Electronic Supplementary Information (ESI) for Chemical Communications

Supplementary Information

Atmospheric microplasma-functionalized 3D microfluidic strips within dense carbon nanotube arrays confine Au nanodots for SERS sensing

Samuel Yick, Zhao Jun Han and Kostya (Ken) Ostrikov

Table of Contents

1. Experimental Details

Growth of vertically aligned carbon nanotubes (VA-CNTs)

VA-CNTs were synthesized *via* a thermal chemical vapor deposition (TCVD) process. Briefly, a silicon wafer with a 500 nm thick oxide layer was cleaned by bath sonication in acetone and isopropyl alcohol. The wafer was then washed with deionized water and baked at 110 °C for 5 minutes. A 10 nm buffer layer of alumina was deposited by reactive sputtering of an Al target in the Ar/O_2 gas mixture. The catalyst layer was then formed by sputtering 1.8 nm thick iron layer onto the alumina-coated wafer. The catalyst containing Si wafer was cut into $1x1cm^2$ pieces and inserted into the thermal furnace (MTI, OTF-1200X with a quartz tube 50 mm in diameter) and heated to 700°C in 35 min under an 800 sccm flow of argon gas. Upon reaching the desired temperature, acetylene and hydrogen were introduced at a rate of 56 and 240 sccm, respectively. The growth of VA-CNTs lasted for 10 minutes before both the H_2 and C_2H_2 gases were terminated. The samples were finally cooled to room temperature in Ar flow.

Plasma modification of VA-CNTs

To modify the VA-CNTs, a home-made microplasma jet was employed, which generated plasma using a 355 kHz radio-frequency (RF) power supply at 29 W (see the setup in Fig. S2). The discharge occurred within a syringe where the anode and cathode was separated by 1 cm. Helium at atmospheric pressure was used as the working gas. The gap between the nozzle of the microplasma jet and the VA-CNTs was 0.5 cm. The samples were scanned at a rate of 2 cm/min for 30 seconds to delineate the microfluidic strip. The nozzle of the syringe has a diameter of 1 mm.[S1]

Decoration of the Au nanodots

A 120-μL droplet of the aqueous solution containing colloidal Au NDs stabilised by tannic acid (0.05 mg/mL with a size distribution of 13-15 nm; purchased from PlasmaChem GmbH) was dispersed onto the plasma-modified VA-CNTs and left to dry overnight. 4-aminothiophenol solution (4-ATP; Sigma-Aldrich) was prepared by dissolving the substance into ethanol at a concentration of 10 mM. The Au ND-decorated VA-CNTs were then immersed in the 4-ATP solution for four days. Finally, the samples were washed in deionized water and dried overnight.

Sample Characterization

The microstructure of VA-CNTs was investigated by a field-emission scanning electron microscopy (FE-SEM; Zeiss Auriga) operated at an electron acceleration voltage of 20 kV and a working distance of 4.5 mm. The transmission electron microscope (TEM) samples were prepared by dispersing the as-grown nanotubes into ethanol with 30 min ultrasonication. The nanotube-containing solution was then dropped onto holey-carbon coated copper grids and dried in air. TEM micrographs were obtained using the Philips CM120 system with an electron beam energy of 120 keV. The optical micrograph was obtained by the Olympus BH2 microscope with a 100x objective lens. XPS measurements were taken using the PHI Specs Sage 150 system, where the Mg Kα (at 1253.6 eV) line was used as the excitation source. The Raman spectra were collected by Renishaw *InVia* confocal Raman microscope system with a 50× objective lens. Samples were excited with 633 nm laser at power of ~ 1.5 mW and a spot diameter of ~ 1 μm^2.

