

## Supplementary Information

### **Silver/Graphene oxide nanocomposite film as flexible SERS substrate for reliable quantitative analysis using high-speed spiral scanning spectrometry**

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## Preparation of composite ink

The composition of silver precursor ink used in this study was slightly modified from literature.<sup>47</sup> The modified procedure is as follows: First, pH adjusted ethanolamine solution is prepared by adding 1 mL formic acid into mixture of 5 mL triple distilled water and 5 mL ethanolamine. The resulting pH value of the solution is approximately 10.5. On a separate vial, 0.4 g of silver acetate, 0.750 mL of pH adjusted ethanolamine solution, and 1 mL of 2 M ethylamine in methanol are mixed vigorously on vortex for 30 sec. The as prepared ink is a clear solution with a hint of yellow color, and is free of any precipitate. In preparation of the Ag/GO composite ink, silver precursor ink and 0.1 wt% GO soln. are mixed in 9:1 volume ratio and sonicated for 15 sec prior to use.

GO powder in highly dispersed 0.1 wt% GO solution was prepared following the modified Hummers method.

Graphite powder, Silver acetate ( $\text{CH}_3\text{CO}_2\text{Ag}$ ), and ethylamine ( $\text{C}_2\text{H}_7\text{N}$ ) solution 2.0 M in methanol were purchased from Aldrich. 2-aminoethanol ( $\text{C}_2\text{H}_7\text{NO}$ ) was purchased from KAN. All chemicals and solvents were analytical grade and used without further purification. Glass cover slips and adhesive tape used in this study were purchased from Marienfeld-Superior and 3 M, respectively.

Design factors of Ag/GO composite ink are as follows:

### *pH*

Formic acid functions as both pH controller and reducing agent. Based on a few experimental investigations, any pH higher than 10.5 requires higher temperature for the ink to completely decompose to form a film, and any pH lower than 10.5 features bad stability of the prepared ink, easily reducing silver ions into precipitates, leading to great loss of silver content within the ink.

### *Silver precursor*

The acetate part of silver acetate completely decomposes together with complexing agents upon heating, leaving the resulting film free of unwanted impurities.

The amount of silver precursor that we used gives the maximum silver loading in the resulting Ag/GO composite ink. Any larger amount leads to precipitation of reduced silver particles within the bottle, resulting in great loss of silver.

### *Complexing agents*

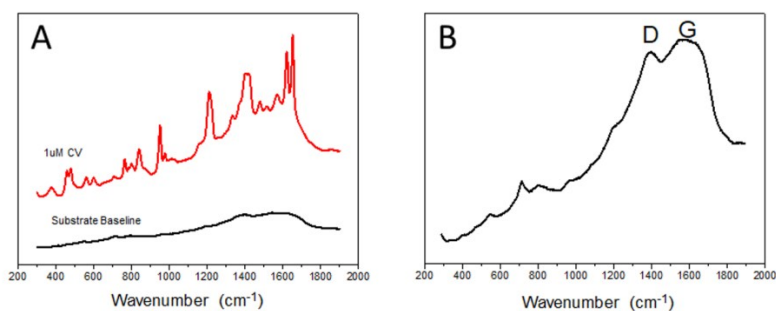
Ethanolamine and ethylamine are both short-chained complexing agents with binding sites for silver ion. They weakly bind to the silver ions and readily decompose at low temperature.

Design factors of Ag/GO SERS tape:

