

Supporting Information

Stimulating Multiple SERS Mechanisms by a Nanofibrous 3-D Network Structure of Titanium Dioxide (TiO₂)

*Dmitry Maznichenko, † Krishnan Venkatakrishnan, † Bo Tan, ‡**

†Department of Mechanical and Industrial Engineering, Ryerson University, 350 Victoria St.,
Toronto, ON M5B 2K3, Canada

‡Dep. of Aerospace Eng., Ryerson University, 350 Victoria St., Toronto, ON M5B 2K3, Canada

Corresponding Author

*Email: tanbo@ryerson.ca, Tel: +1-416-979-5000 ext. 4879, Fax: +1-416-979-5056.

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S1. RAMAN ENHANCEMENT FACTOR CALCULATION

The Raman Enhancement Factor (EF) is typically determined with EM simulations by using generalized Mie theory (GMT)^{1,2} and Finite Difference Time Domain techniques such as 2D-FDTD³ and 3D-FDTD.^{4,5} However, these techniques are computationally limited to simple geometric systems such two-nanoparticle clusters of perfect spheres. In the present case, it is more appropriate to analyze the 3-D nanofibrous network structure experimentally. The following Raman EF equation is the most accepted in literature:⁶

$$EF_{SERS} = \frac{I_{SERS}/N_{surf}}{I_{ref}/N_{bulk}} \quad \text{Eq. S1}$$

I_{SERS} represents the Raman SERS intensity, I_{ref} represents the Raman intensity without the TiO₂ nanofibrous substrate, N_{bulk} represents the number of molecules present under the confocal volume and N_{surf} represents the number of molecules responsible for the SERS response. From Figure 7, $I_{SERS} = 6039$ and $I_{ref} = 113$ at 1623 cm⁻¹ (shifted from 1621 cm⁻¹). The 1621 cm⁻¹ wavenumber is the strongest CV vibrational mode which is used in such EF calculations.^{7,8} The following equation is used to calculate N_{bulk} :

$$N_{bulk} = \pi r^2 h c N_A \quad \text{Eq. S2}$$

In this case, r represents the Raman laser spot radius (1.5 μm), h represents half the Depth of Field (DOF) of the 50x magnified laser used in this study (10/2 μm), c represents the crystal violet (CV) applied concentration (8.1x10⁻³ M) and N_A is the Avogadro constant. Following Eq. S2, N_{bulk} is calculated to be 1.7x10⁸ molecules. To calculate N_{surf} , knowledge of the nanofibrous surface area and CV adsorption to rutile TiO₂ are necessary. Surface area is expected to be similar to electrospun TiO₂ nanowires as summarized by Table S1. From Table S1, the most conservative estimate of the most relevant architecture and phase is 2 m²/g.

Table S1. TiO₂ nanowires compared to the present study nanofibers.

Author	Architecture †	Size (nm)	Phase	BET* (m ² /g)
present study	ds nanofiber	82+/-68	rutile	ca. 2.0
(Alves et al. 2009) ⁹	dr	203+/-122	rutile	2.0
(Chuangchote et al. 2009) ¹⁰	cr	264+/-86	mostly rutile	56
(Wang et al. 2011) ¹¹	dr	250+/-50	R/A = 0.61-2.43	32+/-8
(Hristovski et al. 2008) ¹²	ds	65+/-35	anatase and rutile	126
(Doh et al. 2007) ¹³	ds	194+/-71	anatase	26
(Madhugiri et al. 2004) ¹⁴	ds	650+/-50	anatase	32
(Ray and Lalman 2011) ¹⁵	cs	39+/-7	anatase	259+/-23

† d, discontinuous; c, continuous; s, smooth; r, rough.

*Brunauer–Emmett–Teller surface area model.

To determine the actual surface area within the laser sampling volume, it is necessary to determine the mass of TiO₂ within that region. Similarity relationships are used since it is not practical to weigh cubic micrometer volumes. Firstly, the mass of a rutile crystal is determined that would fit within the Raman sampling volume (Eq. S3).

$$m_1 = \pi r^2 h \rho \quad \text{Eq. S3}$$

Rutile density ρ is 4.249 g/cm³.¹⁶ The new surface area SA₂ is then determined by using the BET surface area from Table S1. By geometric similarity, the effective rutile TiO₂ nanofiber mass that is within the Raman sampling volume is determined by Eq. S4.

$$m_2 = m_1 / \left(1 - \frac{SA_1 - SA_2}{2\pi r h} \right) \quad \text{Eq. S4}$$

Therefore, by using the mass result of Eq. S4 again with the BET surface area, the effective rutile TiO₂ nanofiber surface area within the Raman sampling volume is $SA_{\text{eff}} = 5.0 \times 10^{-11} \text{ m}^2$. For N_{surf} , it is also necessary to determine the adsorption concentration of the CV dye to rutile TiO₂. Table S2 summarizes the literature review for CV adsorption on TiO₂.

Table S2. CV to TiO₂ adsorption equilibrium from UV-vis spectrophotometer measurements.