2. TEM of the VA-CNTs

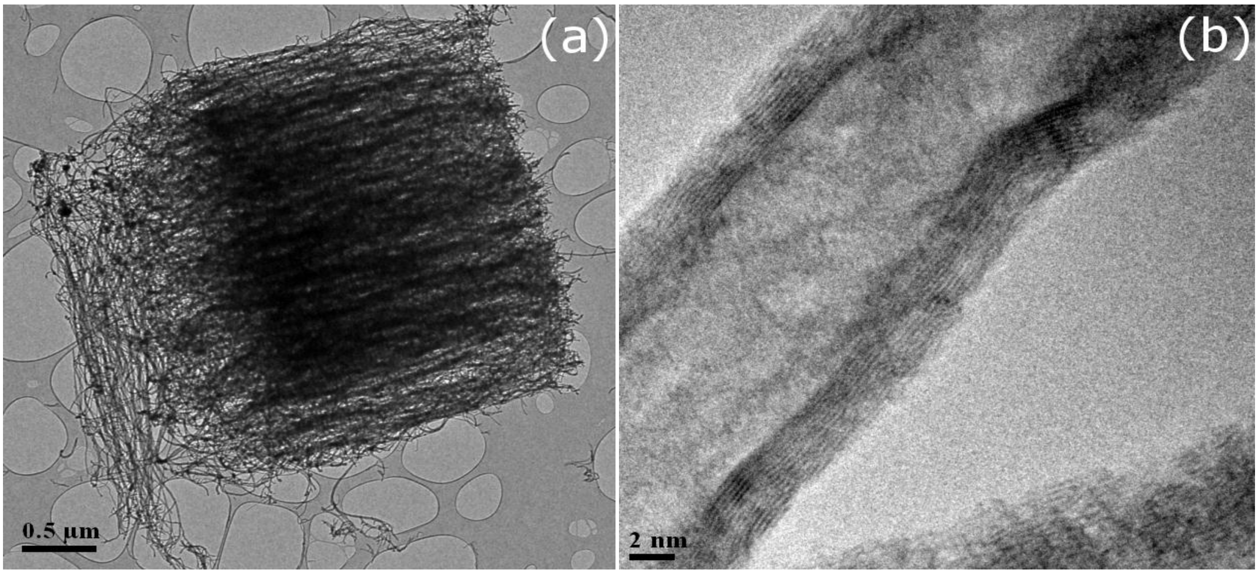

Fig. S1 TEM images of (a) a section of the VA-CNTs and (b) an individual CNT.

3. Schematics of the APMPJ

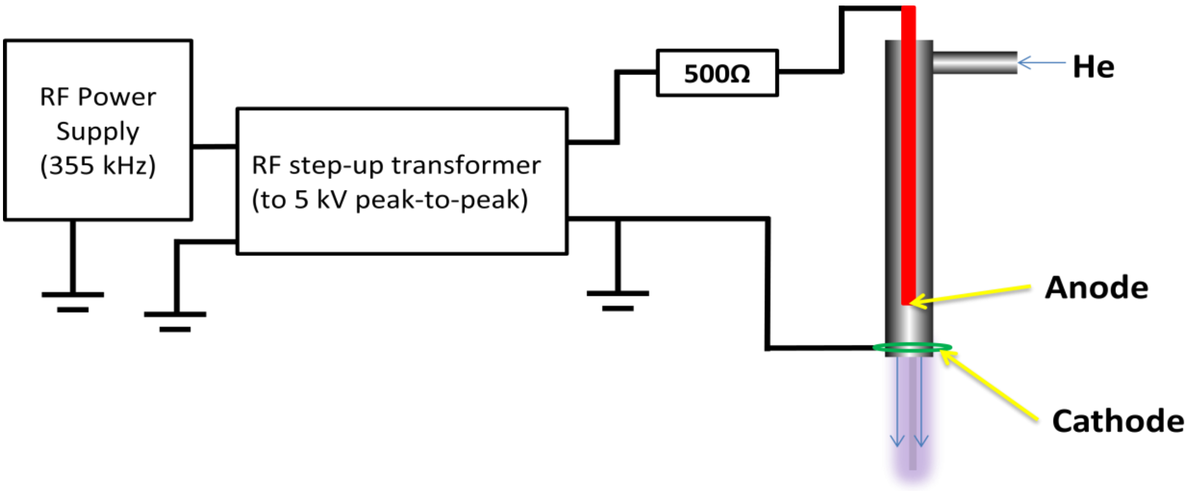

Fig. S2 Schematic of the cold APMPJ. The system consists of a low voltage 350 kHz radio-frequency (RF) power supply with an integrated matching circuit, a step-up transformer, and a current limiting resistor. The maximum output of the power supply system was 5 kV peak-to-peak. The discharge occurred within a syringe where the anode and cathode was separated by 1 cm. Helium was used as the working gas for the discharge.

