

Electronic Supplementary Information for

SERS Platform Based on Diatomite Modified by Gold Nanoparticles Using a Combination of Layer-by-Layer Assembly and Freezing-Induced Loading Method

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SERS measurements justification

1. Choosing traces of Raman scattering

For each diatomite-based sample type, 9-10 measurements were taken. Then for each sample type intensity distributions of the modes around 1362 and 1507 cm^{-1} were analyzed (see Figure S1), and measurements with amplitudes in the lower quartile (1-2 measurements per sample type) were excluded. Therefore, each sample type had 7-9 measurements that were used for further calculation of mean trace and its standard deviation, represented in Figure 7.

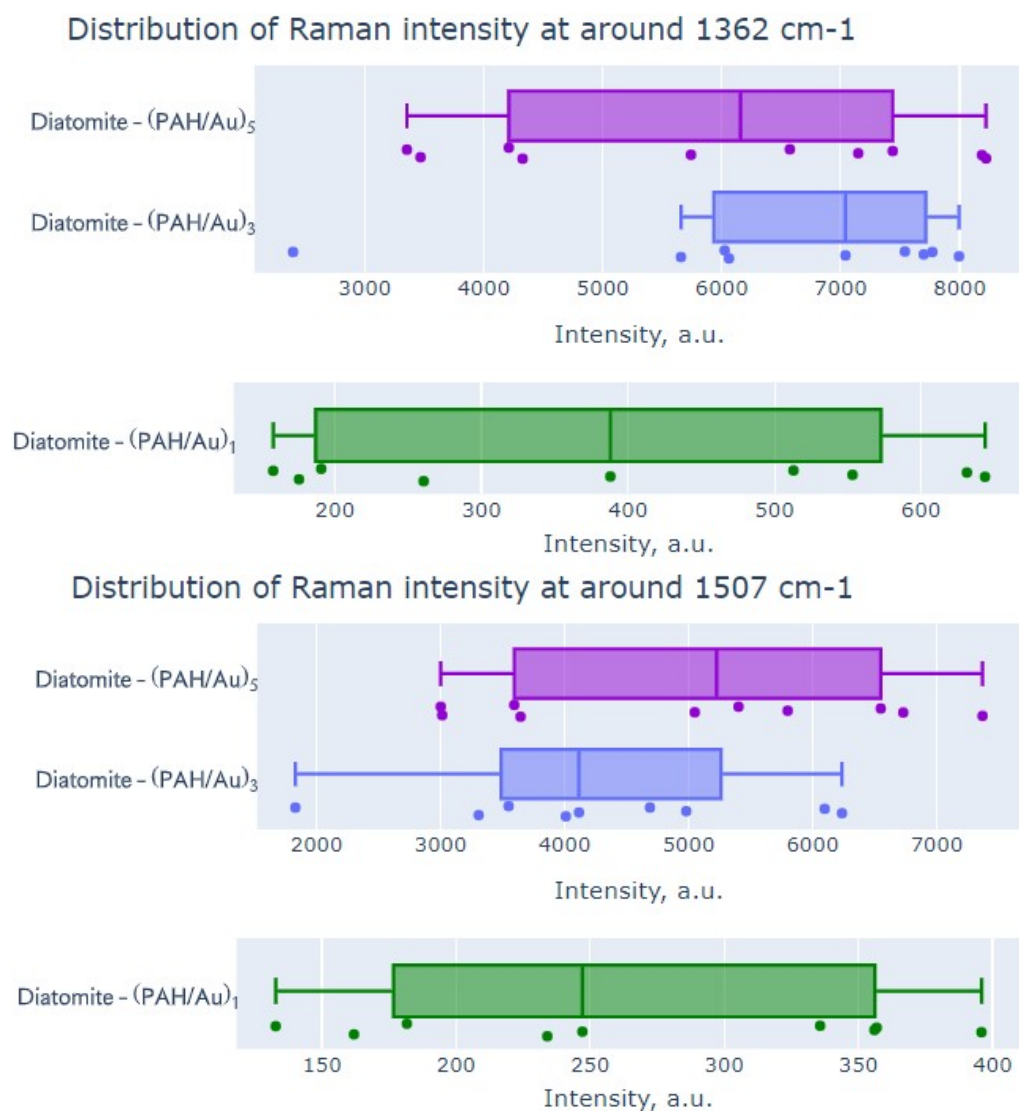


Figure S1. Distributions of peak intensities of two prominent peaks of R6G

In Table S1, mean intensity values and their relative standard deviations are calculated for each pair of prominent Rhodamine 6G (R6G) Raman peaks detected. For a general enhancement factor (EF) estimation

for the substrates, Raman modes at 1362 and 1509 cm^{-1} were used, as they correspond to benzene ring stretching and are the most prominent ones.

Table S1. Raman and SERS intensities

R6G			Diatomite-(PAH/Au) ₃				Diatomite-(PAH/Au) ₅			
Peak position, cm^{-1}	Mean intensity I_{RS} , a.u.	RSD	Peak position, cm^{-1}	Mean intensity I_{SERS} , a.u.	RSD	$\frac{I_{SERS}}{I_{RS}}$	Peak position, cm^{-1}	Mean intensity I_{SERS} , a.u.	RSD	$\frac{I_{SERS}}{I_{RS}}$
1368	122	41%	1363	7081	11%	58	1362	6426	26%	53
1512	120	44%	1509	4723	22%	39	1507	5523	27%	46

2. Enhancement Factor Calculation

The enhancement factor (EF) was calculated as follows:

$$EF = \frac{I_{SERS}/N_{surf}}{I_{RS}/N_{vol}} \quad (1)$$

where I_{RS} , I_{SERS} are Raman and SERS intensities of R6G, N_{surf} is the average number of R6G molecules adsorbed onto the gold-coated diatomite composite in the scattering area for the SERS measurements, and N_{vol} is the number of R6G molecules present in the bulk scattering volume for spontaneous Raman scattering measurements.