Pertinence-Author	Interface, crystal or amorphous†	Adsorption (M)	Time (min)
present study	R, crystal	2.9×10^{-6}	ca. 1
(Hachem et al. 2001) ¹⁷	Degussa P25, R/A=0.429, crystal	2.9×10^{-6}	45 - 90
(Kanna et al. 2010) ¹⁸	Degussa P25, R/A=0.250, crystal	2.5×10^{-5}	30
(Dong et al. 2012) ¹⁹	Degussa P25, crystal	5.0×10^{-8}	15
(Senthilkumaar and Porkodi 2005) ²⁰	A, crystal	1.9×10^{-6}	60
(Senthilkumaar and Porkodi 2005) ²⁰	A, crystal	1.0×10^{-5}	60
(Kanna et al. 2010) ¹⁸	A, amorphous	1.0×10^{-4}	30

† R, rutile; A, anatase

Firstly, no CV dye adsorption on pure rutile data was found. In part, this has to do with the difficulty of synthesizing rutile. The most relevant studies used Degussa P25 that has a mix of both phases. Secondly, Senthilkumaar and Porkodi demonstrated that surface adsorption reduces significantly with increasing CV concentration (the concentration used in the present study was nearly 100 times greater). Thirdly, the SERS experiments were carried out immediately after CV

dye application, whereas adsorption equilibrium is expected to take at least 15 min (Table S2). Therefore, the most conservative estimate of surface adsorption is to use $c_{\text{ads}} = 2.9 \times 10^{-6}$ M. Eq. S5 represents the number of CV molecules adsorbed to the TiO₂ nanofibrous network.

$$N_{\text{surf}} = SA_{\text{eff}} \left(c_{\text{ads}} N_A \frac{1000 \text{ L}}{1 \text{ m}^3} \right)^{\frac{2}{3}} \quad \text{Eq. S5}$$

Substituting the variables and matching the parameter dimensions, $N_{\text{surf}} = 7.2 \times 10^3$ molecules. Finally, inserting all the values back into Eq. S1, the TiO₂ enhancement factor is calculated to be $EF_{\text{SERS}} = 1.3 \times 10^6$. At this point, it should be noted that there are many sources of error when applying Eq. S1 to determine the analytical Raman EF (Table S3).

Table S3. Sources of error when calculating the analytical Raman EF.

Easier to Standardize	Harder to Standardize
dye /wavenumber used for calculation	laser tweezers effect on local concentration
laser focusing accuracy and precision	adsorption factor
time for adsorption equilibrium	variations in surface area after dye application
anatase to rutile TiO ₂ ratio and crystallinity	effect of fluorescence
the exact concentration of the dye	

Table S3 suggests that it is challenging to calculate an exact experimental Raman enhancement factor. Nonetheless, even the most conservative estimate of the nanofibrous TiO₂ 3-D network implies an appreciable 10^6 order enhancement. This is already a major result given that only Ag and Au were previously thought to achieve such EM and charge transfer activity.

S2. COMPLETE CRYSTAL VIOLET DYE EXPERIMENTS

Raman spectroscopy is not currently a standardized method for molecular detection. The first step was therefore to determine the appropriate exposure time, power and edge filter settings.

Figure S1 demonstrates the importance of choosing a proper exposure time and power.

