Investigation of silica sol-gel materials doped with graphene oxide (GO) and TiO_2 as substrates for plasmon-free surface enhanced Raman spectroscopy

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Introduction

Surface enhanced Raman spectroscopy (SERS) is a non-invasive characterization technique where a substrate enhances the Raman scattering of a molecule. SERS is obtained through either electromagnetic enhancement, or chemical enhancement. Most SERS substrates are based on noble metals such as Au, Ag, and Cu, which enhance Raman scattering through surface plasmon resonance. These tend to be expensive, have a short shelf life, and they are not recyclable. Substrates based on non-conductive materials tend to have a smaller enhancement effect than their noble metal counterparts because they can only enhance the signal through chemical enhancement (mainly through charge transfer).

SERS activity has been observed in TiO_2 macroporous structures, graphene, and TiO_2-graphene composite materials (1-4), were Raman scattering was enhanced through both enhanced charge transfer and enhanced light-matter coupling. In this project, these two processes were emulated by using mesoporous silica sol-gel materials doped with graphene oxide (GO) and TiO_2 nanoparticles. GO was detected and reduced within the silica matrix, improving the signal-to-noise ratio for the reduced sol-gel materials.

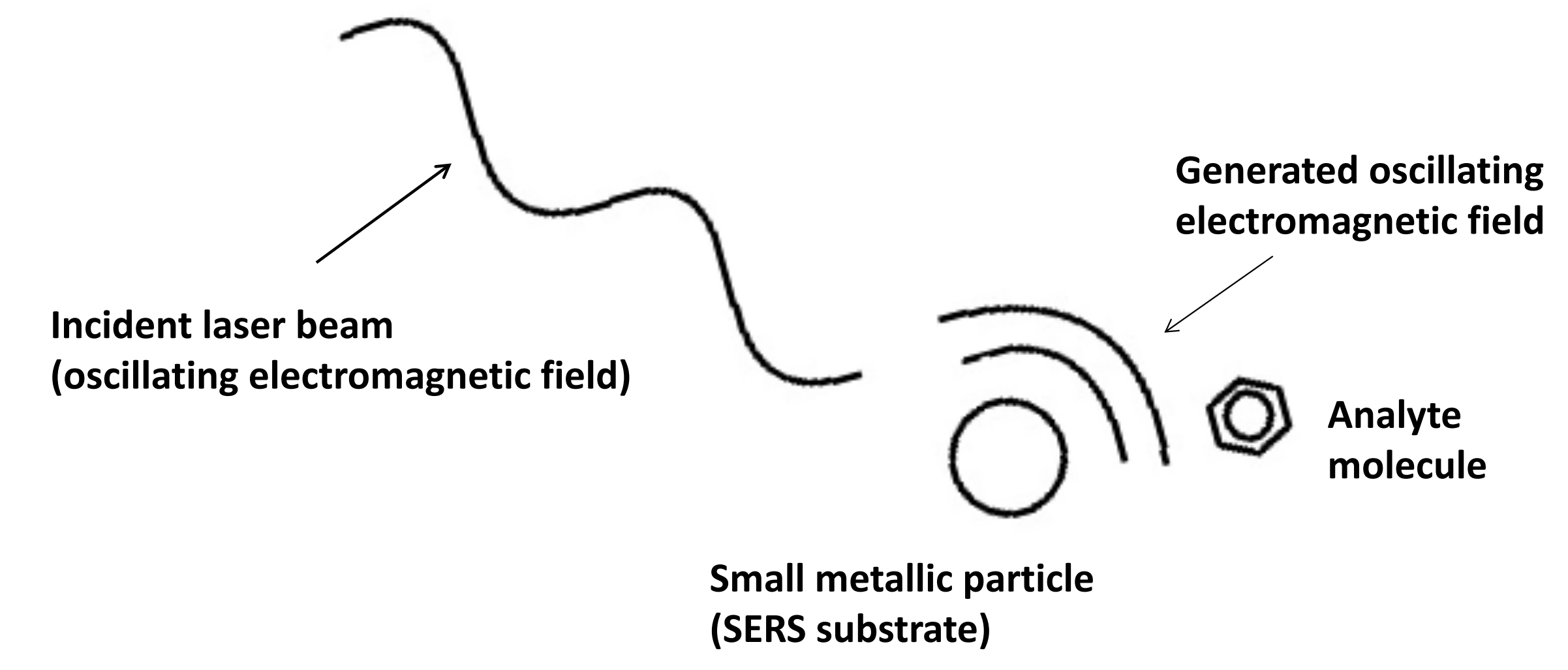

Figure 1. Enhancement of Raman scattering on a metal substrate (nanoparticle) through surface plasmon resonance (5)