4. XPS spectra of the treated VA-CNTs

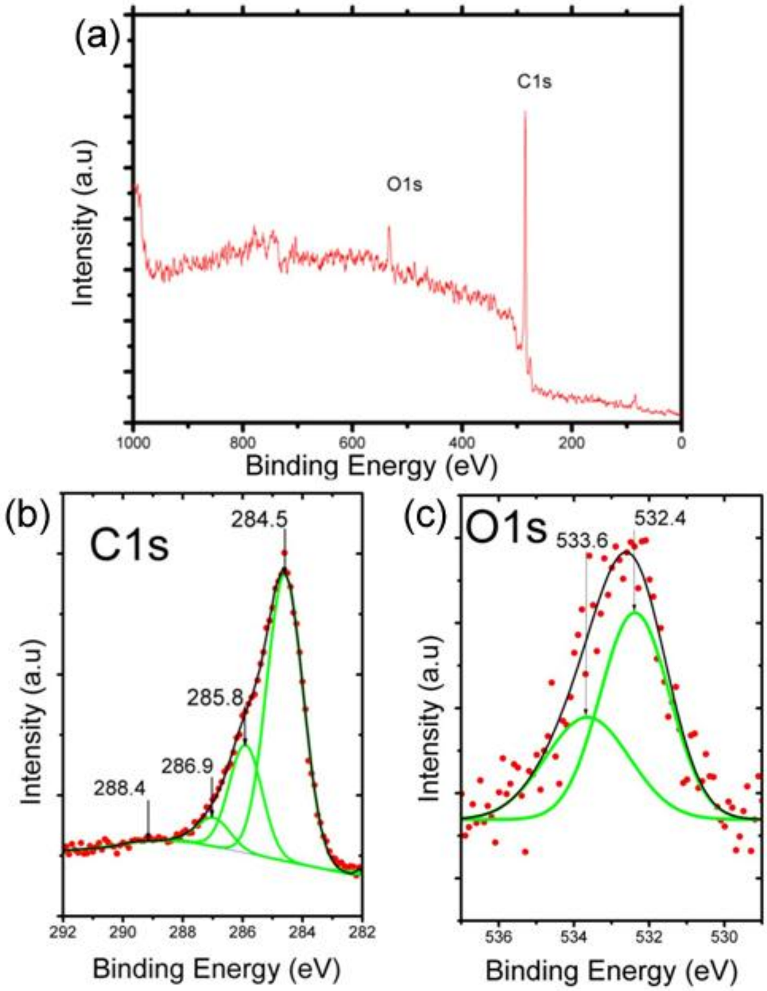

Fig. S3 XPS spectra of (a) survey, (b) C *1s* and (c) O *1s* of the APMPJ-treated VA-CNTs. Four peaks at binding energies of 284.5, 285.8, 286.9 and 288.4 eV are observed in (b), corresponding to the carbon atoms in the sp^2, sp^3, C-O and O-C=O bonding configurations, respectively.[S2] Two peaks at 532.4 and 533.6 eV in (c) correspond to the oxygen atoms in the O-C=O and -OH bonding states, respectively.[S3]

