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Tracking Airborne Molecules from Afar: Three-Dimensional Metal–Organic Framework-Surface-Enhanced Raman Scattering Platform for Stand-Off and Real-Time Atmospheric Monitoring

Gia Chuong Phan-Quang,[†] Ningchen Yang,[†] Hiang Kwee Lee,[†,‡] Howard Yi Fan Sim,[†] Charlynn Sher Lin Koh,[†] Ya-Chuan Kao,[†] Zhao Cai Wong,[†] Eddie Khay Ming Tan,[§] Yue-E Miao,[∥] Wei Fan,[∥] Tianxi Liu,[⊥] In Yee Phang,[*,#] and Xing Yi Ling[*,†]

Why ?

- Rise in polluted air, it is necessary to monitor the changes in the concentration of these pollutants
- Remote sensing, fast and portable

What ?

- Laser induced decarboxylation releases CO_2, this CO_2 can be adsorbed by neighbouring MOF@Agnp and can be tracked

Background

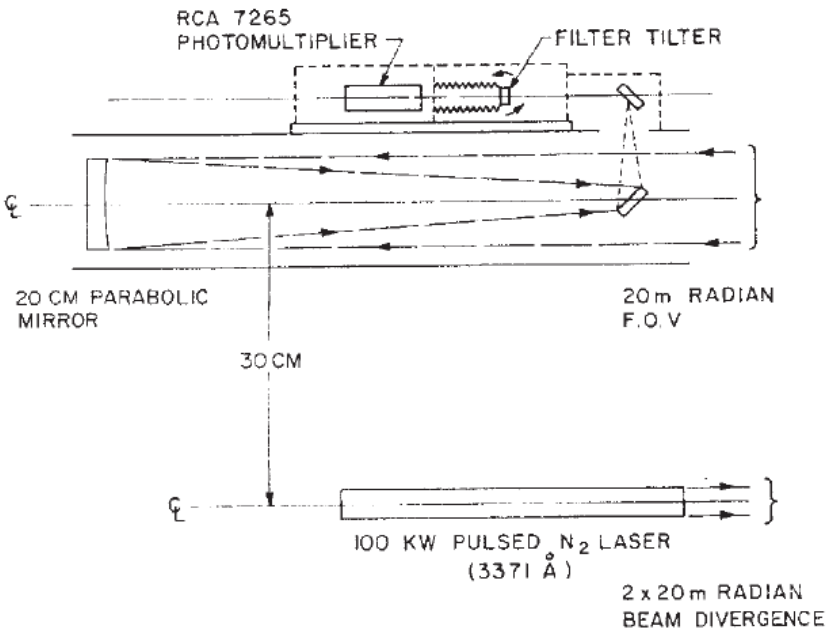


Fig. 1. Schematic diagram of the apparatus used to observe atmospheric Raman scattering.

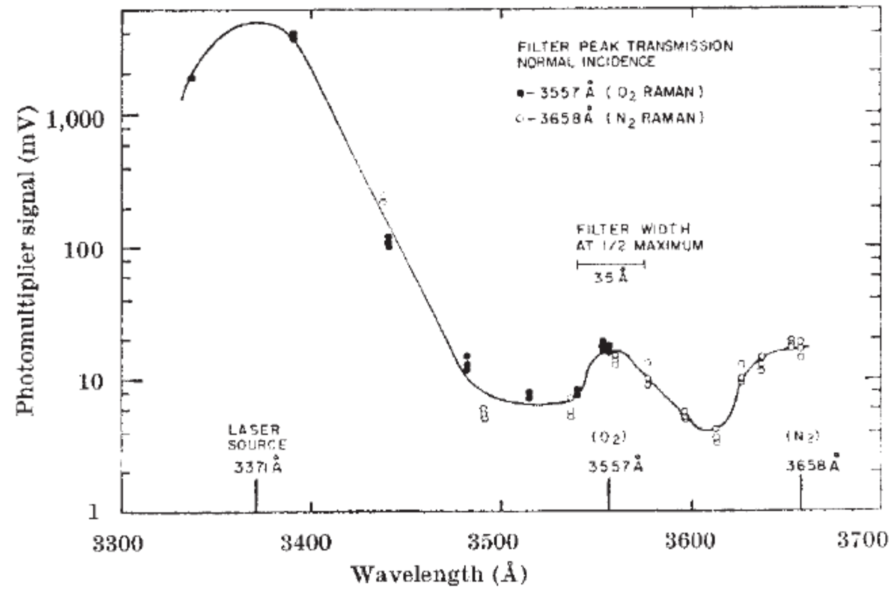
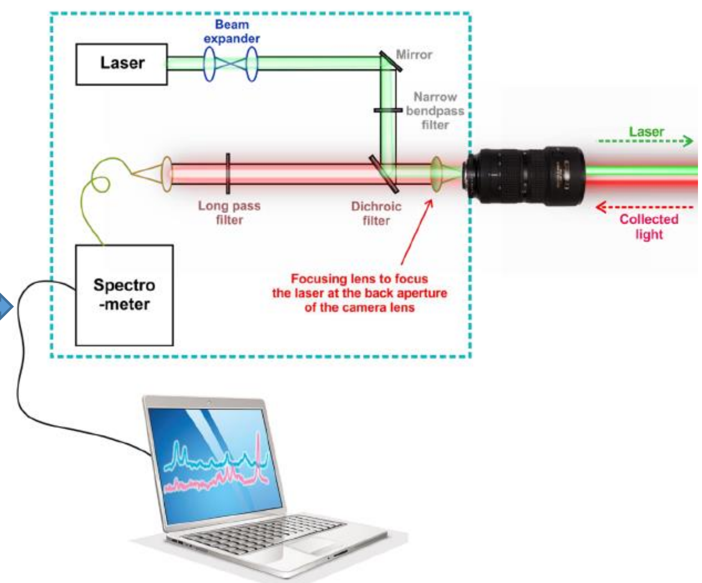


