SERS detection of graphene oxide in acid-catalyzed sol-gels

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Introduction

Overview: Graphene oxide has shown promise as a sensor due to its many interesting physical and chemical properties, including its ability to induce strong chemical enhancement[1] and its high adsorption properties[2]. Moreover, graphene oxide is known to be detectable using surface-enhanced Raman spectroscopy (SERS)[3], a surface-sensitive spectroscopic technique with many applications in the chemical and biological fields[4]. The ability to detect graphene oxides presence while integrated in a silica sol-gel could be an important step in testing its effectiveness as a sensor.

Sol-gel materials: Silica Sol-gel and aerogels are very low density solids, composed of a highly porous matrix of metal-oxide bonds that provide a cage-like structure, allowing for the entrapment of desired target molecules. Silica gels can be synthesized using a variety of different catalysts[5-7]. The synthesis method used involves an acid-catalyzed reaction using TMOS[5], which acts as the building blocks for structure of the porous silica gel.

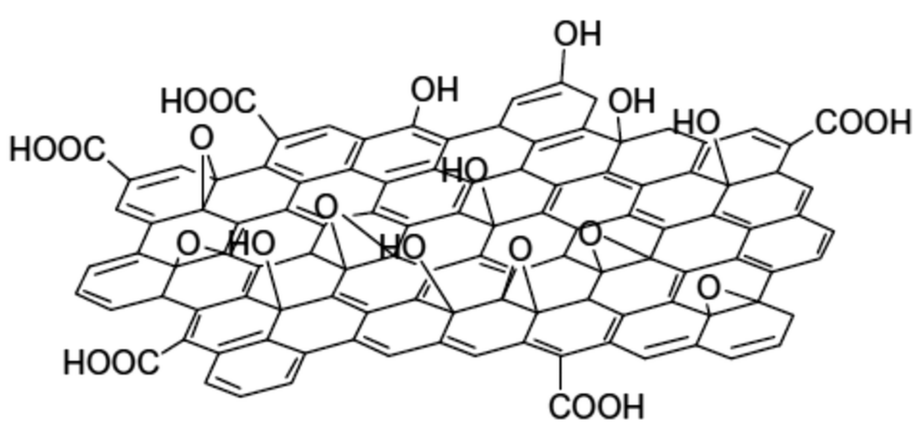

Figure 1: The structure of the target molecule, graphene oxide.[8]

Goal: Little work has been done to investigate the detection of graphene oxide while encaged in a sol-gel, nor as a sensor in an aerogel. Herein, the authors present an acid-catalyzed silica sol-gel preparation that incorporates graphene oxide and silver nanoparticles while using SERS to monitor the efficiency of the graphene oxide uptake. The concentration effect of graphene oxide loading was monitored by SERS. In addition, the impact of the silver nanoparticles size on the graphene oxide SERS spectrum was observed.

Methods

Chemicals:
- Graphene oxide
- Tetramethyl orthosilicate (TMOS)
- Silver nitrate, dihydrate sodium citrate, and citric acid monohydrate
- Chemicals were purchased from Sigma-Aldrich (St. Louis, MO). All materials were used as received.

Procedures:
- Silica sol-gels were prepared by the acid-catalyzed hydrolysis of TMOS[5].
- Silver nanoparticles were prepared using a modified citrate reduction method[9]. Silver nitrate (50 mL, 1 mM) and deionized water (25 mL) were mixed and brought to a boil. Sodium citrate (7.0 mL, 1% w/v) was added and the mixture was refluxed (30 min).
- Graphene oxide (1.0 mL, 2 mg/mL) was added to deionized water (6.5 mL) and the solution sonicated until homogenous. Citrate buffer (0.035 mL, 0.4M, 4.6 pH) and TMOS (4.62 mL) were then added to the mixture and further sonicated (10 min). Silver colloid (3.0 mL), Was added to the solution and sonicated a final time (5 min).
- Gels were aged (24 h).
- Aged gels were washed several times in ethanol, followed by acetone over three days.

