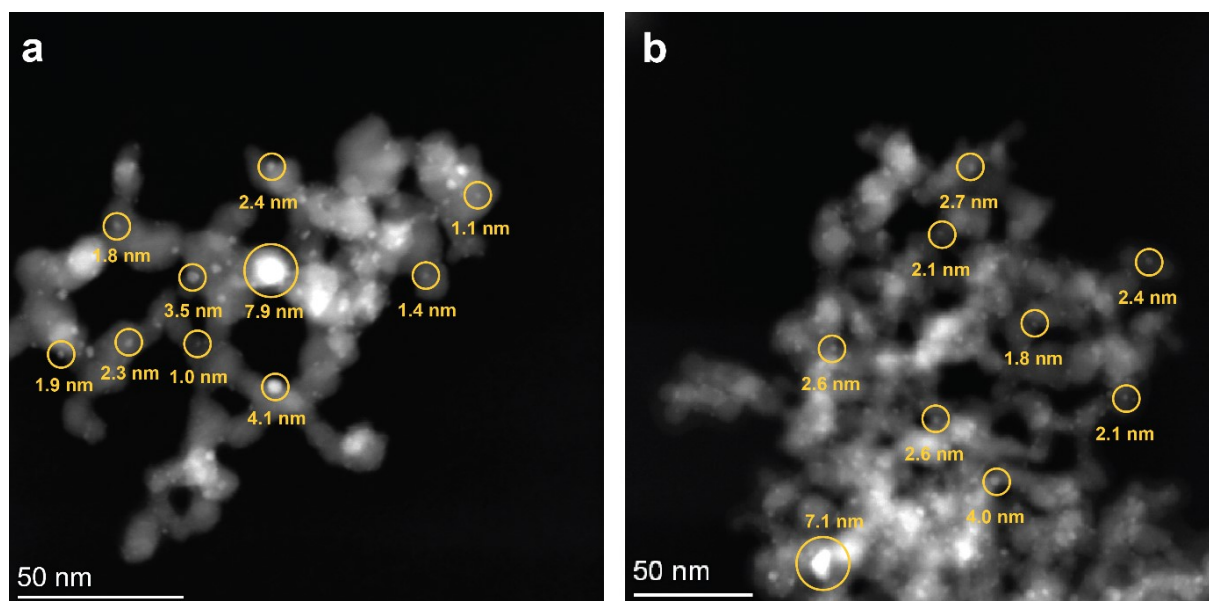
Material characterization for TiO₂

The TiO₂ nanoparticles (darker in **Fig. 1b**) at 4 wt% Ag/AgO_x are faceted and quite aggregated, as indicated by visible sinter necks formed probably during the annealing at 500 °C for 5 h. The TiO₂ particles consist primarily (88 wt%) of the anatase phase, as identified by XRD (**Fig. 1d**, circles) and in line with literature⁷⁰. The remainder is rutile phase (squares). Note that at 20 wt% Ag/AgO_x, also titanium suboxides (i.e. Ti₃O₅, downward triangles, and Ti₄O₇, upward triangles) are observed, in agreement with literature¹⁹. At 4 wt% Ag/AgO_x, the average particle size of 13 nm (as determined by N₂ adsorption) is quite similar to the anatase and rutile crystal sizes (both 12 nm) suggesting monocrystallinity, as observed consistently for all Ag loadings (**ESI Fig. 8**).