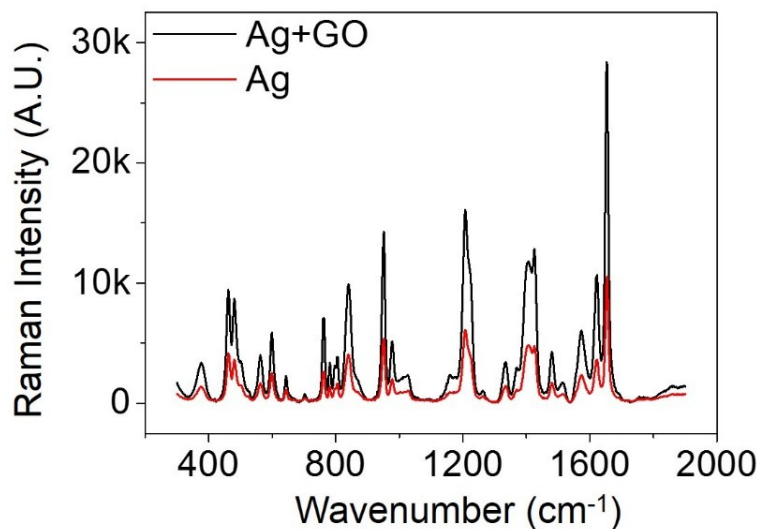
During the preparation of Ag/GO SERS tape we found a number of conditions that had important influence on the quality of the obtained SERS tape.

#### *Effect of GO*

In order to investigate the effect of GO on the SERS performance of Ag/GO SERS tape, SERS tape prepared from Ag ink alone was prepared as control. The content of GO in Ag/GO ink was carefully controlled from 0.001 to 1 wt% to yield optimal dispersion at highest possible concentration. Any GO concentration higher than 0.01 wt% resulted in significant agglomeration of GO upon addition to Ag precursor ink. The ratio of GO solution to Ag precursor ink in Ag/GO ink was chosen in a range where silver loading was not significantly lessened and retained the optimal viscosity for spin-coating.



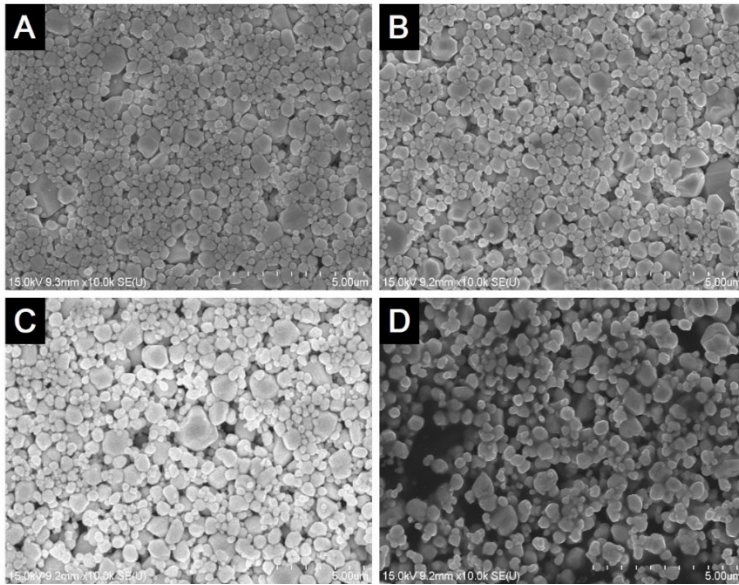
**Figure S 1.** A: SERS spectra of 1 μM CV on Ag/GO SERS tape (red) and substrate baseline (pure Ag/GO SERS tape) (black). Spectra of pure Ag/GO SERS tape is considered a substrate baseline, and was corrected in all spectra data for clearer presentation of data. B: enlarged spectra of the substrate baseline, confirming the presence of GO from the D and G-bands.



**Figure S 2.** SERS profile of 1  $\mu\text{M}$  CV on Ag SERS tape and Ag/GO SERS tape. The SERS enhancement of Ag/GO SERS tape is two to threefold of that of Ag SERS tape, confirming the enhancing effect of GO. Thus, the presence of GO plays a significant part.

*Effect of heating condition*

As the Ag/GO SERS tape in this paper is prepared by simple thermal decomposition, heating conditions were controlled to produce films of different morphology. Sintering temperature and time was optimized through repeated experiments within the range of boiling point of the complexing agents in the ink and melting point of Ag nanoparticles. In addition to sintering temperature and time, effect of different heating rate was investigated.