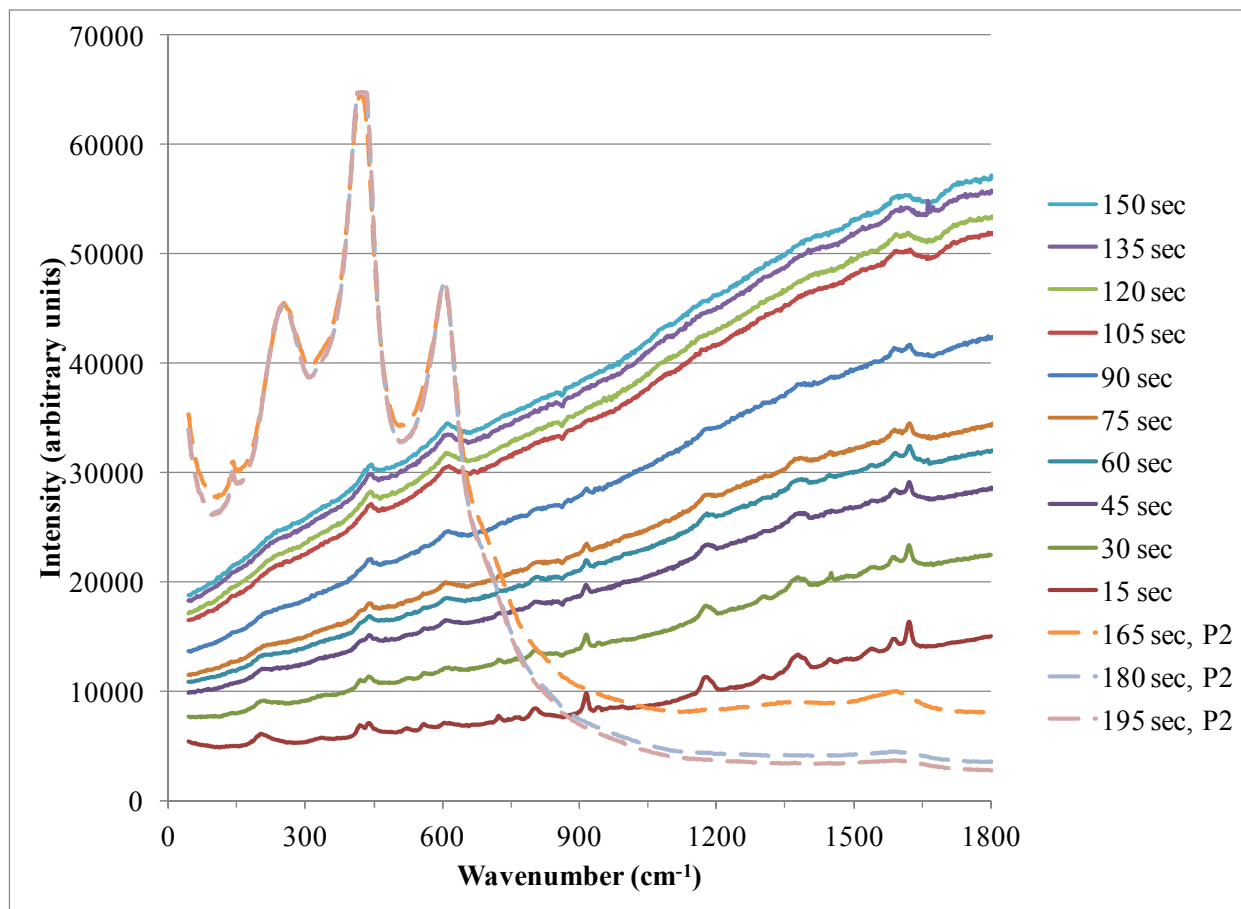


Figure S1. Degradation summary of the CV dye with continuous exposure when using the 26 MHz -15 msec TiO_2 substrate. P2 represents increased power from 1 mW to 79 mW by changing the laser filter attenuation.

At first, Figure S1 shows a fair response at 15 sec (i.e. 5 sec exposure time with a three time accumulation) from CV when applied over the nanofibrous TiO_2 3-D network. However, increased exposure time steadily degrades the CV solution. While this occurs, the overall Raman

intensity is increasing due to increasing fluorescence. When the power is increased at 165 sec, the rutile TiO_2 spectrum dominates the Raman response. Seeing the unprecedented intensity of these rutile peaks makes it important to also recognize that this procedure may have great potential for further enhancement of the TiO_2 nanofibrous network if the resultant substrate is used for subsequent molecular detection. Once the parameters were chosen, the TiO_2 substrates were tested for CV detection capacity. Figure S2 shows such experimentation.