Fig. 2. Photomultiplier signal from atmospheric backscatter as a function of wavelength. Each data point represents a single measurement obtained with one laser pulse.

100 kW N_2 laser, range of 1.2 km data in microS

Current set-up



H. Heard. *Nature*, 16, **1967**, 667.

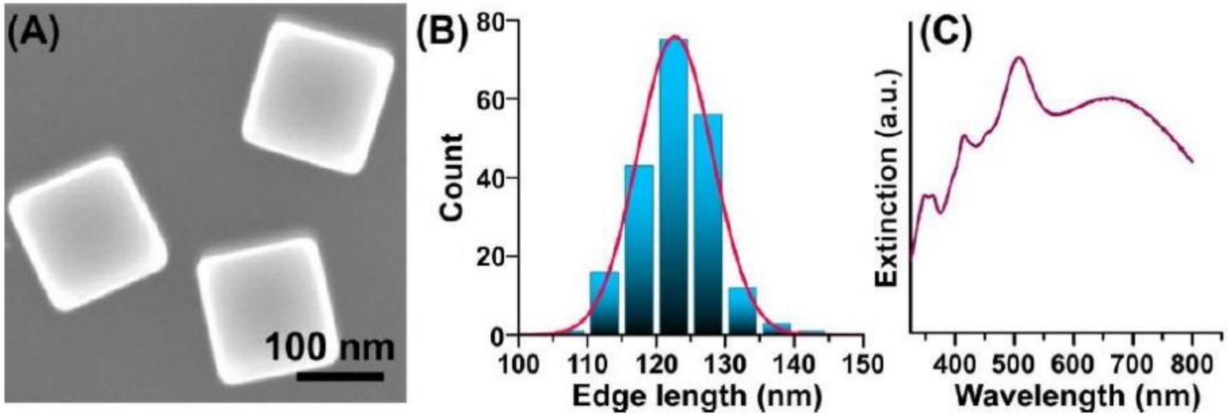
Experimental section

Synthesis and Purification of Silver Nanocubes

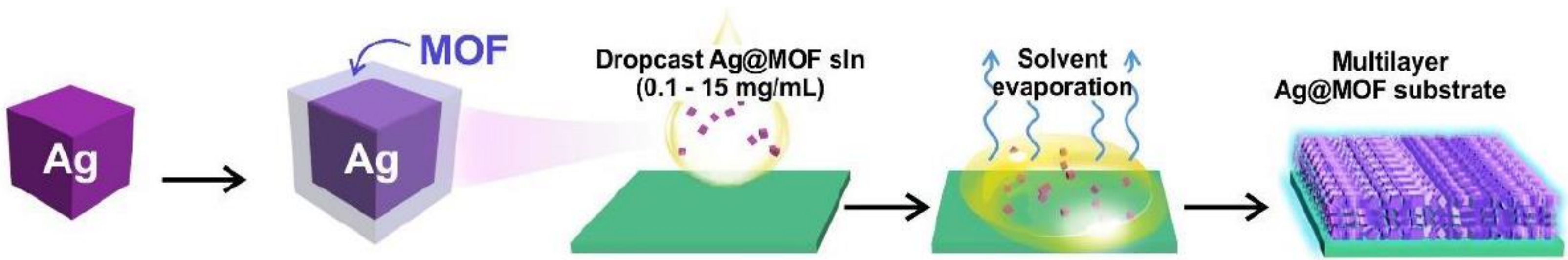
20 mL of 1,5-pentanediol in a 100 mL round bottomed flask was heated to 190 °C for 10 min. A 250 µL portion of poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s, while 500 µL silver nitrate precursor was injected every minute using a quick addition. The addition process continued until the greenish coloration of the reaction mixture faded off. Further purified by multiple centrifugation steps and filtration.