2.1. Determination of N_{surf}

To determine the average number of R6G molecules adsorbed onto the gold-coated diatomite composite in the scattering area, concentrations of bulk R6G before and after incubation with Diatomite-(PAH/Au)₃ layers were estimated by means of the calibration curve built for R6G absorption at 500 nm. A diatomite sample coated with three PAH/AuNPs bilayers was chosen, since sample with five PAH/AuNPs bilayers didn't demonstrate stronger enhancement.

To absorb R6G on diatomite with PAH/AuNPs layers, 120 μL of 200 μM R6G, that equals to 24 nmoles, were mixed with $V_{Dt} = 120 \mu\text{L}$ of Diatomite-(PAH/Au)₃ with concentration $c_{Dt} = 1.3 \cdot 10^8$ particles/mL, that equals to $N_{Dt} = 1.56 \cdot 10^7$ particles in solution.

According to spectroscopic data obtained, the concentration of non-absorbed R6G after incubation with gold-coated diatomite was 72 μM , that equals to 17.3 nmoles. We presume that the rest of R6G molecules, $n_{R6G}^{abs} = 6.7$ nmol, were absorbed on diatomites, therefore on average 1 diatomite adsorbed $2.6 \cdot 10^8$ particles:

$$\frac{N_{R6G}}{N_{Dt}} = \frac{n_{R6G}^{abs} \cdot N_A}{c_{Dt} \cdot V_{Dt}} = 2.6 \cdot 10^8 \text{ molecules/particle}$$

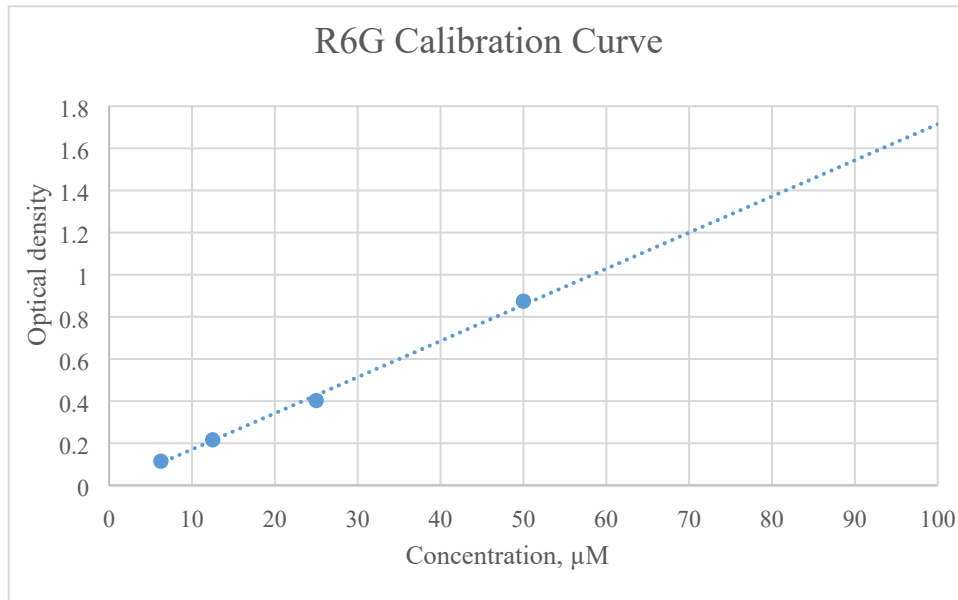


Figure S2. Calibration curve for R6G

Raman spectrometer was equipped with an objective having magnification $M = 10$ and the pinhole size Φ was set to $100 \mu\text{M}$. Therefore the laser spot size radius may be estimated as [Tomba et al. 2007, DOI: 10.1366/000370207779947477]:

$$r \approx \frac{\Phi}{2 \cdot 1.4 \cdot M} = 3.6 \mu\text{m}$$

Then the laser spot area

$$S = \pi r^2 = 40 \mu\text{m}^2$$

That is obviously greater than the diatomite size (see Figure 3), therefore we assume that we get a SERS signal from a single diatom. We also assume that we collect only a half of intensity that could be obtained from one diatomite, as irradiation and detection is provided from just one side, in a backscattering mode. Furthermore, only molecules in vicinity of AuNPs are enhanced, and according to SEM images (Figure 3) 15.5% of diatomite surface is covered with AuNPs, therefore

$$N_{surf} = \frac{1}{2} \cdot \frac{N_{R6G}}{N_{Dt}} * 0.155 = 2 \cdot 10^7 \text{ molecules}$$

2.2. Determination of N_{vol}

Liquid drop height h is around 0.5 mm . Assuming that for a given objective the whole height participates in Raman scattering, the volume participating may be found as

$$V_{RS} = S \cdot h = 2 \cdot 10^4 \mu\text{m}^3$$

Therefore, the number of R6G molecules participating in Raman scattering is

$$N_{vol} = V_{RS} \cdot c_{R6G} \cdot N_A = 2.4 \cdot 10^9 \text{ molecules}$$

2.3. Determination of the Enhancement Factor

Thus, according to Eq.(1) and data from Table , the EF may be estimated as

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{N_{vol}}{N_{surf}} \approx 6 \cdot 10^3$$