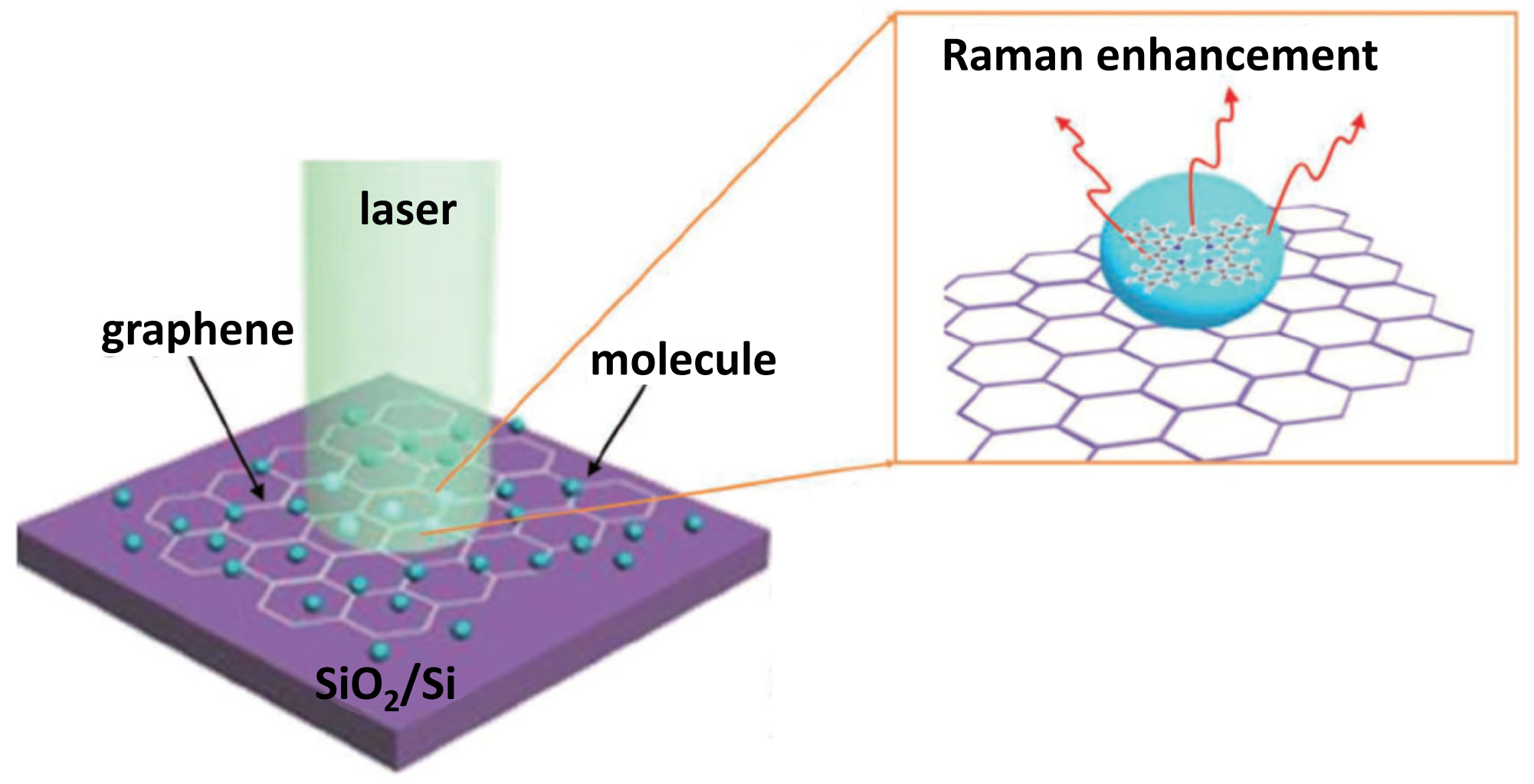

Figure 2. Graphene-mediated enhancement of Raman scattering (GERS) (4).