Synthesis of Ag@ZIF Core−Shell

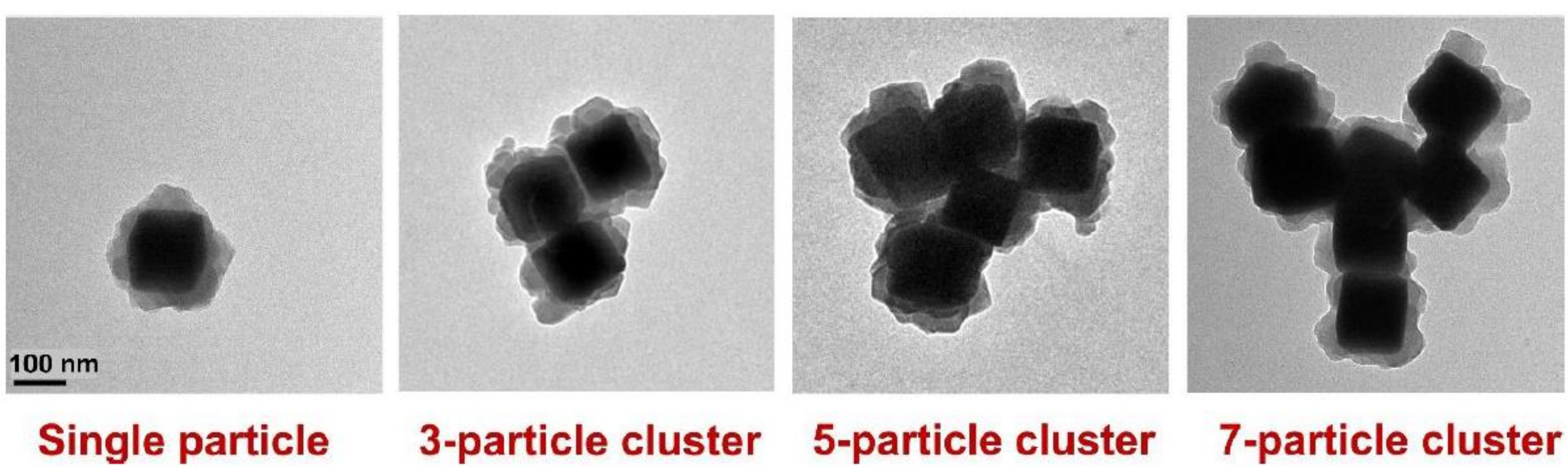
A 250 µL portion of **$Zn(NO_3)_2$** (25 mM) was added to a vial of 1.3 mL of **methanol** and stirred at 500 rpm for 5 min. A 250 µL portion of **methanolic 2-methylimidazole** (50 mM) was then added, followed by the immediate addition of 200 µL of **Ag nanocubes solution** (4.7 mg/mL, Ag nanocubes can be functionalized with 4-MBT to have 4-MBT probe internal standard or HCl treated to remove surface groups). The mixture was stirred for another 90 min at 500 rpm. Excess reagents were removed by centrifugation, and the core−shell nanocubes were then washed twice with methanol and then finally redispersed in methanol.