5. Raman Spectra of the pristine and plasma treated VA-CNTs

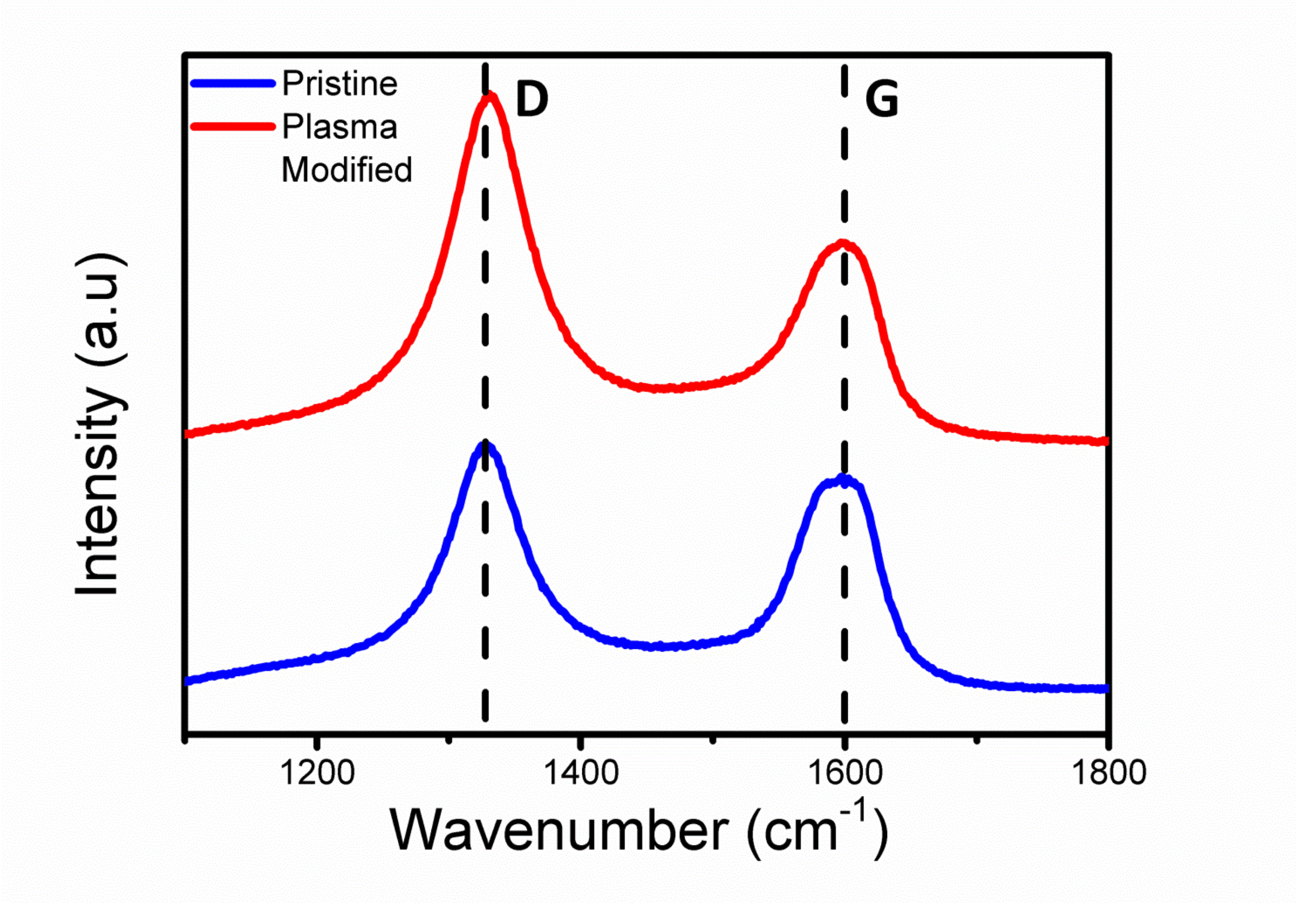

Fig. S4 Raman spectra of the VA-CNTs within and outside the plasma-modified regions, corresponding to areas IV and I in Fig. 2a in the main text, respectively. We observed two prominent peaks in the Raman spectra, the D-band at ~1325 cm^{-1} and the G-band at ~1600 cm^{-1}, which stemmed from the defects and ordered graphitic structures, respectively.[S4]

6. Image of the plasma-generated microfluidic strip

Fig. S5 Using the APMPJ treatment, a thin strip could be created on the surface of the CNT arrays. This microfluidic strip allowed the control of a small volume of liquid at the microscale with high precision. Shown above is an example of the aqueous solution containing Au nanodots dropped onto the microfluidic strip. It was found that the solution was confined within the plasma-generated microfluidic strip.