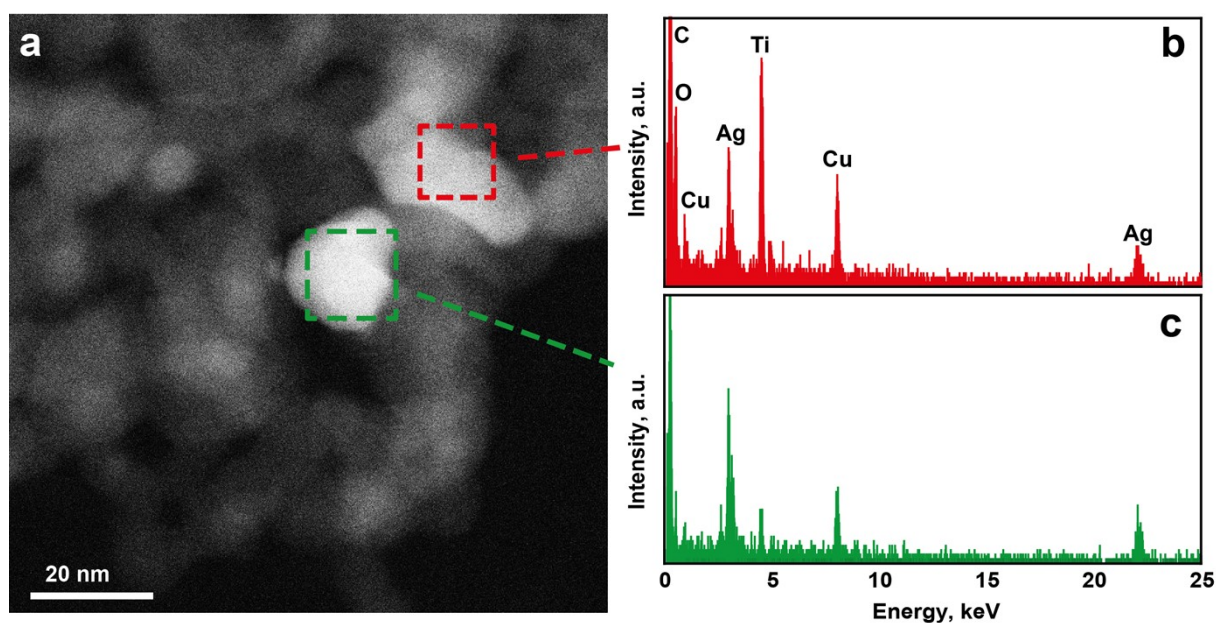
Supplementary References

- 70 Teleki, A., Pratsinis, S. E., Kalyanasundaram, K. & Gouma, P. I. Sensing of organic vapors by flame-made TiO₂ nanoparticles. *Sens. Actuators B* 119, 683-690 (2006).