Instrumentation:
- Custom-built Raman spectrometer using a 532 nm excitation beam and thermoelectrically cooled CCD
- NanoSight LM10 HS
- Shimadzu UV-Vis Spectrophotometer (UV-2600)

Results

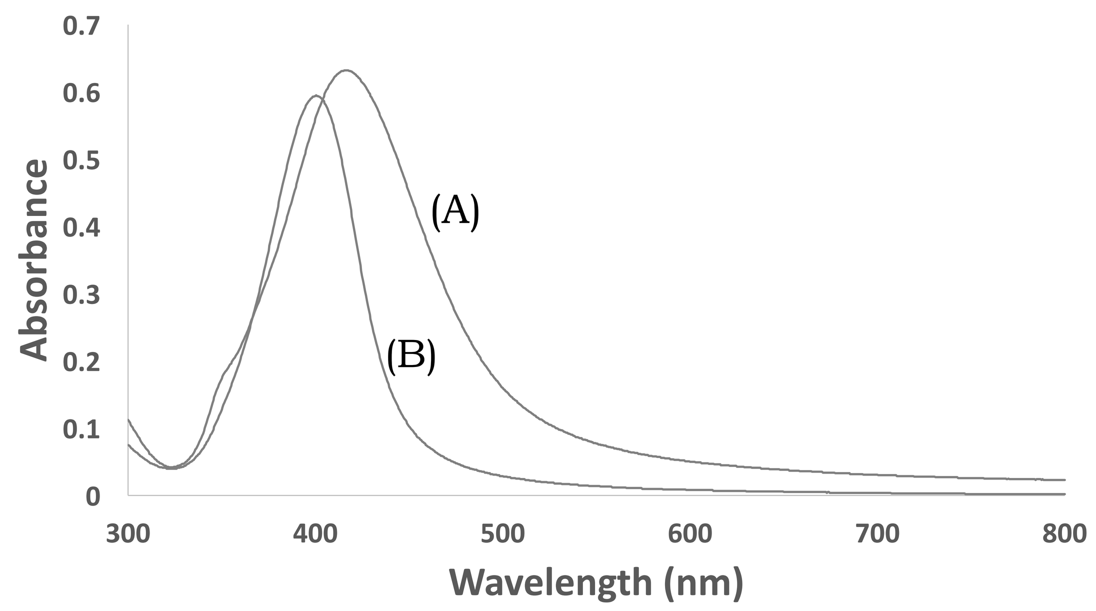

Figure 2: UV-vis spectra for replicate sample preparations of silver nanoparticle solutions. Differences in particle size were observed using full width at half maximum (FWHM) values. The FWHM value for sample (A) was 96.2 nm whereas (B) was 42.3 nm.