7. Cross-sectional SEM of the decorated VA-CNTs

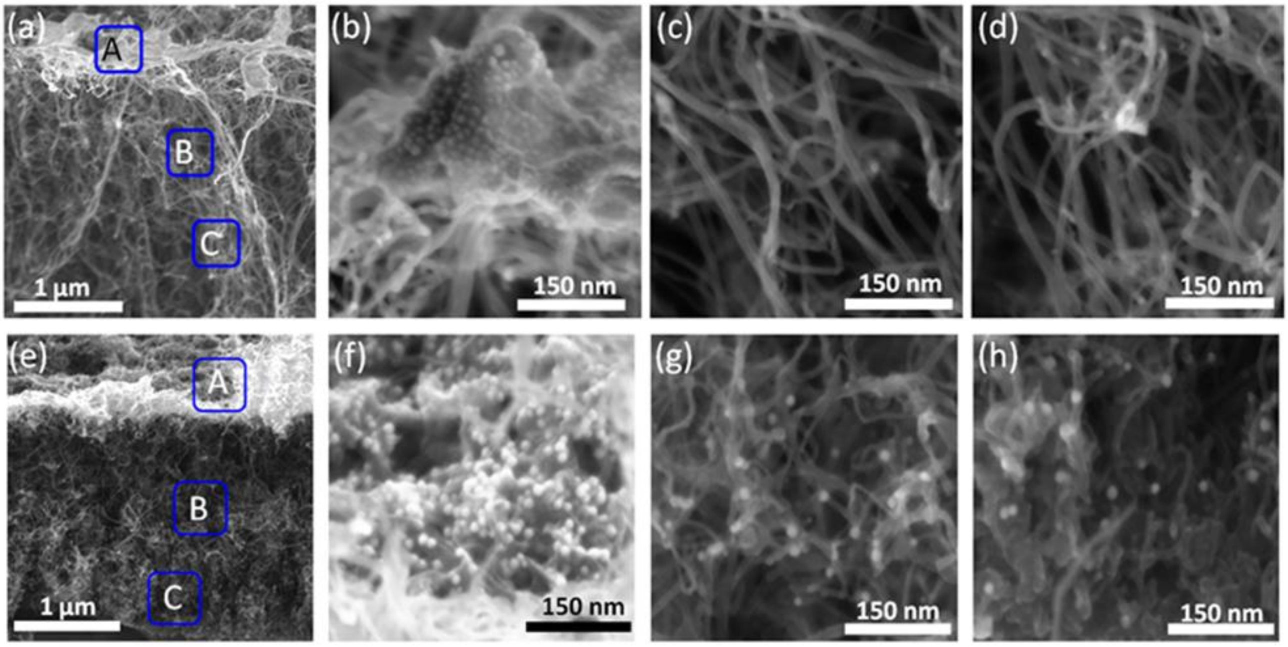

Fig. S6 (a) Cross-sectional SEM images of Au NDs deposited on the pristine CNT arrays. (b-d) High-resolution SEM images taken from squares A-C in (a), respectively. (e) Cross-sectional SEM images of Au NDs deposited on the APMPJ-treated CNT arrays. (f-h) High-resolution SEM images taken from squares A-C in (e), respectively.

References

[S1] W. Yan, Z. J. Han, B. T. Phung and K. Ostrikov, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2637.

[S2] H. Ago, T. Kugler, F. Cacialli, W. R. Salaneck, M. S. P. Shaffer, A. H. Windle and R. H. Friend, *J, Phys. Chem. C*, 1999, **103**, 8116-8121.

[S3] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis and C. Galiotis, *Carbon*, 2008, **46**, 833.

[S4] M. S. Dresselhaus, G. Dresselhaus, R. Saito and A. Jorio, *Phys. Rep.*, 2005, **409**, 47.