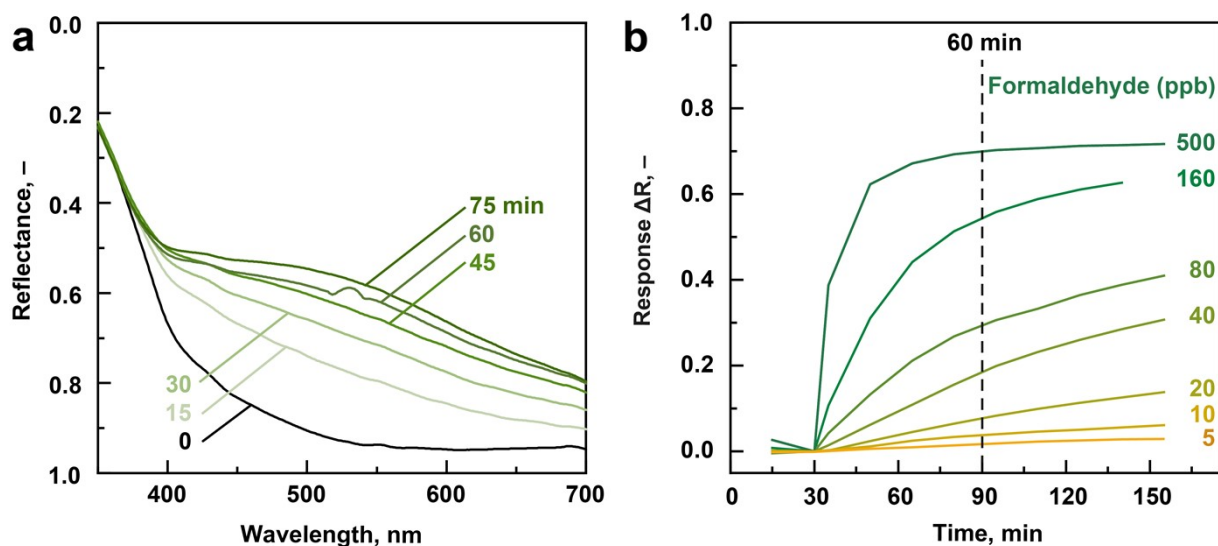
Supplementary Figures



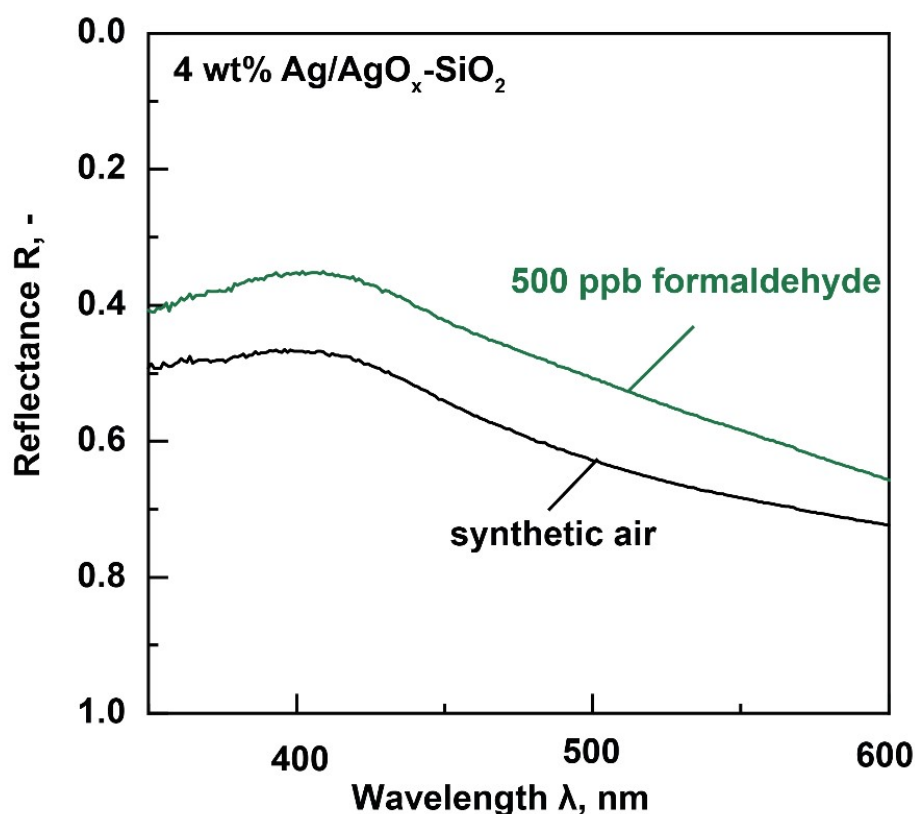
ESI Fig. 1 HAADF-STEM images of Ag/AgO_x clusters. (a,b) Two different HAADF-STEM (Z-contrast) images of 4 wt% Ag/AgO_x on TiO₂ nanohybrids.



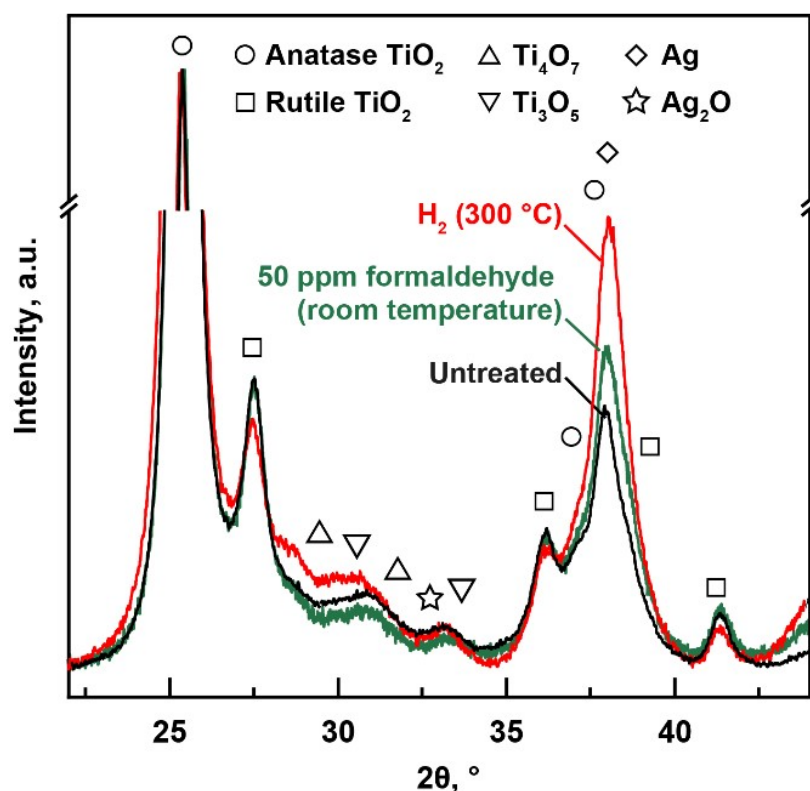
ESI Fig. 2 HAADF-STEM image and EDX spectra. (a) HAADF-STEM image (Z-contrast) of flame-made and annealed (500 °C for 5 h) TiO₂ nanoparticles with nominal 4 wt% Ag. EDX spectra of the marked red (b) and green (c) areas with indicated energies for Ag, Ti and O. Note that the Cu and C are associated to the TEM grid.



