

Electronic Supplementary Information (ESI)

Nanographene oxide-TiO₂ photonic films as plasmon-free substrates for surface-enhanced Raman scattering

Dimitrios Papadakis,^a Angeliki Diamantopoulou,^a Petros-Andreas Pantazopoulos,^a Dimitrios Palles,^b Elias Sakellis,^c Nikos Boukos,^c Nikolaos Stefanou^a and Vlassis Likodimos^{*a}

^a Section of Solid State Physics, Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, 15784, Greece. E-mail: vlikodimos@phys.uoa.gr

^b Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece

^c Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", 15341 Agia Paraskevi, Athens, Greece

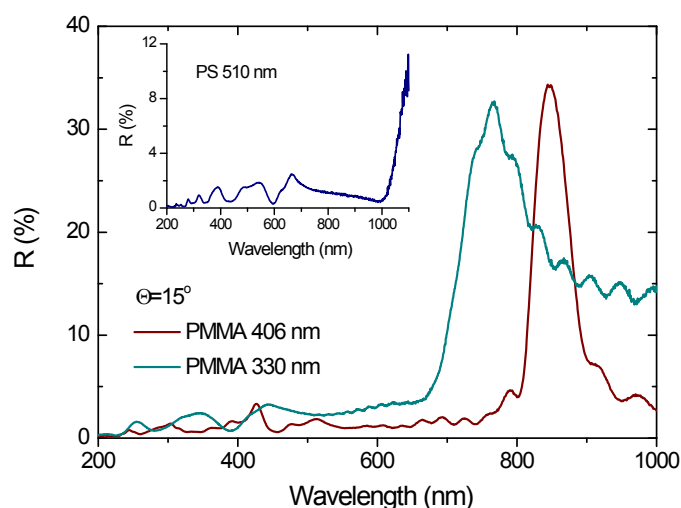


Fig. S1 Specular reflectance spectra for the colloidal opal templates from 330 and 406 nm PMMA spheres. The inset shows the corresponding R% spectrum for the PS 510 nm opal film, where the stop band is expected at 1200 nm.

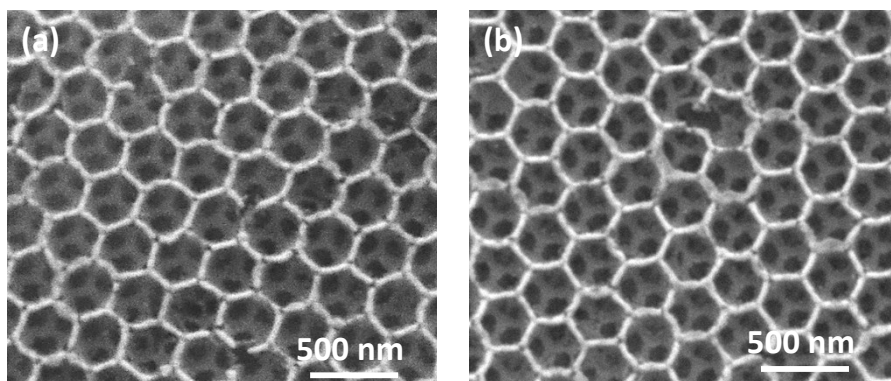


Fig. S2 SEM images for the PC406 inverse opals (a) before and (b) after surface functionalization with GO nanosheets.

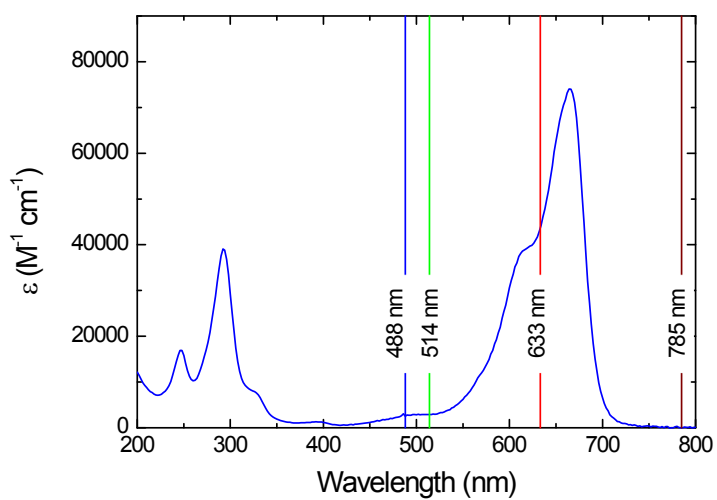


Fig. S3 The molar extinction coefficient of MB determined from 10^{-5} M aqueous solution using a 1 cm path length quartz micro cell. Solid lines depict the different laser excitation wavelengths applied in the present work.