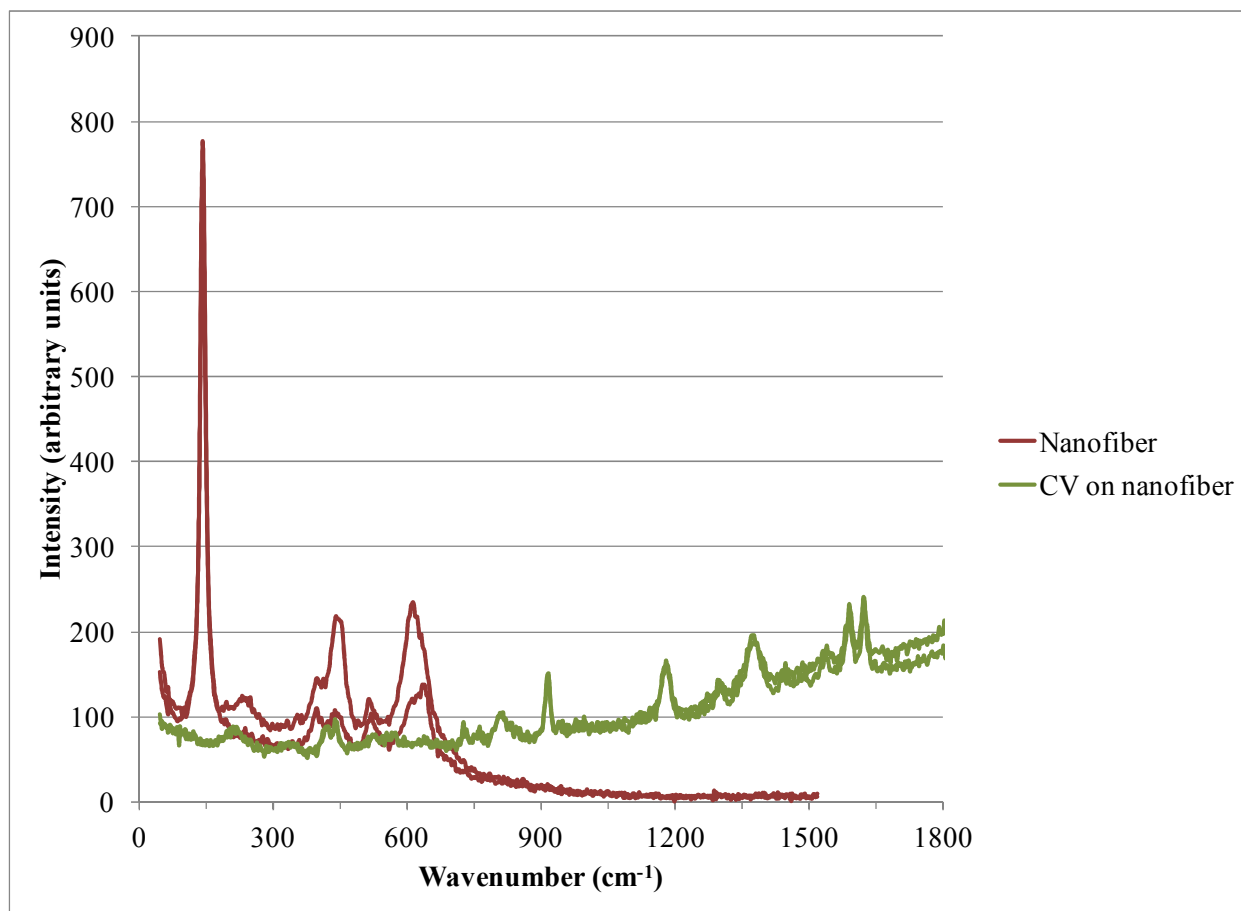


Figure S2. CV- TiO_2 experiments using the 8 MHz -15 msec substrate, four spectra are shown.

From Figure S2, there is no clear enhancement of the CV dye. In addition, the nanofiber rutile spectrum is not clearly defined which indicated the presence of impurities. This affect is more pronounced with Figure S3.