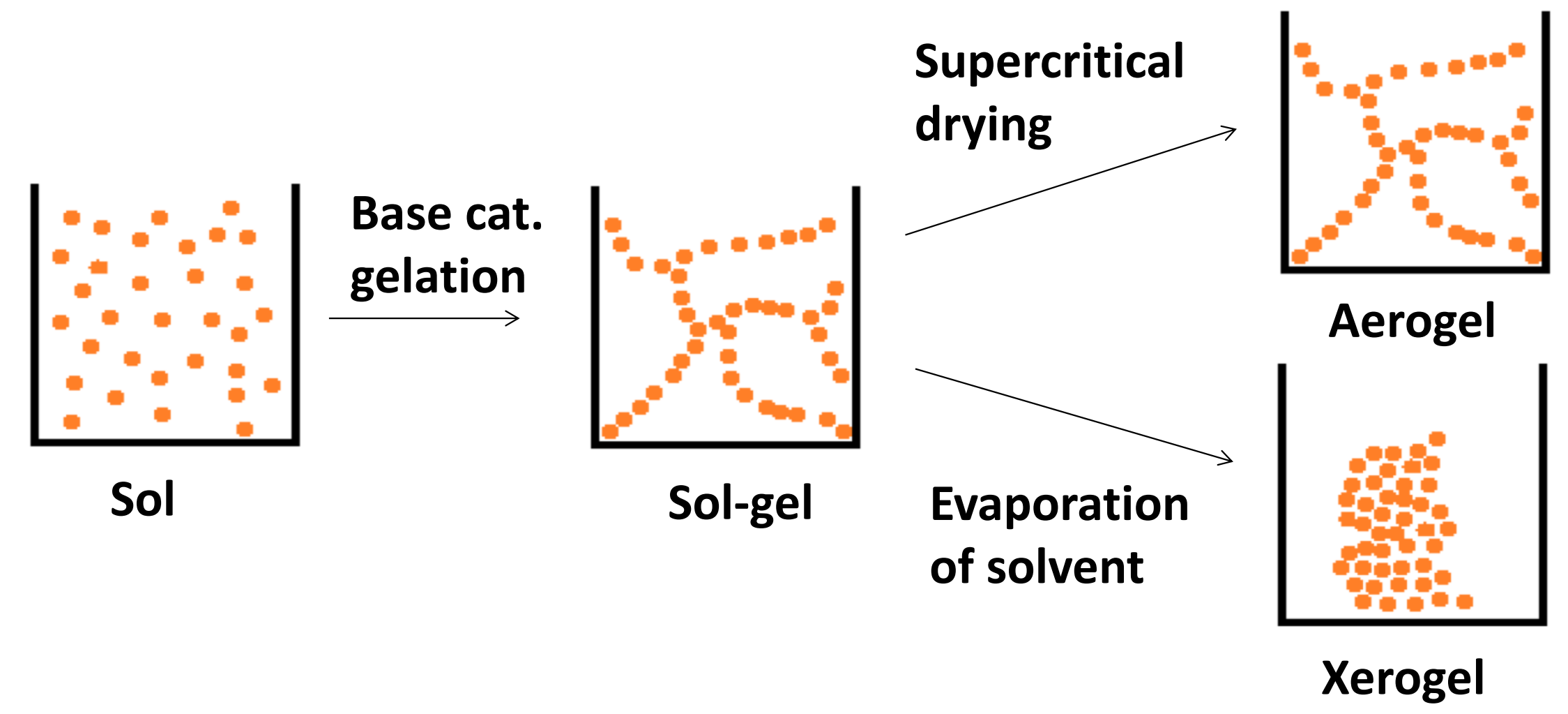

Figure 3. Processing of a sol (solution of dispersed TMOS nanoparticles) into aerogels and xerogels (6).