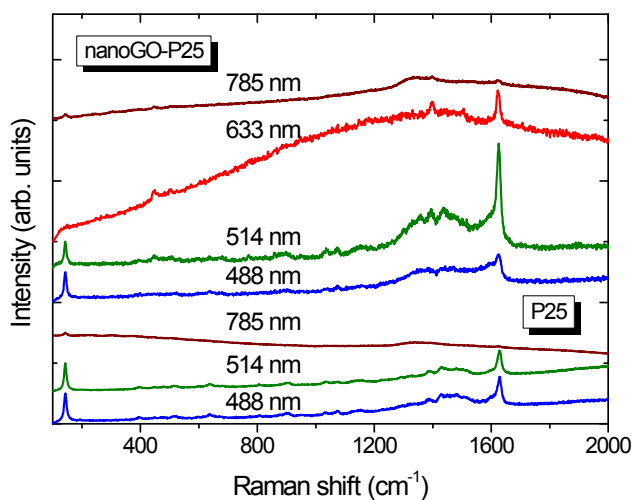


Fig. S4 Raman spectra of 3×10^{-5} M MB adsorbed on pristine and nanoGO-functionalized P25 films at different laser excitations.

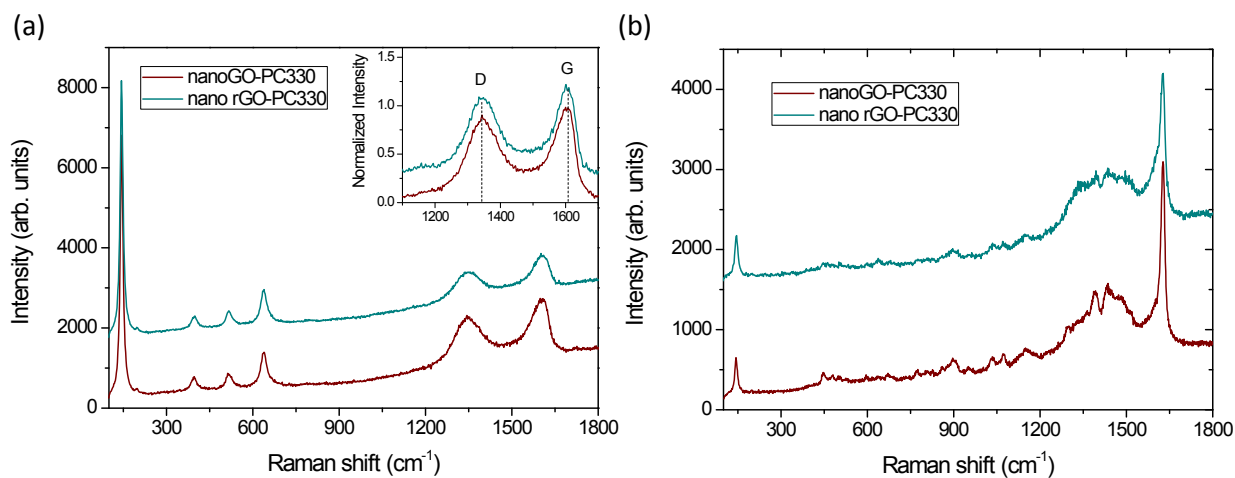


Fig. S5 (a) Raman spectra of nanoGO-PC330 before and after thermal reduction at 200 °C under He flow at 514 nm. (b) MB SERS spectra on nanoGO-PC330 and nano rGO-PC330 films after adsorption using 10^{-4} M MB aqueous solution.

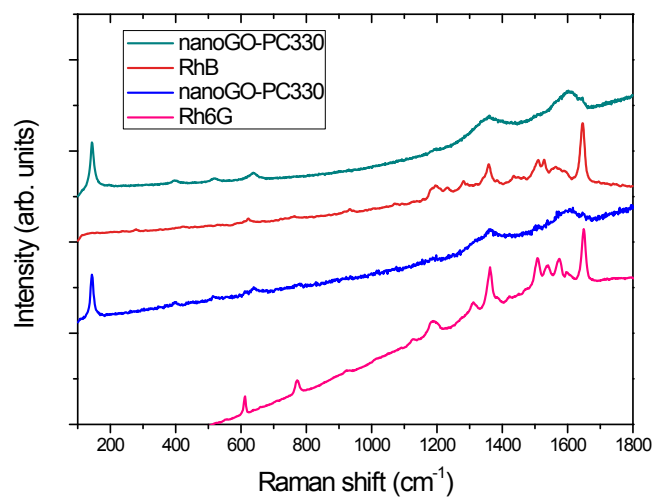


Fig. S6 Raman spectra of RhB and Rh6G dyes adsorbed from 10^{-5} M aqueous solutions on nanoGO-PC330 substrates compared to the corresponding solid powders at 488 and 514 nm, respectively.