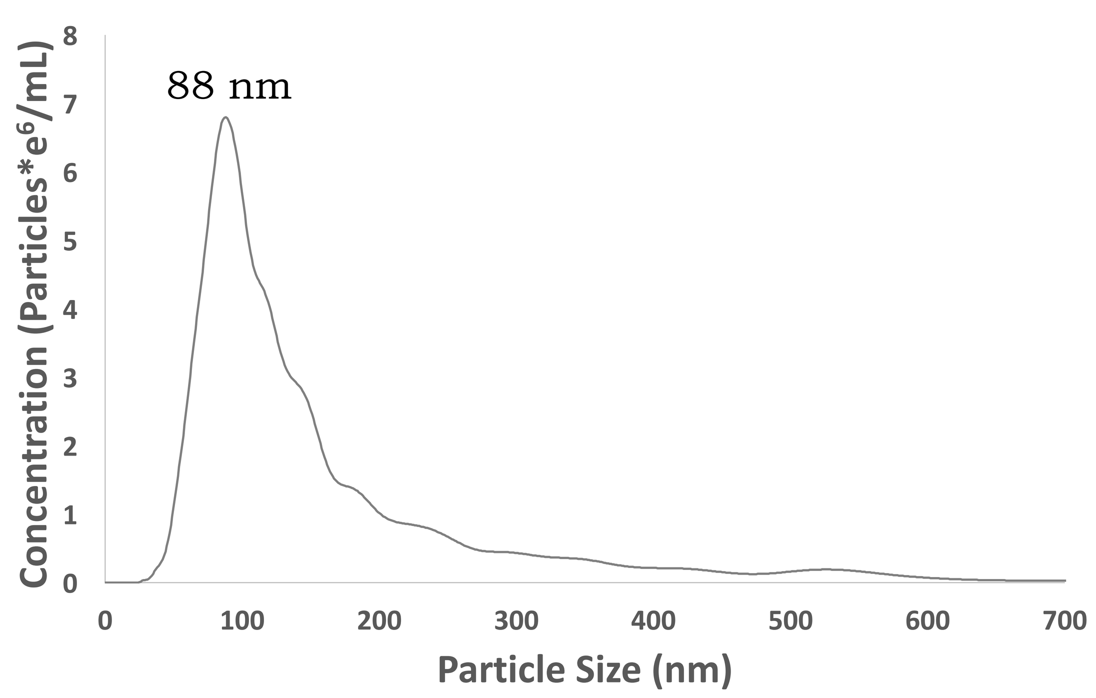

Figure 3: NanoSight spectrum of the various sized silver nanoparticles in solution (A) from Figure 2 with a mean size of 88 nm.

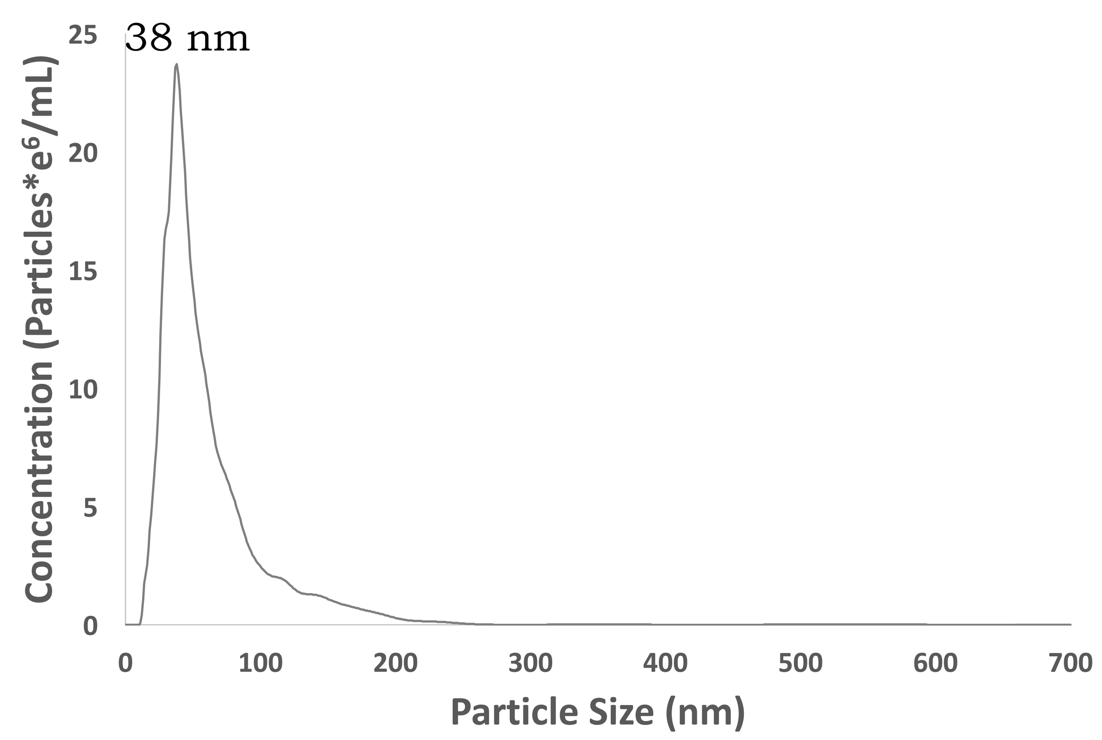

Figure 4: Nanosight spectrum of the various sized silver nanoparticles in solution (B) from Figure 2 with a mean size of 38 nm.