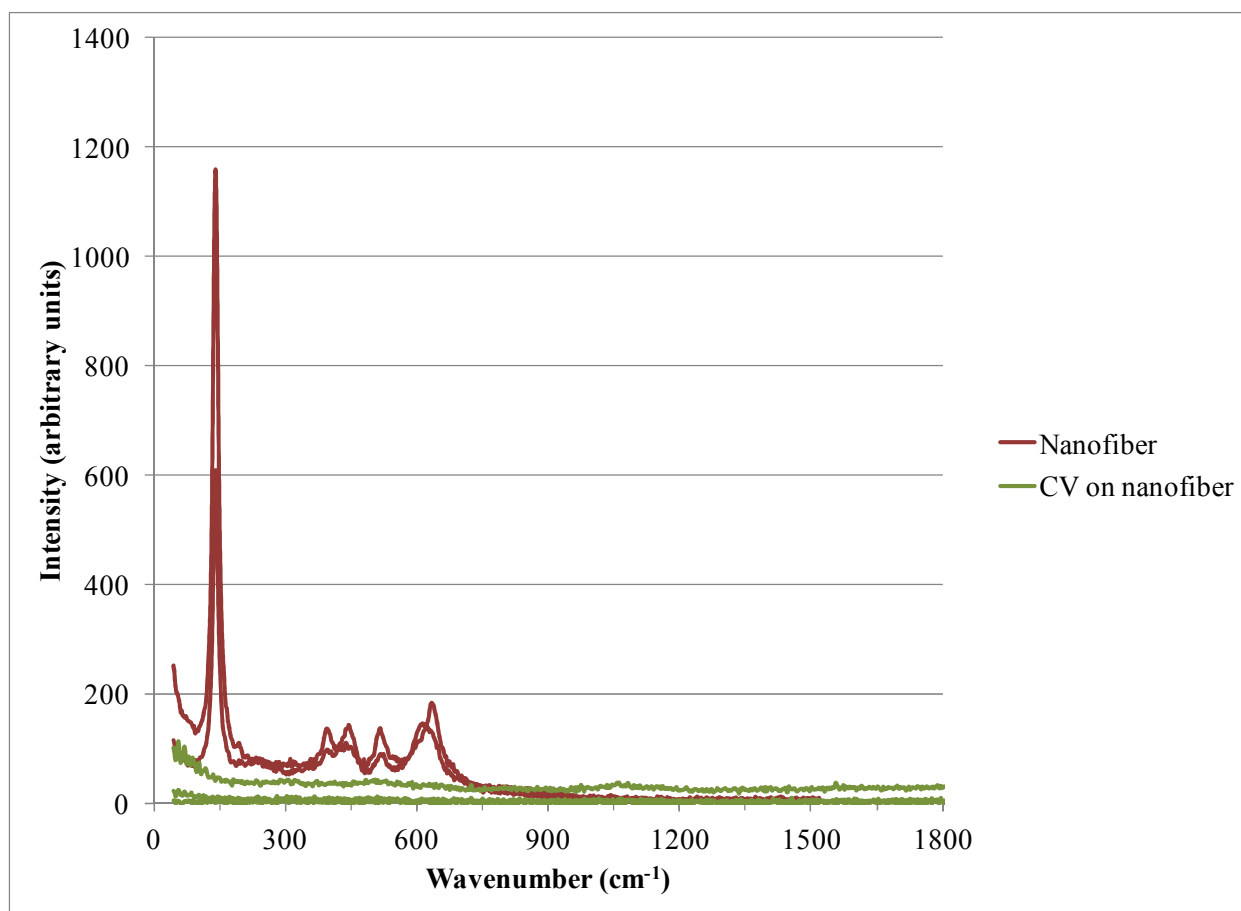


Figure S3. CV-TiO₂ experiments using the 13 MHz -15 msec substrate, four spectra are shown.

As shown by Figure S3, not only is there no enhancement of the CV dye after application, there is a total loss of Raman response. Firstly, the substrate is no longer pure rutile, as anatase wavenumbers begin to appear. Secondly, the stability of the 3-D network with the CV dye may be lower which could result in excessive aggregation and hence loss of any nanofibrous network advantages. The exact justification for such spectra degradation is still speculative and is subject for a thorough investigation in future research. Nonetheless, the majority of substrates did provide a clear Raman response. Figure S4 shows the typical experimental result by using the best Raman laser parameters.

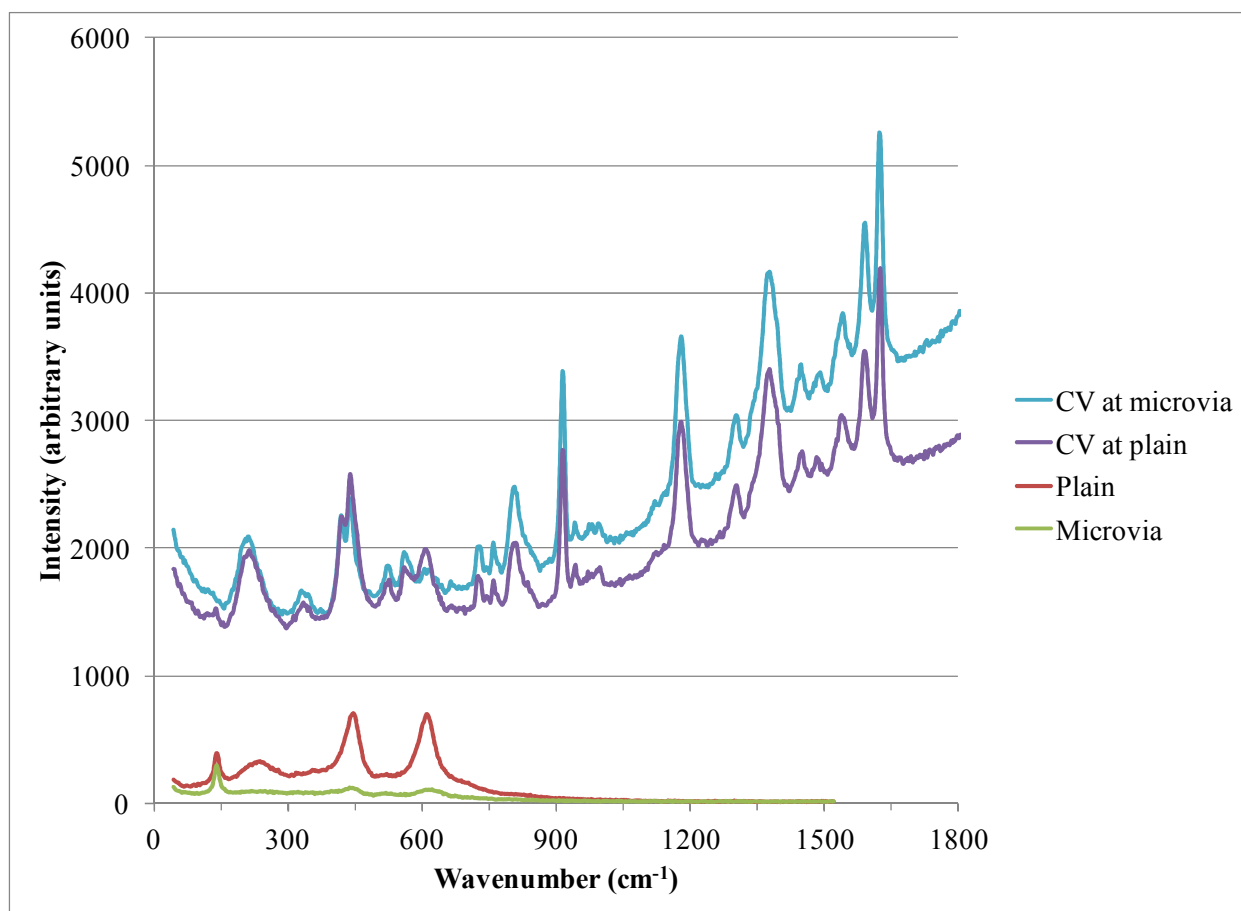


Figure S4. CV-TiO₂ experiments using the 8 MHz -1 msec substrate.