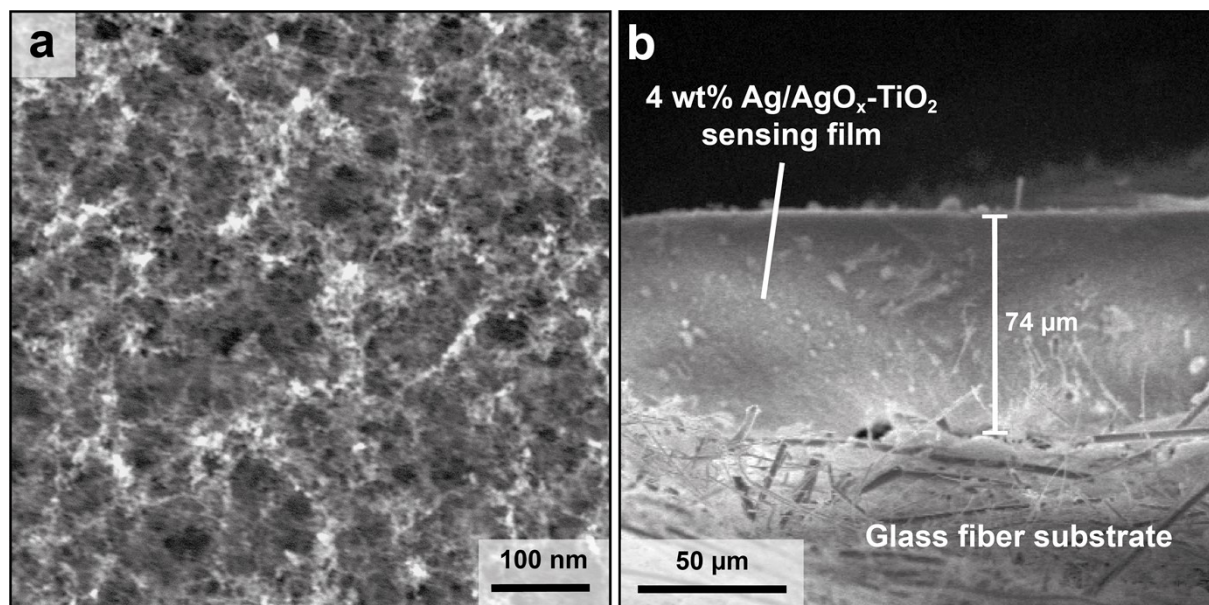
ESI Fig. 3 Transient UV/Vis reflectance spectra and LSPR sensor responses. (a) UV/Vis reflectance spectra of 4 wt% Ag/AgO_x-TiO₂ nanohybrids when exposed for 0 – 75 min to 80 ppb formaldehyde at room temperature and 50% RH in air. (b) LSPR response (at $\lambda_{\text{LSPR}} = 565$ nm) of TiO₂ with nominal 4 wt% Ag to 5 – 500 ppb formaldehyde.



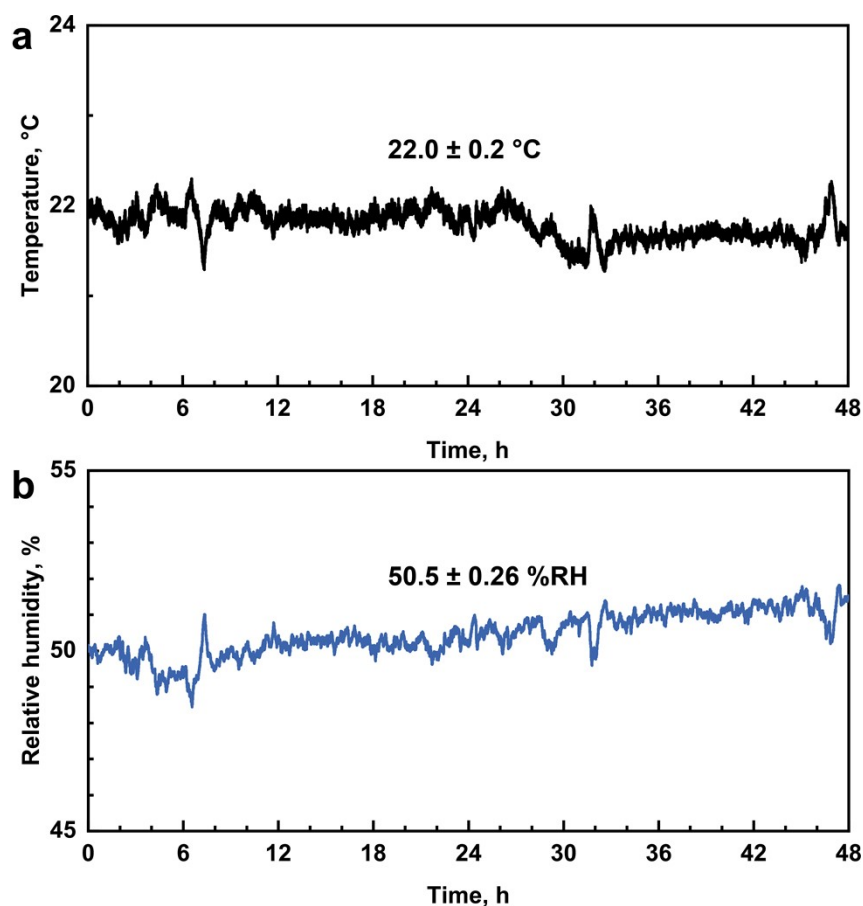
ESI Fig. 4 Reflectance spectra of Ag/AgO_x on SiO₂. UV/Vis reflectance spectra of 4 wt% Ag/AgO_x-SiO₂ nanohybrids at room temperature in air (black line) and when exposed to 500 ppb formaldehyde for 60 min (green) at 50% RH.