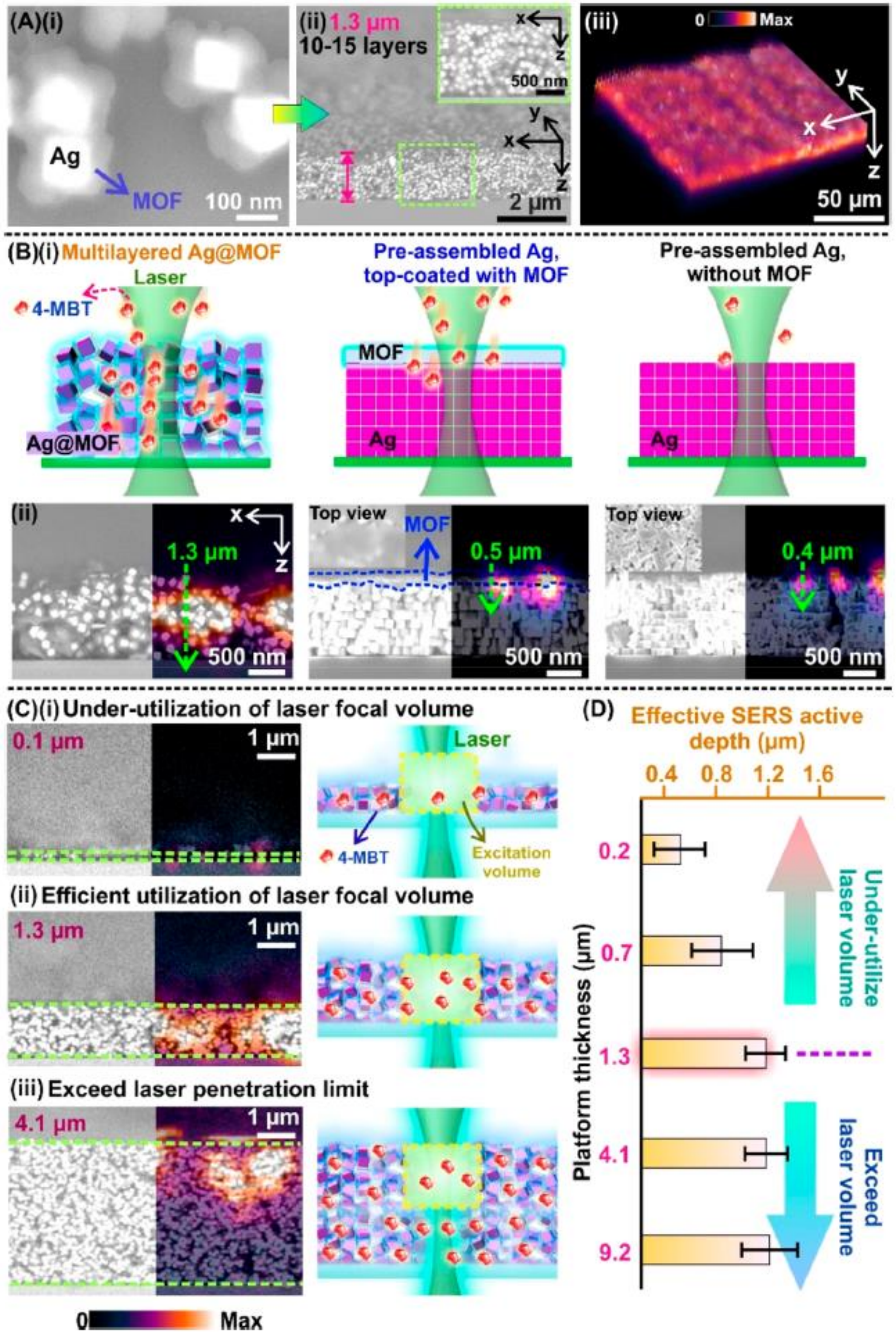


(A) SEM image of as-synthesized Ag nanocubes and (B) its size distribution (121 ± 5 nm). (C) Extinction spectrum of colloidal Ag nanocubes.

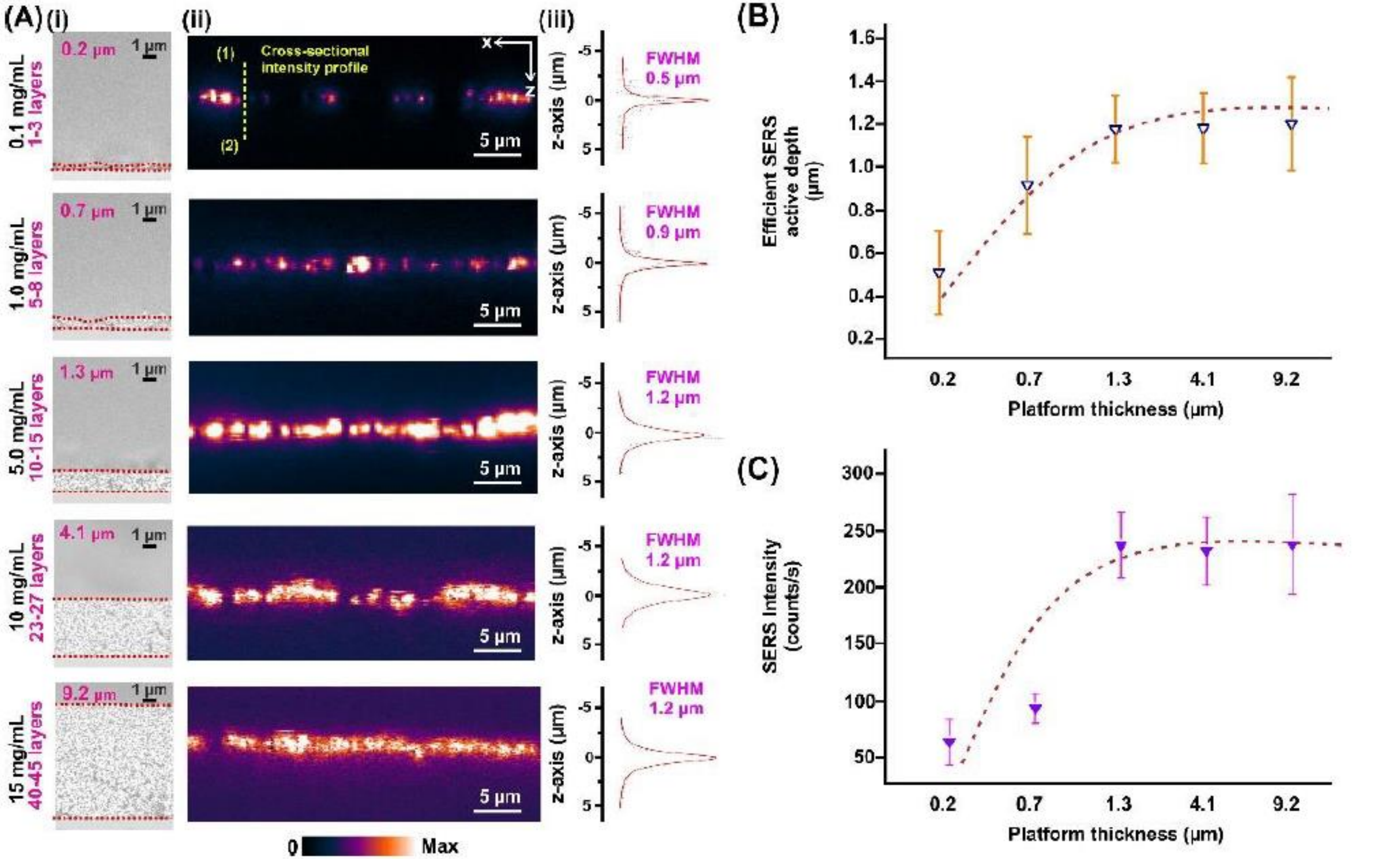


Multilayer substrate fabrication protocol.