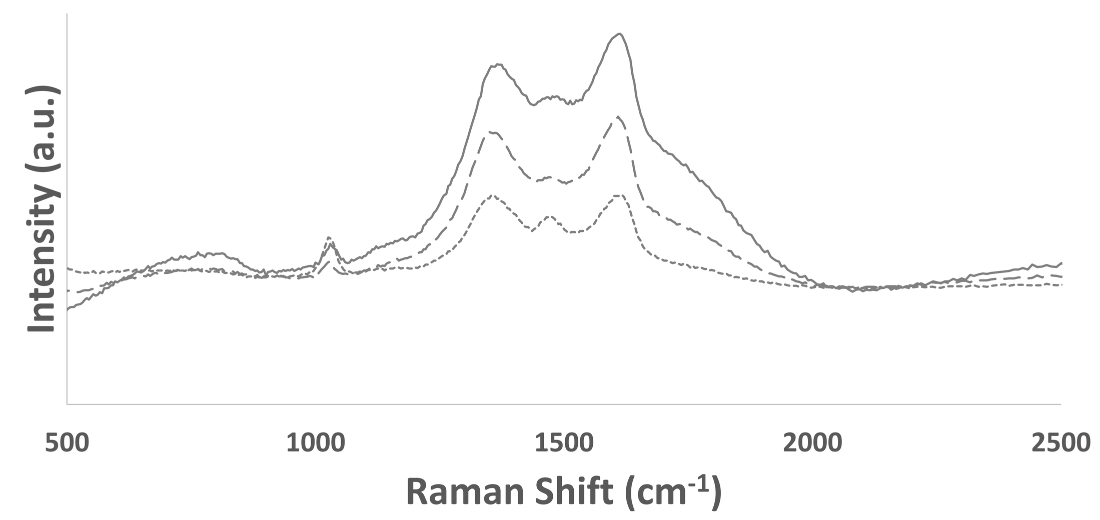

Figure 5: SERS spectra of graphene oxide silica sol-gels using silver nanoparticle solution (A) at various graphene oxide concentrations. Concentrations of graphene oxide were 0.066 mg/mL (· · ·), 0.123 mg/mL (- - -), and 0.198 mg/mL (——).