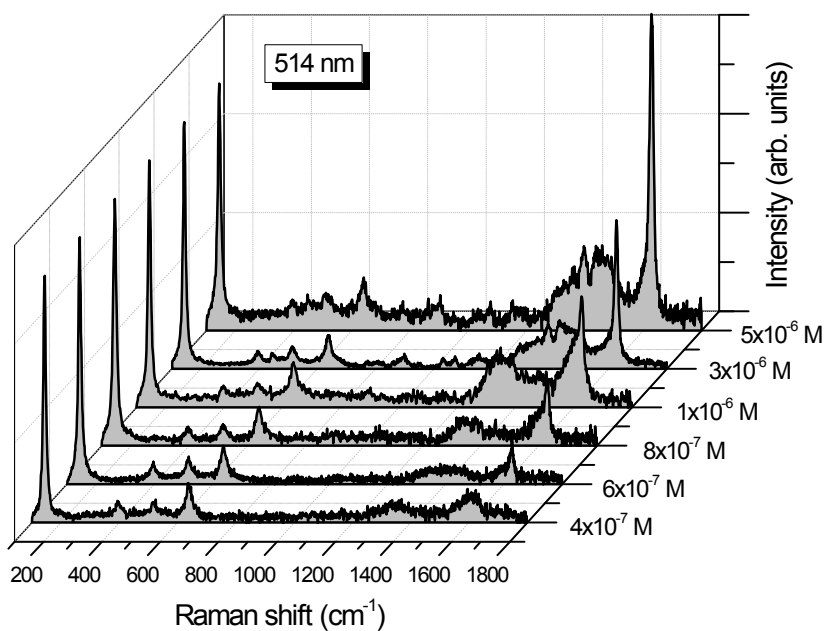


Fig. S7 MB SERS spectra on nanoGO-PC330 after adsorption in MB aqueous solutions of decreasing concentrations at 514 nm.

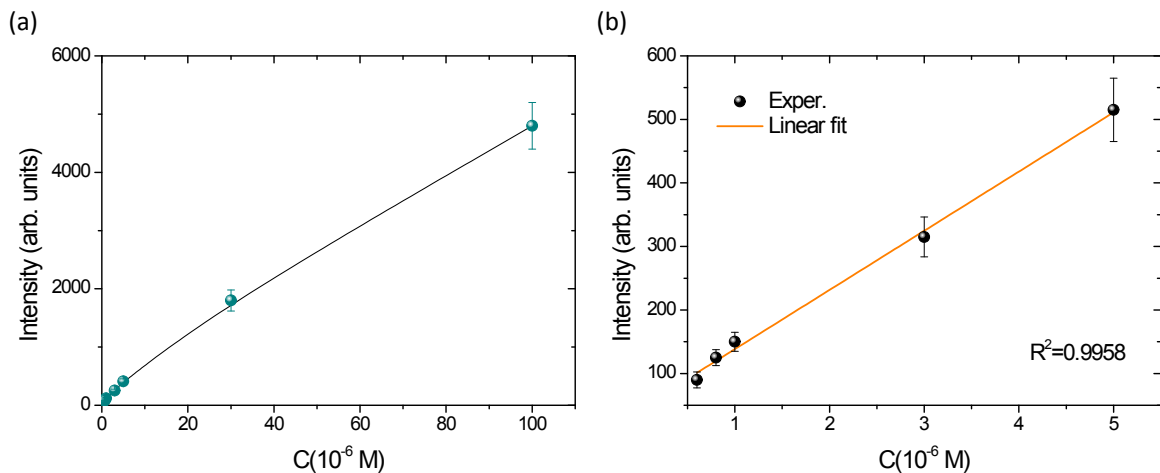


Fig. S8 Concentration dependence of the 1628 cm⁻¹ SERS intensity on nanoGO-PC330 (a) over a broad MB concentration range (10⁻⁴ to 6×10⁻⁷ M) and (b) in the mM range along with the corresponding linear fit. The solid line in (a) serves as a guide to the eye.