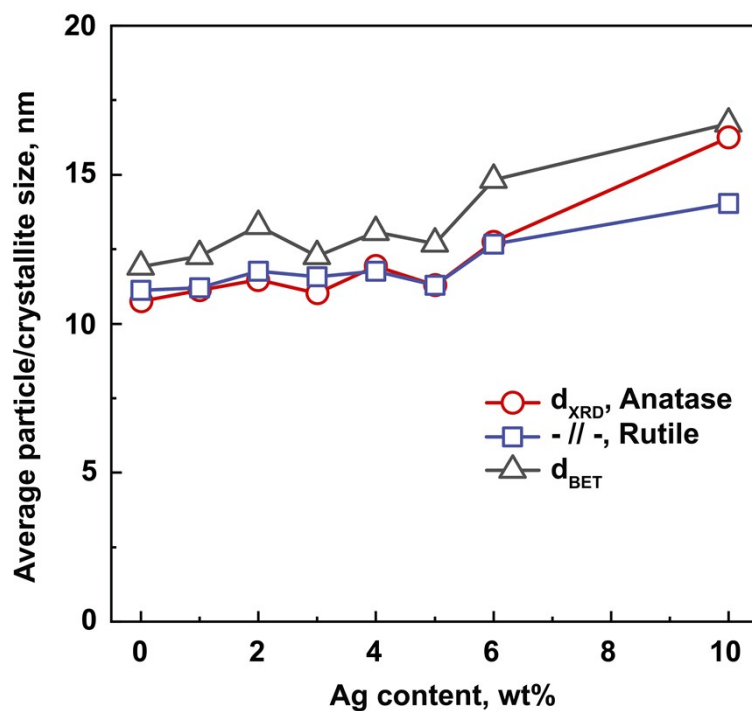
ESI Fig. 5 XRD patterns. TiO_2 with nominal 4 wt% Ag before (black), after exposure to 50 ppm formaldehyde at room temperature (green) and after reduction with a H_2/Ar mixture at 300 °C (red). Reference peak positions of anatase TiO_2 (circles), rutile TiO_2 (squares), Ti_4O_7 (upward triangles), Ti_3O_5 (downward triangles), metallic Ag (diamonds) and Ag_2O (star) are indicated. Note the scale break of the ordinate for better visibility.



ESI Fig. 6 Film morphology. Scanning electron microscopy (a) top and (b) cross-sectional view images of a TiO_2 film with nominal 4 wt% Ag deposited for 16 min onto a glass fiber substrate and annealed at 500 °C for 5 h. The film thickness is $74 \pm 7 \mu\text{m}$.



ESI Fig. 7 Temperature and RH of inlet gas. Temperature (a) and RH (b) upstream of the sensing chamber (blue line) during 48 h of continuous operation.



ESI Fig. 8 Crystal and particle sizes of TiO₂. XRD-measured crystal sizes of anatase (circles) and rutile (squares) TiO₂ with nominal 0 – 10 wt% Ag after annealing at 500 °C for 5 h. Also shown are the corresponding BET-equivalent particle sizes (triangles).