Results

Sol-gels doped with TiO_2 (nanoparticles w/primary size 21 nm) (P25) showed an increase in the Raman signal-to-noise ratio for TiO_2: TMOS molar ratios less than 0.01 when compared to a silica-GO blank, and the same trend was observed for their respective xerogels (Table 1). The signal-to-noise ratio for all aerogels was lower than 0.69, indicating that aerogels are not suitable SERS substrates. An increase in the signal to noise ratio was observed when sol-gels were transformed into xerogels. Thermally reduced xerogels had a higher signal-to-noise ratio than air-dried xerogels (Table 1). The spectra of the reduced xerogels showed a shift of the position of the G peak to the right and a decrease in both the intensity of D' and the I_D/I_G ratio (Table 2, Figure 4).

Table 1. Signal-to-noise ratio for TMOS xerogels doped with P25 with various TiO_2: TMOS molar ratios.

TiO_2: TMOS	Signal-to-noise (sol-gels)	Signal-to-noise ratio (xerogels)	
		Air dried	Thermally reduced
0.0002	1.50	1.52	1.58
0.0005	1.17	1.26	1.42
0	1.05	1.19	1.24
0.001	1.03	1.12	1.13
0.01	0.98	0.72	0.94
0.02	0.95	1.01	1.26

Table 2. Position of the G peak, intensity of D', and I_D/I_G ratio for xerogels analyzed before and after reduction

TiO_2: TMOS	Before			After		
	G peak	D' intensity	I_D/I_G	G peak	D' intensity	I_D/I_G
0.0002	1599	2200.1	0.8904	1604	804.74	0.8323
0.0005	1600	2336.5	0.8440	1605	508.45	0.8082
0.001	1599	2206.0	0.8477	1605	1603.4	0.8306
0.01	1597	2252.0	0.8866	1603	905.77	0.7986
0.02	1599	2269.3	0.8565	1605	1042.2	0.7908
0	1599	2384.4	0.8789	1604	754.2	0.7749