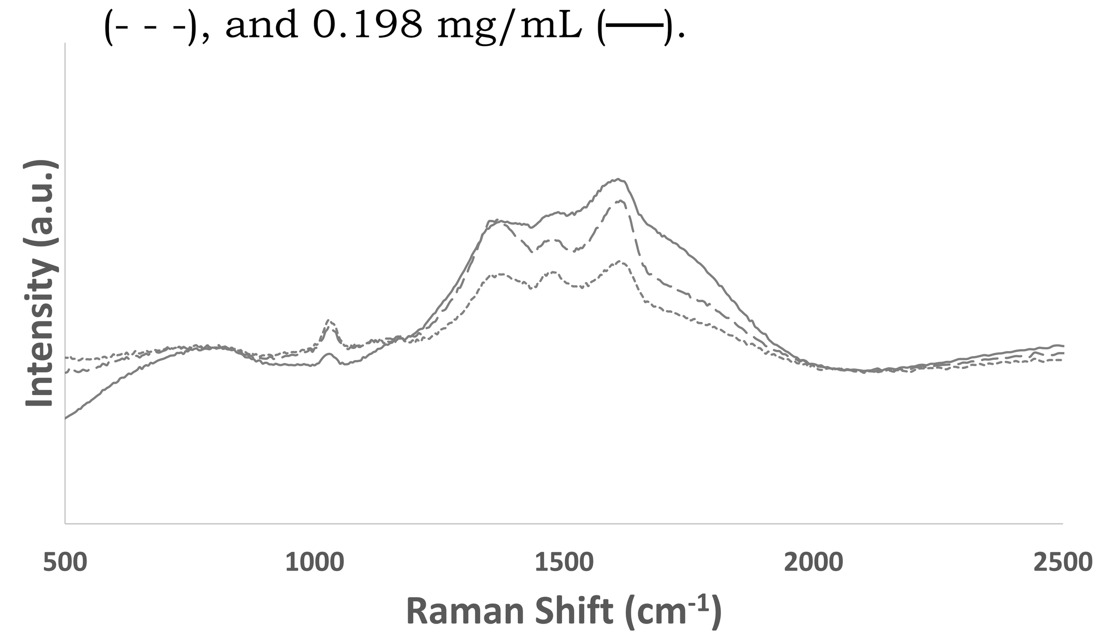

Figure 6: SERS spectra of graphene oxide silica sol-gels using silver nanoparticle solution (B) at various graphene oxide concentrations. Concentrations of graphene oxide were 0.066 mg/mL (· · ·), 0.123 mg/mL (- - -), and 0.198 mg/mL (——).

Discussion

Graphene oxide sol-gels with silver nanoparticles were successfully prepared through a modified acid catalyzed synthesis reaction. The graphene oxide was detectable through SERS (Figure 5, 6) when integrated into the sol-gel matrix at its characteristic peaks (1365 cm^{-1}, 1612 cm^{-1})[3]. Other peaks appear (1030 cm^{-1}, 1476 cm^{-1}) and may be characteristic peaks of methanol, a side product of the modified reaction.

Data suggests that as graphene oxide concentration increases peak intensity also increases (Figure 5, 6). Silver nanoparticle solutions (A) and (B) were synthesized and had an average size of 88 nm and 38 nm, respectively (Figure 3, 4). Figure 2 supports these results by showing that solution (A) is more aggregated with a FWHM value of 96.2 nm, whereas solution (B) had a FWHM value of only 42.3 nm. Figure 5 shows that graphene oxides characteristic peaks are intensified and become more distinct when larger silver nanoparticles are present when compared to those made with smaller silver nanoparticles that are shown in Figure 6. The next step for this research is to dry these sol-gels into aerogels, where graphene oxide can be tested as a sensor.

Conclusions

- Graphene oxide in the presence of silver nanoparticles can be detected by SERS while encapsulated in a silica sol-gel matrix.
- The intensity of graphene oxides characteristic peaks (1365 cm^{-1}, 1612 cm^{-1}) increase as the concentration of graphene oxide increases in the sol-gel matrix.
- Data suggests that larger silver nanoparticles integrated into the silica sol-gels allow for greater intensity of graphene oxide signature peaks.

Acknowledgments

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References

1. X. Ling, L.M. Xie, Y. Fang, H. Xu, H.L. Zhang, J. Kong, M.S. Dresselhaus, J. Zhang, Z.F. Liu. *Nano Lett. 10* **2010** 553–561.
2. A. Wojcik, P.V. Kamat. ACS Nano 4 **2010** 6697–6706
3. G. Ding et al. / *Appl. Surf. Sci.* 345 **2015** 310-318.
4. Schlücker, S. Chem. Int. Ed. 53 **2014** 4756–4795.
5. Rywak, A; Burlitch, *J. Chem. Mater.* **1996**, 8, 60-67
6. Allen. J, Rosenberg,. J, Johnston. E, Hart. C. ACS *Appl. Mater. Interfaces* **2012**, 4, 1573-1584
7. Cai, S; Zhang, Y; Zhang, H; Yan, H; Lv, H; Jiang, B. ACS *Appl. Mater. Interfaces* **2014**, 6, 11470−11475
8. Nasrollahzadeh. M, Babaei. F, Fakhri. P, Jaleh. B. *RSC Adv. 5* **2015** 10782-10789.
9. P.C. Lee, D. Meisel, J. Phys. Chem. 86 **1982** 3391-3395