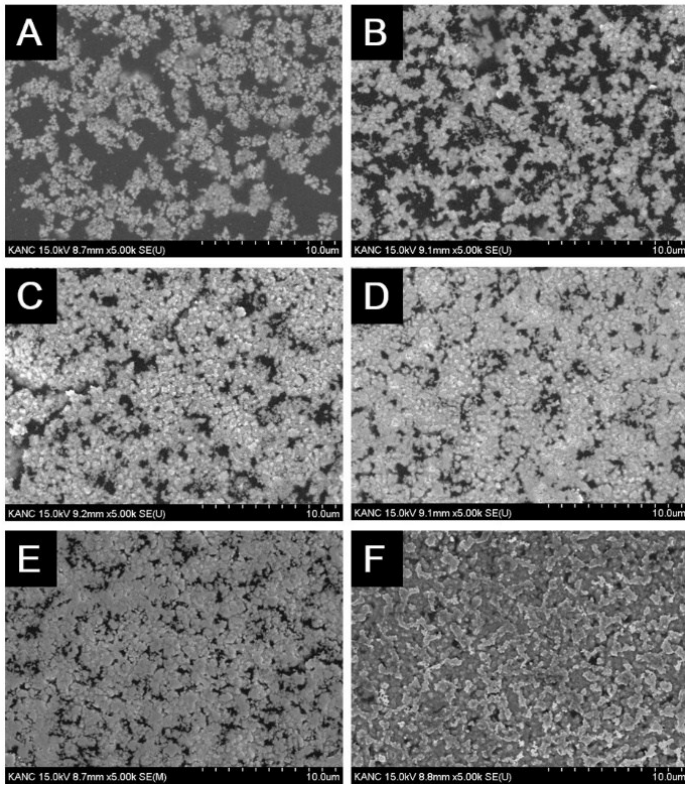


**Figure S 3.** Ag/GO SERS tape prepared at different heating rate (20, 10, 5, 2.5 °C·min<sup>-1</sup>) in a tube furnace. When heated at a higher heating rate, Ag particles were formed in a relatively close-packed surface morphology compared to the rough and seemingly porous morphology of lower heating rates.

Samples heated at higher rate tends to yield with more compact structure because it rapidly bypasses the non-densification regime and directly reaches the densification regime. We aimed to obtain uniform and dense arrangement of nanostructures for most reproducible results. Thus, direct heating on a hot plate was chosen to prepare SERS active film with the most uniform morphology.

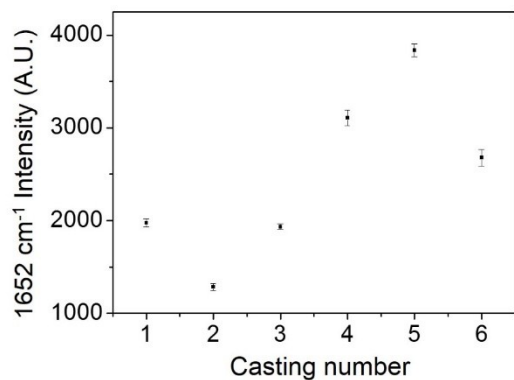
#### *Effect of film density*

Since SERS performance greatly depends on the interparticle space of the substrate which functions as the hot spot for signal enhancement, achieving optimal density of hot spots is essential. Therefore, we attempted to control the density of the film by repetitive casting over sintered films. Our precursor ink being particle free, the ink can infiltrate into the porous structure of pre-formed layers and fill in the empty spaces. The casting number was controlled from one to six. Then, we treated our Ag/GO SERS tape with a common Raman dye (10<sup>-6</sup> M Crystal Violet, CV) to measure the Raman signals.