The Raman sample stage was robotically controlled with micrometer resolution. Together with the built in camera, it was possible to position the Raman laser beam over the microvias or the inter-microvia plains when visible (Figure 1). Firstly, Figure S4 demonstrates enhancement of the CV dye as typical CV intensity with the chosen parameters was on average 150 a.u.. Secondly, there is a noticeable drop in intensity of the TiO₂ substrate when the laser is positioned over the microvia. This is an expected result as the microvia depth can draw the laser out of focus. Nonetheless, the importance of nanofibers is demonstrated after applying the CV dye. Regardless of whether the laser is positioned over the microvias or in between, the intensity remains about the same. Therefore, the nanofibers act as a porous medium to support molecular detection away

from the surface. It is also possible to reduce the effect of microvias if desirable as shown by Figure S6 which will be presented later. The highest attained Raman enhancement of the CV dye is shown by Figure S5.

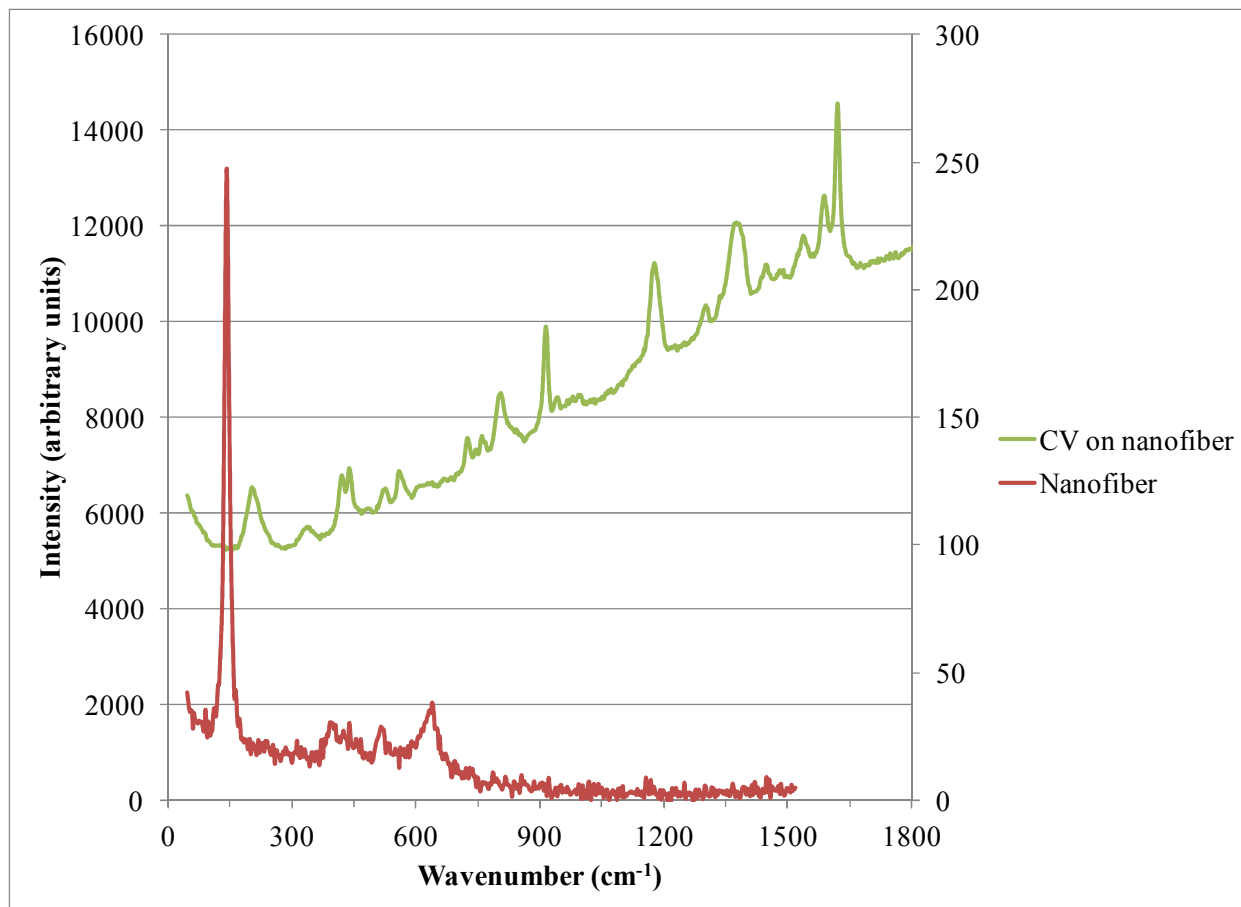


Figure S5. Highest observed enhancement of the CV dye when using the 8 MHz -20 msec TiO₂ substrate, Nanofiber spectra is on the secondary axis.