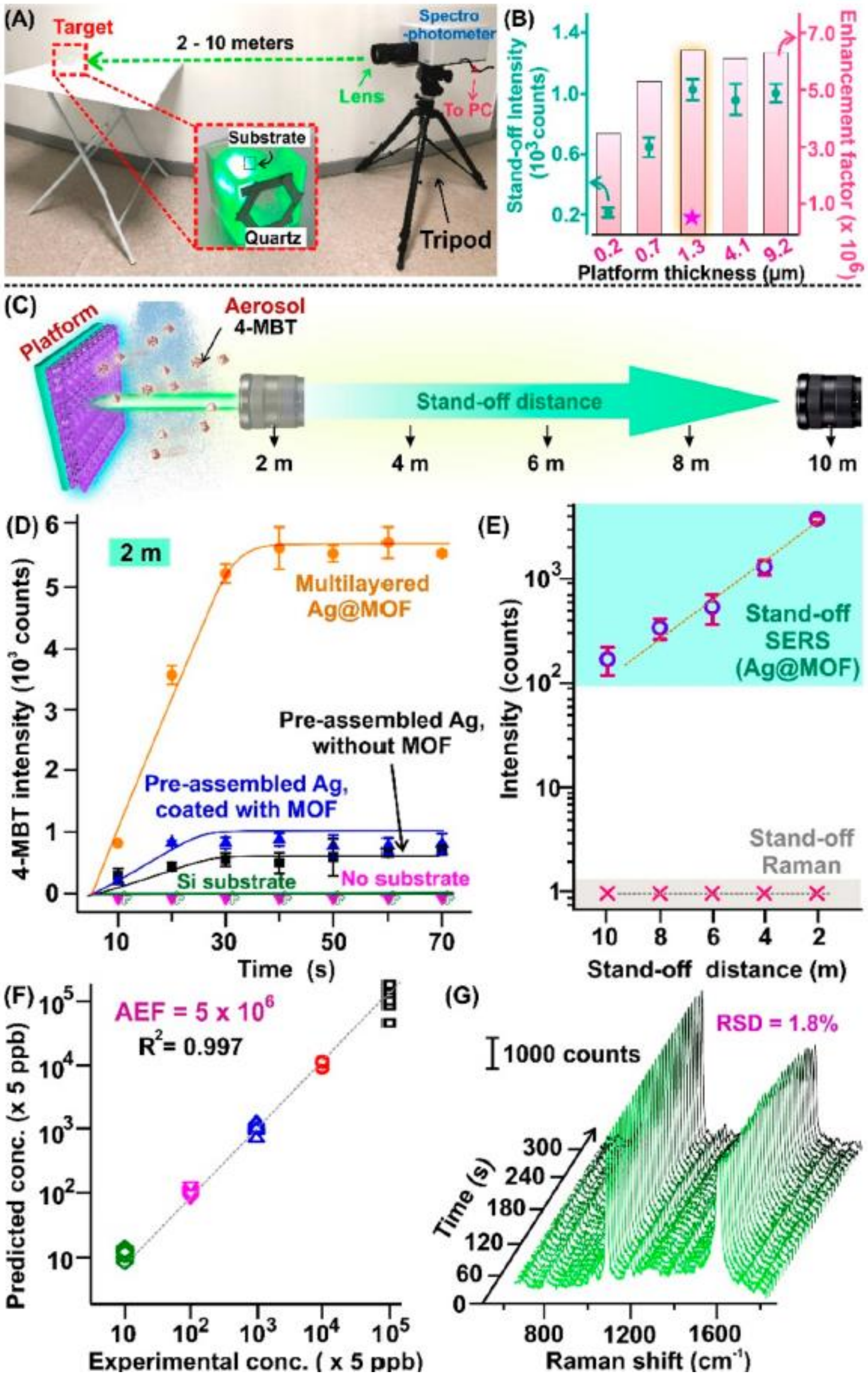




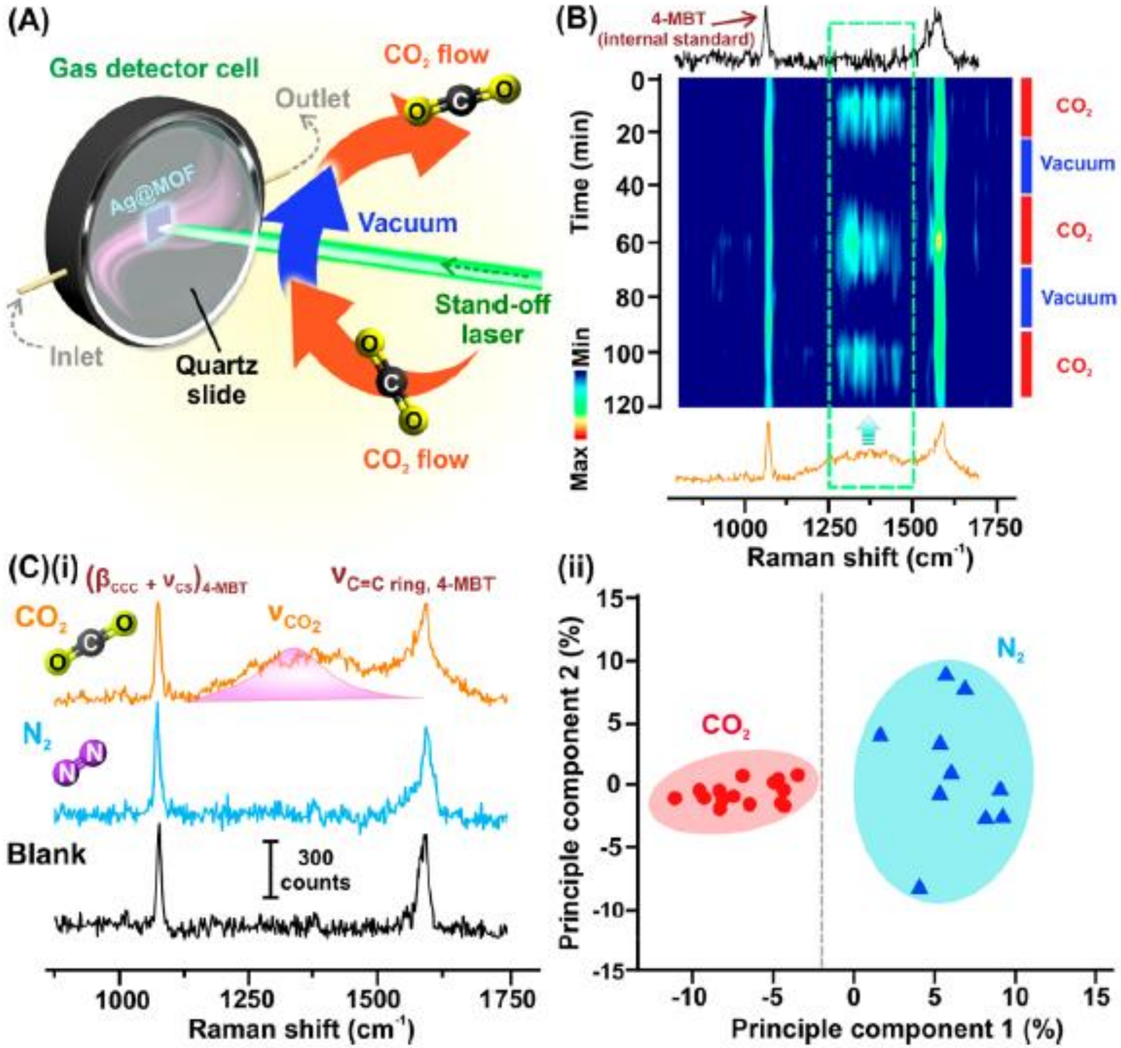
3D MOF-SERS platform. (A) (i) SEM image showing Ag@MOF particles, (ii) cross-sectional SEM image showing the side view of multilayered Ag@MOF platform, and (iii) 3D x−y−z SERS image of a segment of the platform (imaged with 20× objective lens). (B) (i) Schemes and (ii) cross-sectional SEM images showing the structure and how airborne molecules are absorbed and detected in different platform configurations. Half of the images in (ii) are overlapped with x−z SERS hyperspectral images (imaged with 100× objective lens) showing the penetration of gaseous 4-MBT into the platform (Ag in the platforms has no 4-MBT surface groups prior to exposure). (C) (Left) SEM images overlapped with x−z SERS images (imaged with 100× objective lens) of Ag@MOF platforms with increasing thickness and (right) schemes showing the hotspot and analyte density within the fixed laser focal volume where platforms of different thicknesses are used. (D) Effective SERS active depth and stand-off intensity (at 2 m) of 4-MBT's SERS band at 1077 cm^{-1} obtained from platforms with thickness ranging from 0.2−9.2 µm (using Ag pre-functionalized with 4-MBT).