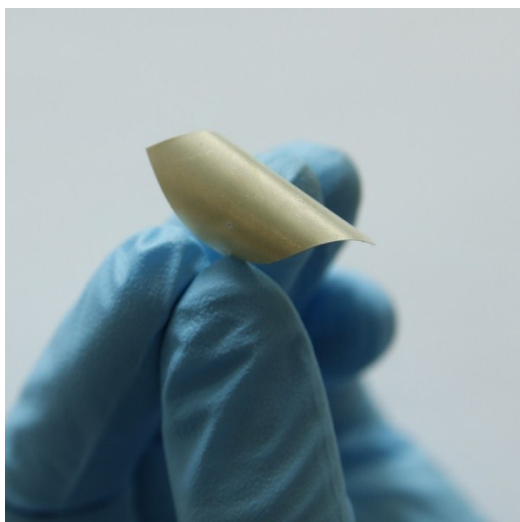


**Figure S 4.** SEM micrographs of Ag/GO SERS tape prepared from 1 to 6 casting number (A to F).

The SEM micrographs of Ag/GO SERS tapes prepared with different casting numbers from one to six are shown in Figure S 4. The SEM micrographs revealed increase in density of silver nanoclusters on the surface without any signs of large morphological changes until five, then further increase in casting number higher than five caused detachment of the film from the glass substrate induced by formation of protruding aggregates on the film-glass interface. The plotted graph in Figure S 5 shows the relationship between casting number and enhancement of CV on Ag/GO SERS tapes.

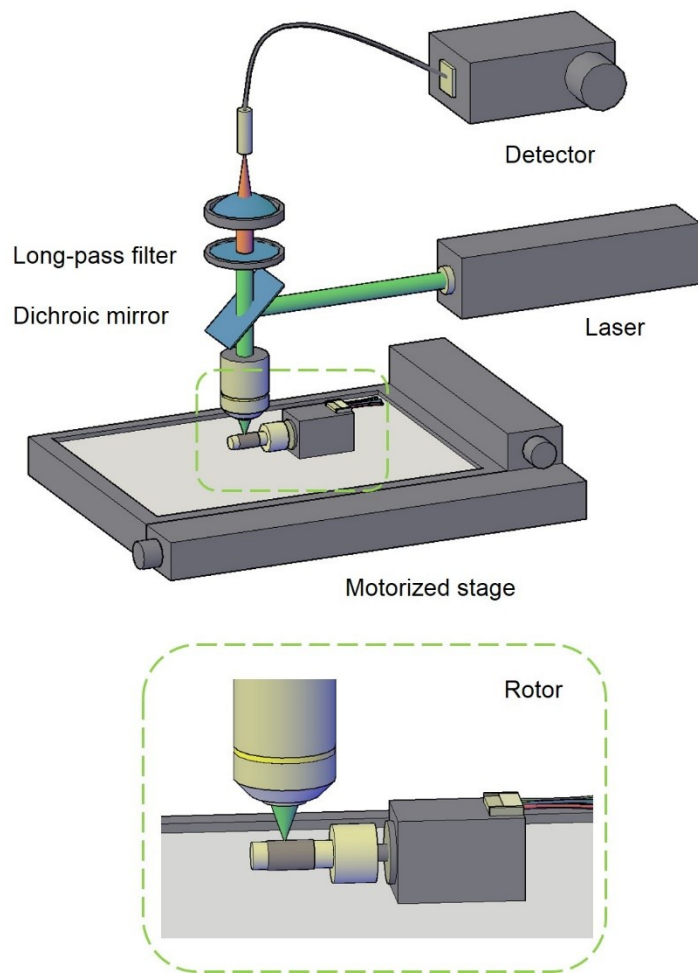


**Figure S 5.** The baseline-corrected peak height of the CV peak located near 1652 cm<sup>-1</sup> region was used as a measure to quantify the SERS response of Ag/GO SERS tape at different coating number from one to six. The intensity of 1652 cm<sup>-1</sup> peak gradually increases as number of casting increases from two to five, then sharply decreases at six, possibly because of the formation of aggregates on the surface of the film observed from the SEM micrograph.