Following the calculation procedure of Supporting Information section S1, the calculated EF of Figure S5 is 3.1×10^6 . However, the rutile nanofiber spectrum once again shows impurities as was seen with Figure S2 and Figure S3. This is an interesting result as such behavior typically results in null spectrum response or at best no enhancement. We chose to present the most consistent enhancement data, as summarized by Figure S6 and Figure 7 in the main text.

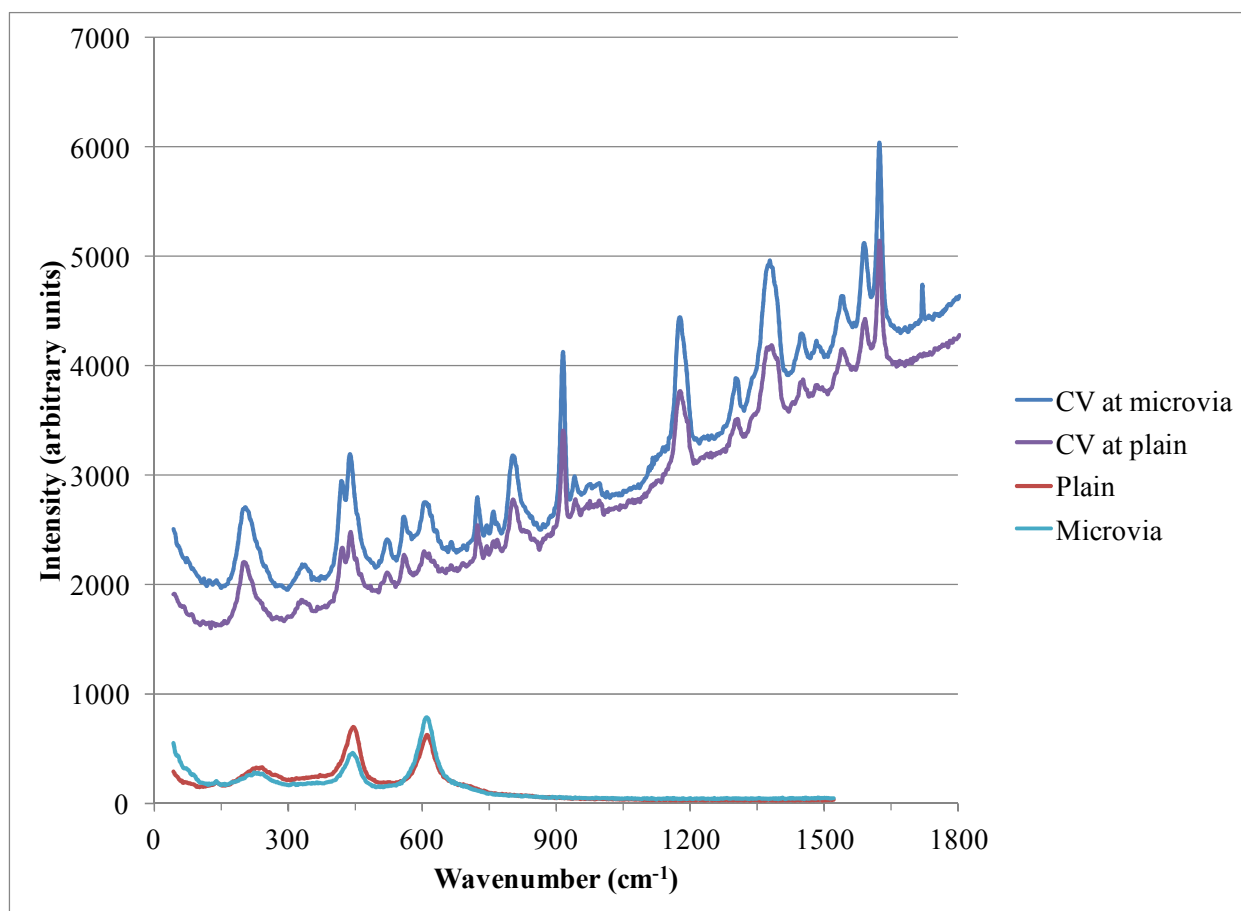


Figure S6. CV-TiO₂ experiments using the 26 MHz -15 msec substrate.

The variations in 3-D nanofibrous porosity, TiO₂ phase composition impurities, crystallinity, nanofiber particle size averages and standard deviations as well as microvia morphology and network depth are all tunable with the femtosecond laser manufacturing technique. Investigating these factors the most is meaningful when developing a sensor for industrial use. The issue is that proving an enhancement for a CV dye may not be applicable, for instance, to aromatic pollutants with much lower Raman cross-sections and different adsorption kinetics. Therefore, it is reasonable to conclude that the 3-D nanofiber network clearly has a significant potential to compete with the most popular Ag and Au substrates which will be subject to future research.