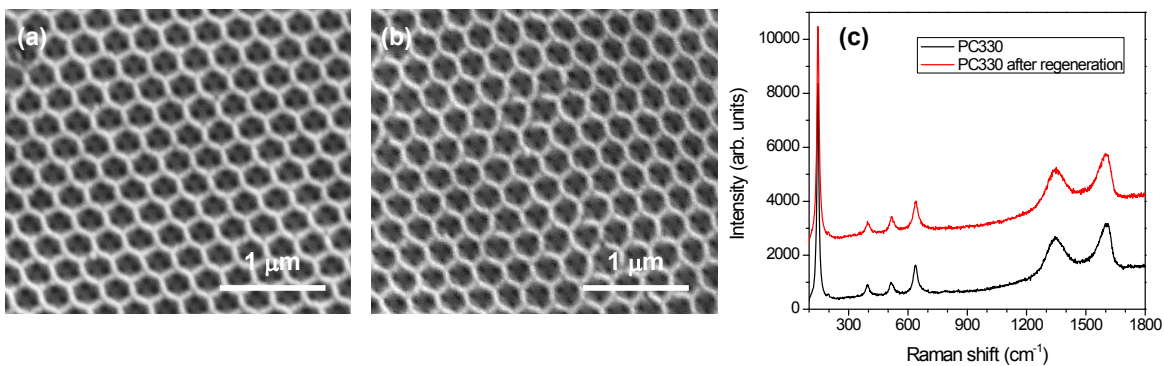


Fig. S9 SEM images of nanoGO-PC330 substrate (a) before and (b) after the 2nd regeneration cycle. (c) The corresponding Raman spectra of the SERS substrates at 514 nm.

Table S1 Raman band frequencies of MB adsorbed on pristine PC330 and nanoGO-PC330 inverse opals compared to those of solid MB powder at 514 nm.

MB powder	PC330	nanoGO-PC330	Assignment [1], [2], [3]
1627 (vs)	1629 (vs)	1630 (vs)	$\nu(\text{C-C})_{\text{ring}}$
1543 (vw)	1546 (vw)	1546 (vw)	$\nu_{\text{asym}}(\text{C-C-C})$
1473 (s)	1482 (s)	1474 (s)	$\nu(\text{C-C})/\delta(\text{C-N-C})$
1440 (m)	1430 (s)	1443 (s)	$\nu(\text{C-C-C})/\nu_{\text{as}}(\text{C-N-C})$
1397 (s)	1394 (s)	1398 (s)	$\nu(\text{C-C})/\nu(\text{NH-C})$
1366 (m)	1366 (vw)	1366 (m)	$\nu(\text{C-N-C})/\delta(\text{C-C-C})$
1303 (m)	1302 (w)	1302 (m)	$\delta(\text{C-N-C})/\beta(\text{C-H})$
1186 (w)	1186 (vw)	1186 (w)	$w(\text{C-H})$
1157 (w)	1157 (vw)	1157 (w)	$\delta(\text{C-C-C})/w(\text{NH})/\beta(\text{CH})$
1076 (m)	1076 (w)	1076 (m)	$w(\text{NH})/w(\text{CH})$
1039 (w)	1037 (m)	1037 (m)	$\nu(\text{C-S-C})/\delta(\text{C-C-C})$
953 (m)	953 (w)	953 (m)	$\nu(\text{C-S-C})$
900 (vw)	900 (m)	900 (m)	
862 (m)	862 (vw)	862 (w)	
828 (vw)	828 (w)	828 (w)	
-	809 (w)	808 (w)	$\delta(\text{C-N-C})/\delta(\text{C-S-C})/\delta(\text{C-C-C})$
772 (m)	771 (w)	772 (m)	
670 (w)	670 (vw)	671 (w)	$\gamma(\text{C-H})$
595 (vw)	597 (w)	597 (w)	$\delta(\text{C-S-C})/\delta(\text{C-C-C})$
502 (w)	502 (w)	502 (vw)	$\delta(\text{C-N-C})$ dimer
-	479 (vw)	479 (vw)	$\beta(\text{C-H})$ monomer
448 (m)	448 (m)	448 (m)	$\delta(\text{C-N-C})$ dimer

Abbreviations: s, strong; m, medium; w, weak; vw, very weak; ν , stretching; β , in-plane bending; γ , out-of-plane bending; δ , skeletal deformation; w, wagging

References

- 1 K. Hutchinson, R. E. Hester, W. J. Albery and A. R. Hillman, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2053-2071.
- 2 W. Xu, M. Aydin, S. Zakia and D. L. Akins, *J. Phys. Chem. B* 2004, **108**, 5588-5593.
- 3 G. N. Xiao and S. Q. Man, *Chem. Phys. Lett.*, 2007, **447**, 305–309.