Supplementary Information

**Oxidized Nitinol Substrate for Interference Enhanced Raman Scattering of Monolayer Graphene**

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Figure S1. Optical Micrograph of graphene on Substrates. (a) T-0 (b) T-30 (c) T-44 (d) T-54 (e) T-65 (f) T-79 and (g) T-139. All micrographs taken with LEICA software. The substrates exhibit colors due to interference of light.
**Figure S2. Raman Maps:** The uniformity of Raman intensity enhancement has been shown. (a,b) T-0 and T-44 at 514 nm laser, respectively (c,d) T-0 and T-54 at 633 nm laser, respectively. Both T-44 and T-54 exhibiting significant enhancement as compare to T-0 and enhancement is almost uniform in selected area of Raman mapping. The scale bar in Figure (a-d) is 5 μm.
Figure S3. SERS of methylene blue (MB). (a) Raman spectrum of $10^{-4}$M MB aqueous solution adsorbed on SiO$_2$/Si substrate. (b) Raman spectrum of $10^{-4}$M MB adsorbed on T-54 substrate. The peak at 1623 cm$^{-1}$, assigned to C-C stretching vibration, considered as characteristic of MB. A substantial Raman enhancement can be observed of MB on T-54.
Multi Reflection Model (MRM)

Multi reflection model has been used to explain the contrast between graphene and SiO$_2$ previously,$^{1,2}$ which explains the interference and multireflection of light through multilayer structure. Later on, few studies carried on to implement this model to describe quantitatively the dependency of Raman intensity of graphene on the thickness of SiO$_2$.$^{3-5}$ We utilized similar model to explain our results, the variation of intensity of Raman bands of graphene with TiO$_2$ thickness.

In MRM for Raman scattering, we consider the absorption of incident light and scattering processes separately, as shown in Figure S4 (a,b). Hence, when incident laser passed through surfaces, light absorbed partially by graphene layer and subsequently by TiO$_2$ layer. During this course, light also underwent through multireflection in graphene and TiO$_2$ layer as shown in Figure S4(a).

All the absorptions during incidence of light can be summed as $F_a$, expressed as

$$F_a = t_1 \left[ \frac{1 + r_2 r_3 e^{-2i\beta_2}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}} \right]$$

Where, $t_1 = 2n_0/(n_1 + n_0)$ is the Fresnel transmittance and $r_1 = (n_0 - n_1)/(n_0 + n_1)$, $r_2 = (n_1 - n_2)/(n_1 + n_2)$, $r_3 = (n_2 - n_3)/(n_2 + n_3)$ are the Fresnel reflection coefficients for the three interfaces between air (refractive index $n_0$), graphene (refractive index $n_1$), TiO$_2$ (refractive index $n_2$) and NiTi (refractive index $n_3$). The term $\beta$ accounts for the phase change of laser light while passing through the particular medium and given by $\beta_{x,1,2} = 2\pi d_{x,1,2} n_{1,1,2}/\lambda$, where $d_1$ and $d_2$ are the thickness of graphene and TiO$_2$ layers, respectively, and $x$ is the depth in graphene from which we are getting all interactions. While $\lambda$ is excitation wavelength of laser.

Correspondingly, for the Raman scattering as a result of multireflection during scattering shown in Figure S4(b), can be represented by term $F_s$ and expressed as

$$F_s = t_1' \left[ \frac{1 + r_2 r_3 e^{-2i\beta_2}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}} \right]$$

Where,$t_1' = 2n_1/(n_1 + n_0)$ Fresnel Transmittance. Here we have taken the approximation of same wavelength of incident laser and Raman bands (scattering), as considered in other studies.$^{3,6}$

Now, as a result of multireflection/interference during absorption and scattering the overall enhancement factor $F$ can be written as$^4$
\[ F = N \int_0^{d_1} |F_a F_s|^2 \, dx \]

Where N is term obtained by calculation of enhancement factor F with consideration of free standing graphene. Figure S4(c) shows the calculated enhancement factor of monolayer graphene bands on TiO\textsubscript{2}/NiTi as a function of thickness of TiO\textsubscript{2} at 514 nm, 633 nm and 785 nm. The enhancement factor F is relative to the free standing graphene. The parameters used in this calculation are, thickness of monolayer graphene \(d_1 = 0.34\text{nm}\), \(n_0 = 1\), \(n_1 = 2.6-1.3i\), \(n_2 = 2.2\) and \(n_3 = 2.66-3.3i\) at 514 nm are the refractive indices of air, graphene, TiO\textsubscript{2} and NiTi, respectively.\textsuperscript{3,7}

**Figure S4. Multireflection Model Schematic.** The schematic of laser light multireflection and interference during transmission through monolayer graphene on TiO\textsubscript{2} capping layer substrate (a) absorption of incident light (b) Raman scattering process integrated with multireflection process (c) calculated enhancement factor of graphene bands as a function of TiO\textsubscript{2} thickness at 514 nm, 633 nm and 785 nm lasers.
References