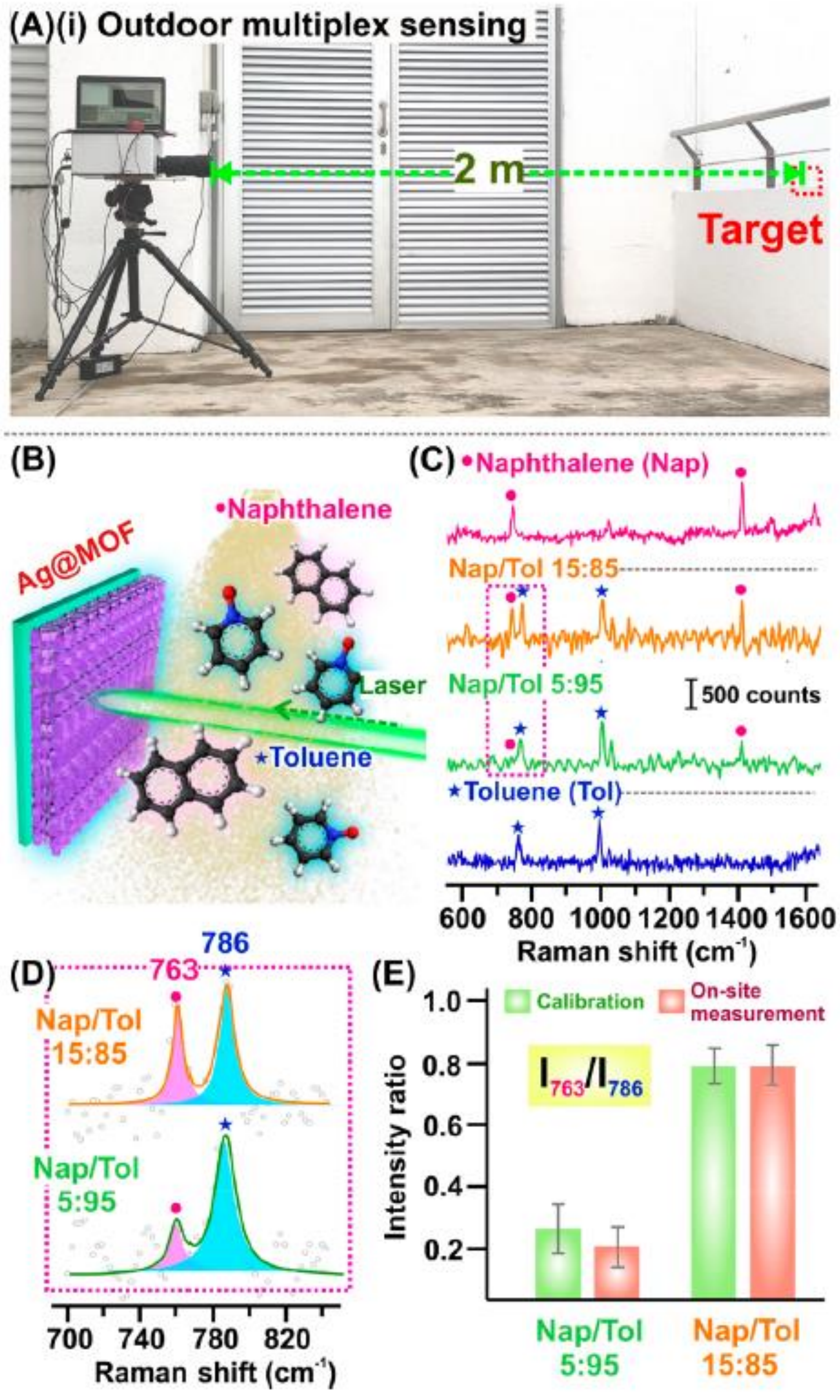
(A)(i) Cross-sectional SEM images, (ii) x-z SERS imaging of the multilayer Ag@MOF substrates of different thickness (Ag surface is modified with probe molecule 4-MBT), and (iii) their respective cross-sectional profile tracing 4-MBT 1077 cm-1 signal from region (1) to (2). (B) The full-width half-maximum of the intensity profiles, showing the efficient SERS-active thickness and (C) SERS intensity of different multilayer platforms