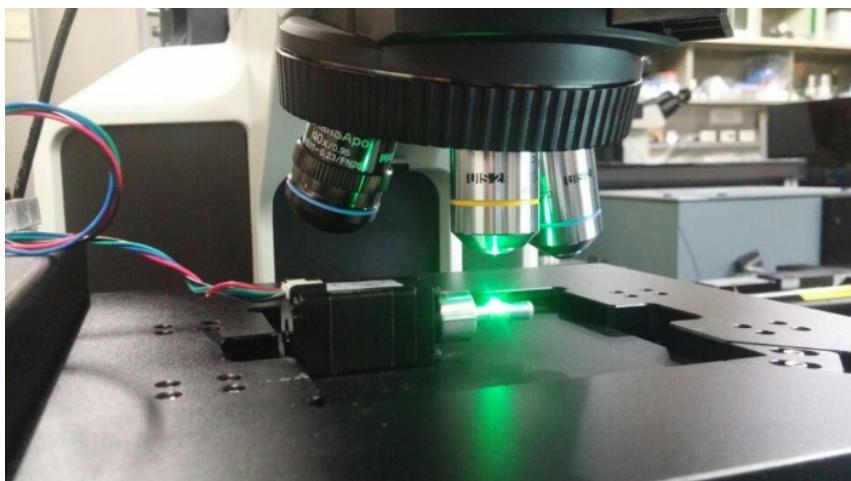


**Figure S 6.** Optical image of Ag/GO SERS tape. The physical exfoliation of Ag/GO film from glass substrate using adhesive tape results in a thin sheet of Ag/GO composite film with a glossy surface that readily bends without any significant structural deformation. The initially exposed surface of the Ag/GO film before exfoliation appears dull without any metallic gloss due to the absence of specular light as light is scattered in other directions upon contact with the rough surface.