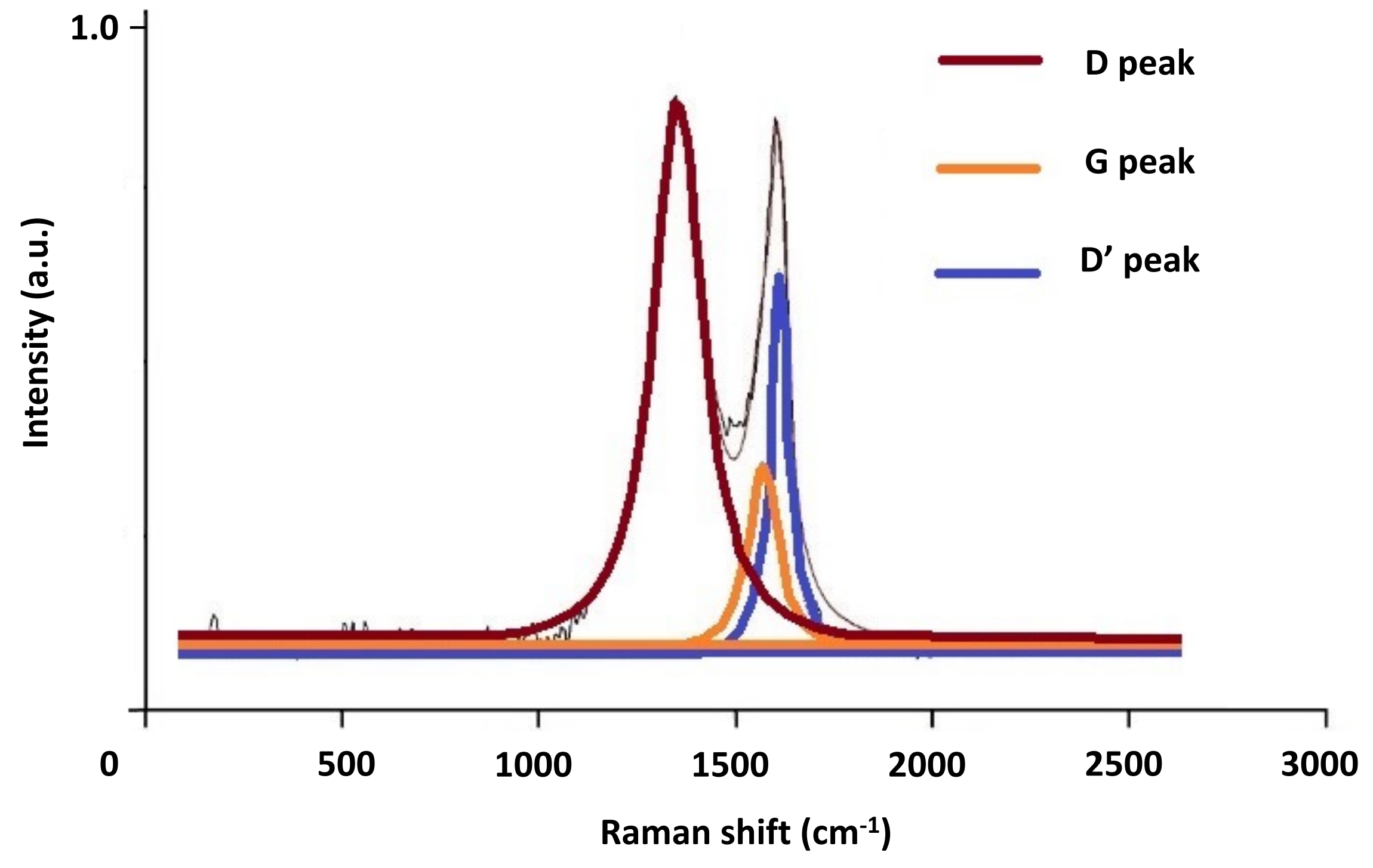

Figure 4. Peak assignment for the Raman spectra of a typical, air-dried TMOS xerogel.

Discussion

The observed signal-to-noise ratio for different sol-gel materials suggests that sol-gels and xerogels are better suited as plasmon-free SERS substrates than aerogels. The photocatalytic properties of the TiO_2 nanoparticles make these substrates recyclable. The spectral analysis of thermally reduced xerogels doped with graphene oxide (GO) indicated that the oxygen content for GO is decreasing and the sp^2 carbon network is being partially reformed (6). Thermally reduced xerogels had a higher signal-to-noise ratio than air-dried xerogels (Table 1).

Graphene has a flat and smooth surface that allows it to interact through π-π bonding interactions, thus promoting charge transfer (1, 4). The disappearance of the oxygen functionalities found on graphene oxide also allows for more graphene- TiO_2 interactions. GO reduction inside the silica matrix provides a stable surface for GO to promote charge transfer and enhance Raman scattering. These results indicate that improved enhancement is obtained when graphitization takes place. The improvement of the charge transfer within the silica/titania composite reduced xerogels doped with GO enhanced their Raman signal-to-noise ratio.

Conclusions

The signal-to-noise ratio for the Raman spectrum of GO was optimized by doping silica sol-gels with P25 for TiO_2:TMOS molar ratios less than 0.01. Thermally reduced xerogels showed a higher Raman enhancement due to the partial reformation of the sp^2 carbon network trapped in the silica matrix, which appears to enhance the graphene-TiO_2 interactions, promoting charge transfer. Silica sol-gels and xerogels doped with TiO_2/GO were successfully used as plasmon-free, label-free SERS substrates. Their Raman signal enhancement and enhanced photocatalytic properties (7) render these materials potential candidates for the production of highly stable, reusable, biologically-compatible, metal-free SERS substrates.

Methods

Chemicals: Silver nitrate (99.8%), tetramethyl orthosilicate (TMOS, 98%), titanium (IV) propoxide (TPOT, 98%), titanium (IV) oxide (nanopowder, primary particle size of 21 nm) (P25), methanol (≥99.9), ammonium hydroxide (30%), sodium citrate (90%), and graphene oxide (2 mg/mL, dispersion in water) (GO) were purchased from Sigma Aldrich (Milwaukee, WI).

Synthesis: Sol-gels were prepared using a TMOS: H_2O: MeOH: NH_4OH molar ratio of 1: 30: 9: 0.25, a constant concentration of GO, and various amounts of either TPOT or P25. Sol-gels were transformed into aerogels by supercritical CO_2 drying. Xerogels were obtained by air-drying the sol-gels or heating them in a tube furnace at 400 °C (heating rate 5 °C/min) for one hour (Figure 1).

Analysis: Raman spectra were obtained using a custom-built Raman spectrometer with a 532 nm laser. Spectra were acquired using KestralSpec with 5 second acquisitions, a slit width of 50 nm and automatic background subtraction. The spectrum of both the air-dried and thermally reduced xerogels was fitted using Origin 9.

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