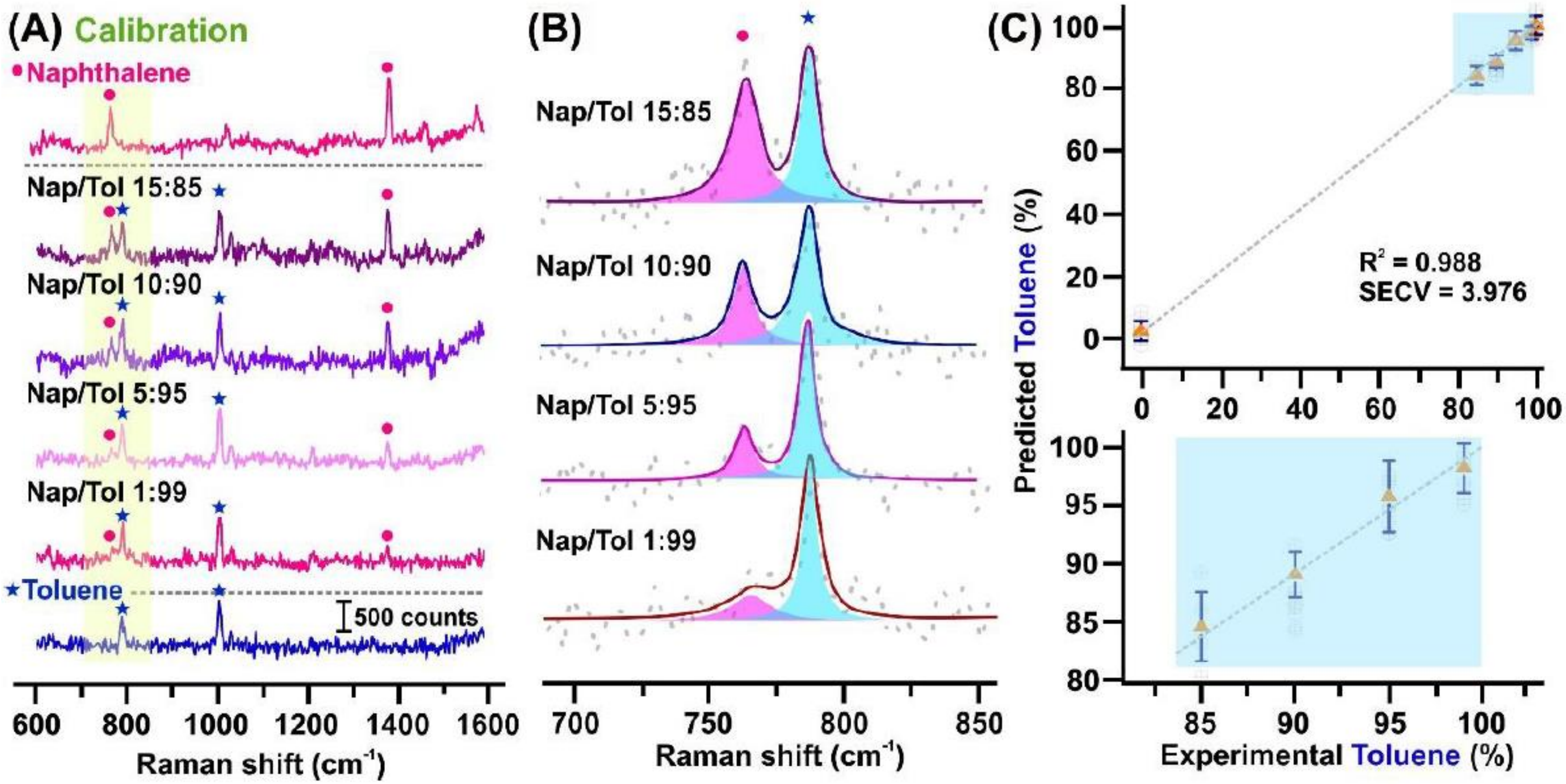
Stand-off SERS using 3D MOF-SERS platform. (A) Set-up of our stand-off SERS system. (B) Stand-off intensity (at 2 m) of 4-MBT's 1077 cm^{-1} obtained from platforms of thickness ranging from 0.2–9.2 µm (with Ag pre-functionalized with 4-MBT). (C) Scheme showing the stand-off SERS detection of aerosolized 4-MBT (500 ppm, Ag in the platforms has no 4-MBT surface groups). (D) Real-time 4-MBT intensity obtained in the stand-off SERS detection using different platforms. (E) 4-MBT intensities obtained at distances from 2 to 10 m using our Ag@ MOF SERS platform and normal Raman detection. (F) Partial least-squares calibration graph of different 4-MBT airborne concentrations detected using our stand-off SERS system (at 2 m). (G) Consistent real-time stand-off SERS spectra of 4-MBT recorded on Ag@MOF substrate for a continuous period of 300 s after the substrate has reached saturation.



Remote SERS-based gas detector. (A) Scheme showing remote tracking of CO_2 in real time for several cycles using multilayered Ag@ MOFplatform. (B) Time-resolved SERS intensity profile of 1360 cm^{-1} band, showing the absorption and detection of CO_2 in several cycles. (C) (i) Spectroscopic observation of CO_2 vibrational modes (shown with respect to internal standard peak of 4-MBT grafted on the Ag particle) in the detection of CO_2, which is not observed in the control experiments with N_2 flow and no gas (blank), (ii) Principle component analysis (PCA) score plot of stand-off SERS spectra observed in the presence of CO_2 or N_2.



Outdoor remote sensing of airborne polycyclic aromatic hydrocarbon (PAH) mixture. (A) (i) Outdoor stand-off detection set-up. (B) Scheme showing the stand-off detection of aerosolized toluene and naphthalene. (C) Stand-off multiplex spectra obtained in outdoor condition with natural light, for Nap/Tol 5:95 and 15:85 mixture, with reference to individual naphthalene and toluene SERS spectra. (D) Spectral analysis of characteristic signals of the analytes within the dotted region in (C). (E) Comparison of Nap/Tol signal intensity ratio between calibration spectra and outdoor spectra, using 763 and 786 cm^{-1} signals.



Calibration of multiplex (poly)aromatic hydrocarbon detection (indoor) (A) Stand-off multiplex SERS spectra obtained with just toluene (Tol), naphthalene (Nap) and Nap/Tol mixture at different composition for calibration (performed indoor, within 100 µL of Tol aerosol, accounting for 7000 pm Tol and 97-1700 ppm of Nap). (B) Spectrum deconvolution of the yellow-highlighted area in (A), showing the relative ratio between Nap 763 cm^{-1} and Tol 786 cm^{-1} signals at different composition. (C) Calibrated PLS prediction model constructed from the SERS spectra of various Nap/Tol composition from 0 to 100% (with a blue-highlighted magnification of Nap/Tol 85 to 99% region).

Conclusion

- Real-time stand-off SERS detection of airborne molecules by integrating stand-off Raman with a 3D Ag@MOF platform possessing micron-scale hotspot volume and high molecule sorbing ability was achieved.

- Stand-off SERS system enables rapid quantitative detection of aerosolized chemicals with parts per billion (ppb) detection limit at a remote distance of 2−10 m.

- Ability to rapidly track chemical changes in atmospheric content when CO2 gas is exposed to the platform in repeated cycles.

- 8-fold lower laser power (≤55 mW) than other common stand-off Raman techniques with ultrahigh laser power of >400 mW

Thank you