**Figure S 7.** Illustrative image of the in-house cylindrical/spiral scanning system.



**Figure S 8.** Optical image of in-house cylindrical/scanning system.

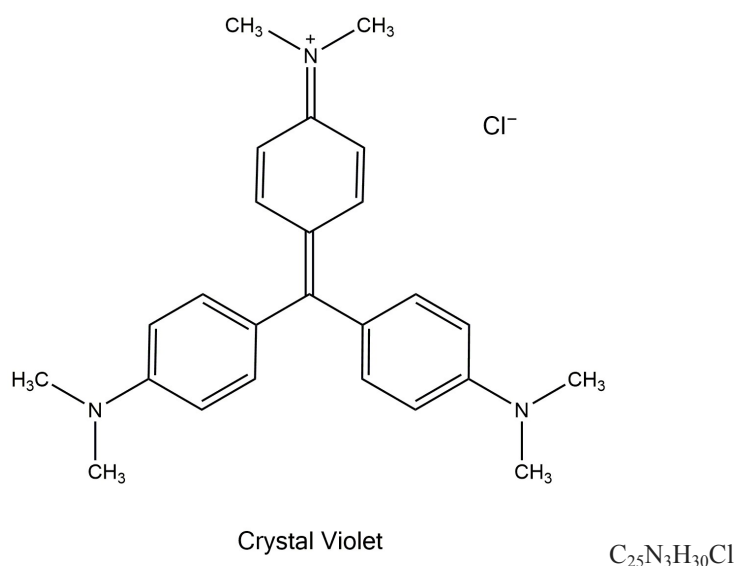
### *SERS measurements on Ag/GO film*

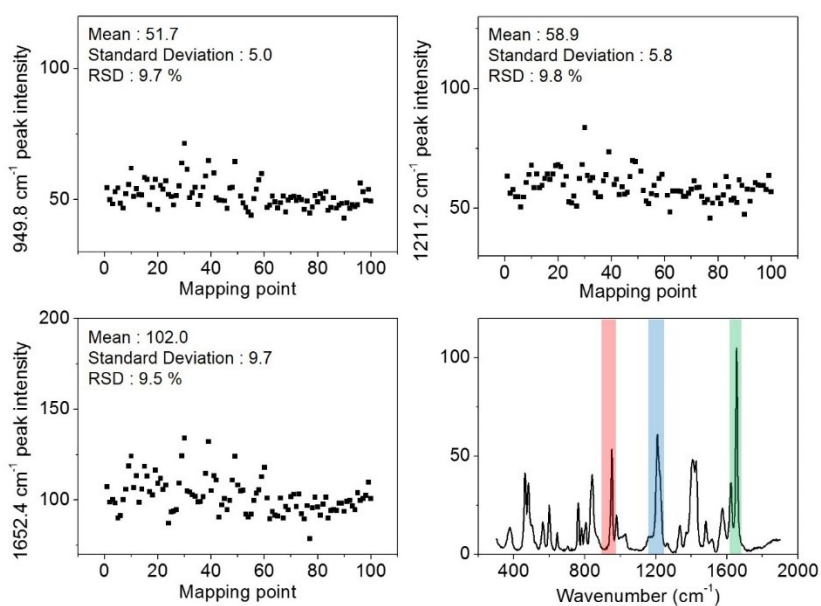
SERS was conducted with an in-house Raman system incorporating high speed rotor and motorized stage. The Raman system consists of a commercial upright microscope (Olympus, BX53), an Ar ion laser, and a polychromator (Andor, Shamrock 303i) equipped with scientific grade CCD (Andor, DU420A-BEX2\_DD). Analyte samples were excited using the Ar ion laser with a fixed wavelength at 514.5 nm of 1 mW output at samples. Raman signals were measured by collecting back-scattered light. To avoid signals by unwanted lights, we used dichroic beamsplitter (Semrock Di02-514) and long pass filter (Semrock LP02-514RE).

The high-speed rotor system is composed of a rotor, a step motor, and a motor driver (Arduino uno R3) controlled by LABVIEW software. SERS substrates were immobilized on the cylindrical rotor using double sided tape (3M 3136). The rotor system was then mounted on the motorized stage of the upright microscope. The step motor employed in the rotor system was programmed with Arduino and step motor driver, and its operation was synchronized with CCD and microscope motorized stage by LABVIEW software. Raman signals were epi-detected with an upright microscope and 10× objective lens was used with ~50 μm beam diameter.

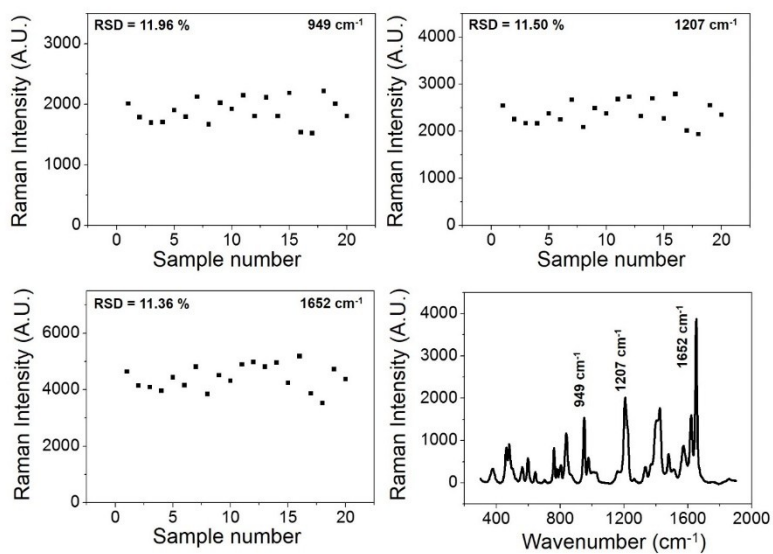
After data acquisition, baseline correction was carried out using asymmetric least square (AsLs) method to remove the broad background signals coming from the substrates itself.

Crystal Violet (CV), a popular Raman probe molecule, was selected as a model dye to evaluate the SERS performance of the Ag/GO SERS substrate and the cylindrical system. The reagent was purchased from Tokyo Chemical Industry Co., Ltd., and was used directly as received.