S3. CROSS-SECTION ANALYSIS

Since the TiO_2 nanofibers were mobile with respect to the AFM scanning probe, it was possible to scan the cross-section view of the microvias (Figure S7). The flat lines at 0 μm are saturated responses from the AFM scanning head since the maximum scanning depth was limited to ca. 5 μm . The depth can be controlled by reducing the synthesis laser repetition rate and dwell time (Figure 1). The microvia depth is expected to have a positive correlation with the depth of the nanofiber network. However, SEM cross sections showing the nanofibers proved to be much more difficult.

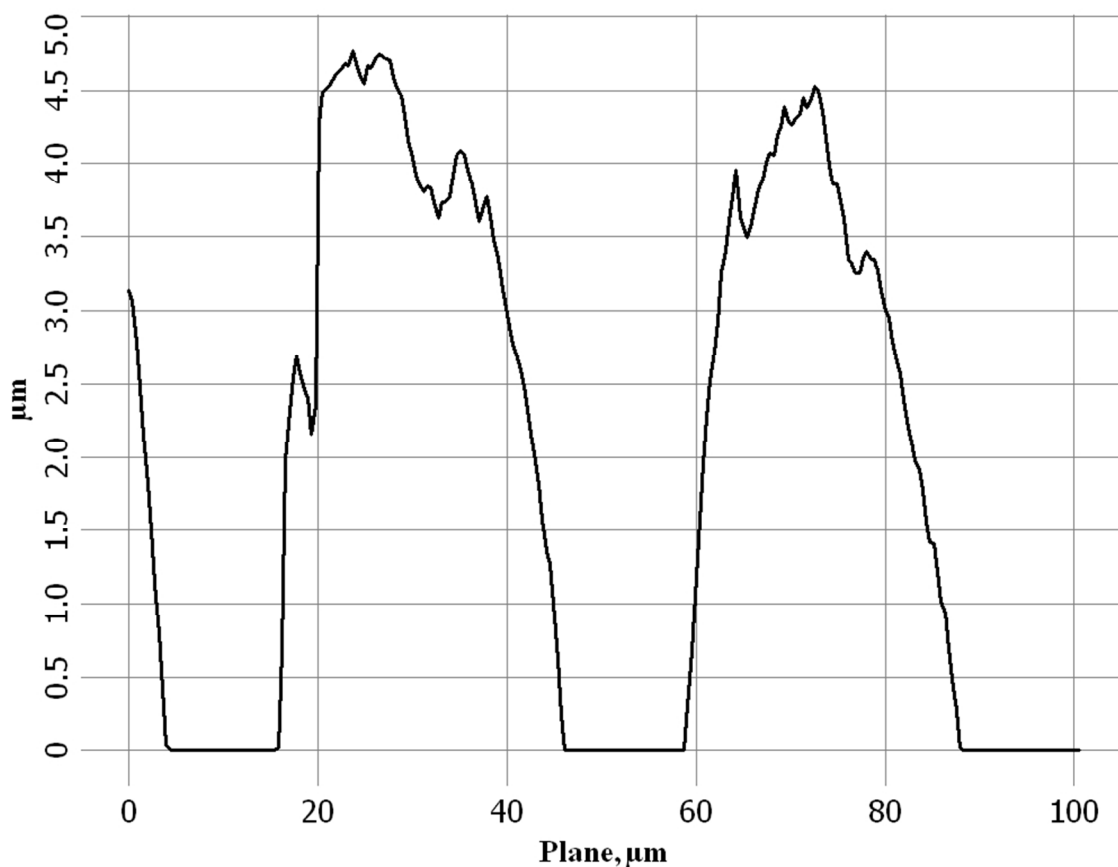


Figure S7. AFM cross-sectional view of the top left substrate in Figure 6 (first cross section from the bottom of the AFM scan).

Titanium is a cumbersome material to machine. The commercial Ti sample used was 0.75 in thick. Various methods were attempted at cutting a cross section. Mechanical material removal processes such as sawing were not capable at cutting through the thickness. As a result, only diamond blade grinding could be used. The problem is that liquid coolant is required which inevitably washes away the nanofibers. Another method was considered to irradiate the sample on the edge. There were two major problems with this technique. Firstly, the heat dissipation is different resulting in plasma dynamics different from a standard surface. Second, there were significant safety concerns as the laser can scatter off the edge of the Ti sample and potentially damage laboratory equipment and cause harm to the operators. Ti foil was used to alleviate the thickness problem. However, the intense heat from laser irradiation during synthesis heavily warped the foil. As a result, the surface did not have a consistent laser focus and could not generate the TiO₂ nanofiber network.

Nonetheless, we were previously able to make cross sectional views on silicon. Polished silicon wafers of 550 μm thickness were brittle and thin enough such that normal scribe and break methods resulted in reasonable SEM images. A cross section of Si nanofibers within the microvias was previously presented by Tavangar et al., 2010.²¹ A cross section of a more developed nanofibrous 3-D network was presented by Sivakumar et al., 2010.²² It is expected that the nanofibrous network will appear similar to the later work as it appears similar to TiO₂ nanofibrous networks from plan view.

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