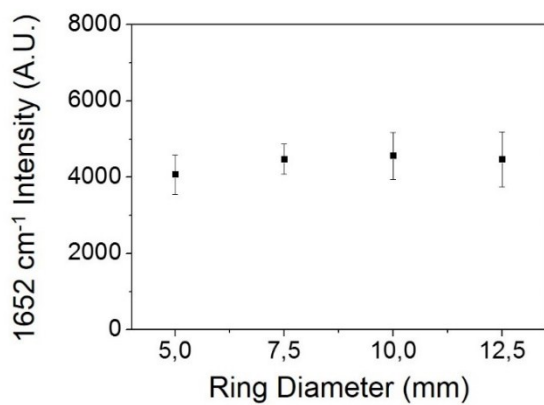




**Figure S 9.** SERS spectra intensity of  $10^{-5}$ M CV at  $949\text{ cm}^{-1}$ ,  $1207\text{ cm}^{-1}$ , and  $1652\text{ cm}^{-1}$  collected from 100 mapping points of Ag/GO SERS tape.

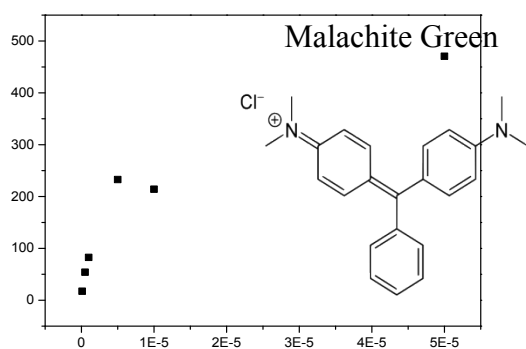


**Figure S 10.** SERS spectra intensity of  $10^{-5}$  M CV at  $949\text{ cm}^{-1}$ ,  $1207\text{ cm}^{-1}$ , and  $1652\text{ cm}^{-1}$  collected from spiral scanning 20 different batches of Ag/GO SERS tape.

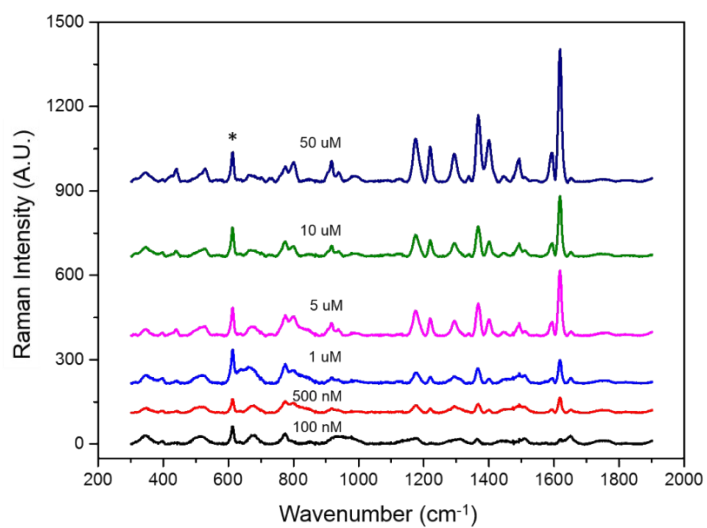
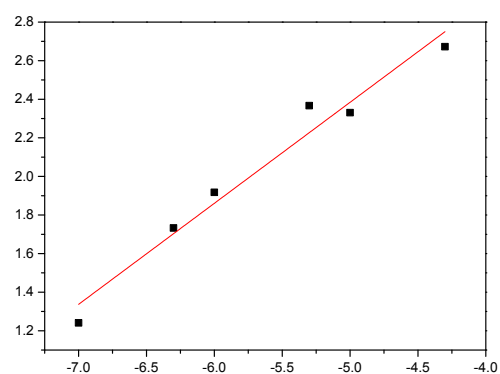


**Figure S 11.** Intensity of baseline corrected 1652 cm<sup>-1</sup> peak of CV on Ag/GO SERS tape plotted against rotor sizes (diameter): 5.0, 7.5, 10.0, 12.5 mm.

**Real concentration and SERS intensity  
at  $1618\text{ cm}^{-1}$**



**Logarithmic concentration and  
SERS intensity at  $1618\text{ cm}^{-1}$**



**Figure S 12.** SERS measurements of Malachite Green on Ag/GO SERS tape ranging from  $1 \times 10^{-5}$  M to  $5 \times 10^{-8}$  M.