

Supplementary Information

Optothermal microbubble assisted manufacturing of nanogap-rich structures for active chemical sensing

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Work flow of nanogap-rich structure fabrication and active analyte sensing with an OGMB

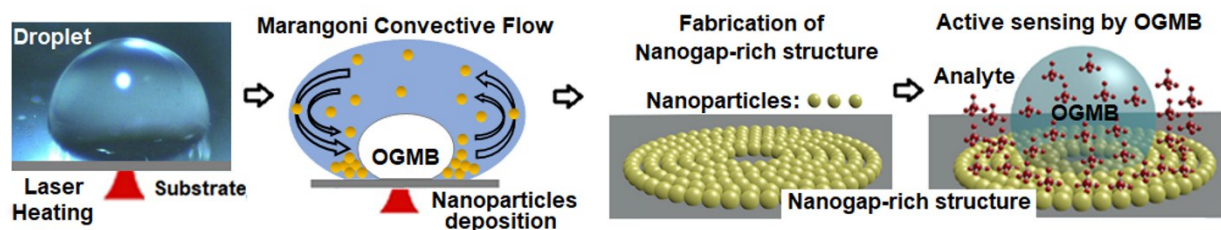


Fig. S1 Schematic of step-by-step procedures of manufacturing of nanogap-rich structure and active sensing of analytes through an OGMB

An OGMB is not only able to rapidly fabricate nanogap-rich structure through the accumulation of metallic nanoparticles but also guide and concentrate analytes towards the nanogap-rich structure for active sensing of analytes. Fig. S1 shows the work flow of this method as follows:

- 1) A droplet of nanoparticle solution is placed on a gold-coated cover glass. Fig. S1(a) shows an optical image of such a droplet.
- 2) An OGMB is generated inside the droplet of nanoparticle solution by laser heating. OGMB helps to fabricate nanogap-rich structure by accumulating nanoparticles on the gold-coated cover glass due to the convective flow around the OGMB as schematically shown in Fig. S1(b).
- 3) Fig. S1(c) schematically shows a nanogap-rich structure that is fabricated on a gold-coated cover glass. Optical images of such nanogap-rich structures can be found in Fig. 1(b) and Fig. 1(e) in the text of main article.
- 4) Analyte solution is then placed on top of the nanogap-rich structure for SERS detection with both passive sensing and active sensing.

Passive sensing: Analytes are let freely diffuse to the nanogap-rich structure and then SERS spectra of the analytes are obtained from the surface of the nanogap-rich structure. The schematic of passive sensing method is shown in the inset of Fig. 2 (b) and Fig. 3(b) of the of main article.

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Active sensing: Analytes are guided and concentrated towards the nanogap-rich structure by generating an OGMB from analyte solution on the nanogap-rich structure. SERS spectra of the analytes are then obtained from the surface of the nanogap-rich structures. Active sensing of analytes is schematically shown in Fig. S1 and in the inset of Fig. 2 (d) and Fig. 3(d) of the of main article.

Movie S1

Movie S1 demonstrates how nanoparticles are attracted towards an OGMB due to the Marangoni convective flow and deposited on the substrate to rapidly fabricate a ring-shaped nanogap-rich structure.

Stability of nanogap-rich structure

Stability of nanogap-rich structures is tested by sonicating the nanogap-rich structure for 10 minutes in DI water. Fig. S2(a) and Fig. S2(b) show a nanogap-rich structure before and after sonication, respectively which demonstrates a stable nanogap-rich structure after 10 minutes of sonication.

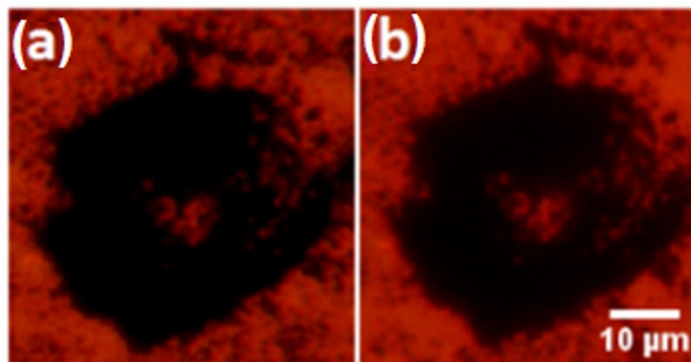


Fig. S2 Nanogap-rich structure (a) before sonication (b) after 10 minutes sonication.

Enhancement factor (EF) of nanogap-rich structures due to passive sensing

Before we apply the active sensing method of analytes, the average SERS enhancement factors of two nanogap-rich structures were calculated due to the passive sensing of analytes. The average SERS enhancement factors (EF) of two nanogap-rich structures, i.e. gold-nanosphere-structure and gold-nanoshell-structure, were calculated through the comparison of the Raman signals collected from R6G at a concentration of 10 mM in the absence of the nanogap-rich structures and the SERS signals obtained from 0.1 μM R6G on the nanogap-rich structures according to the following formula: ^{1,2}

$$EF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}} \quad (1)$$

Where, I_{SERS} = Raman intensities of R6G at 1364 cm^{-1} on the nanogap-rich structure.

$I_{RS=}$ Raman intensities of R6G at 1364 cm^{-1} in the absence of nanogap-rich structure.

$C_{RS} = 10 \times 10^{-3}$ M is the concentration of R6G solution for normal Raman spectrum measurement.

$C_{SERS} = 1 \times 10^{-7}$ M is the concentration of R6G solution for SERS measurement.

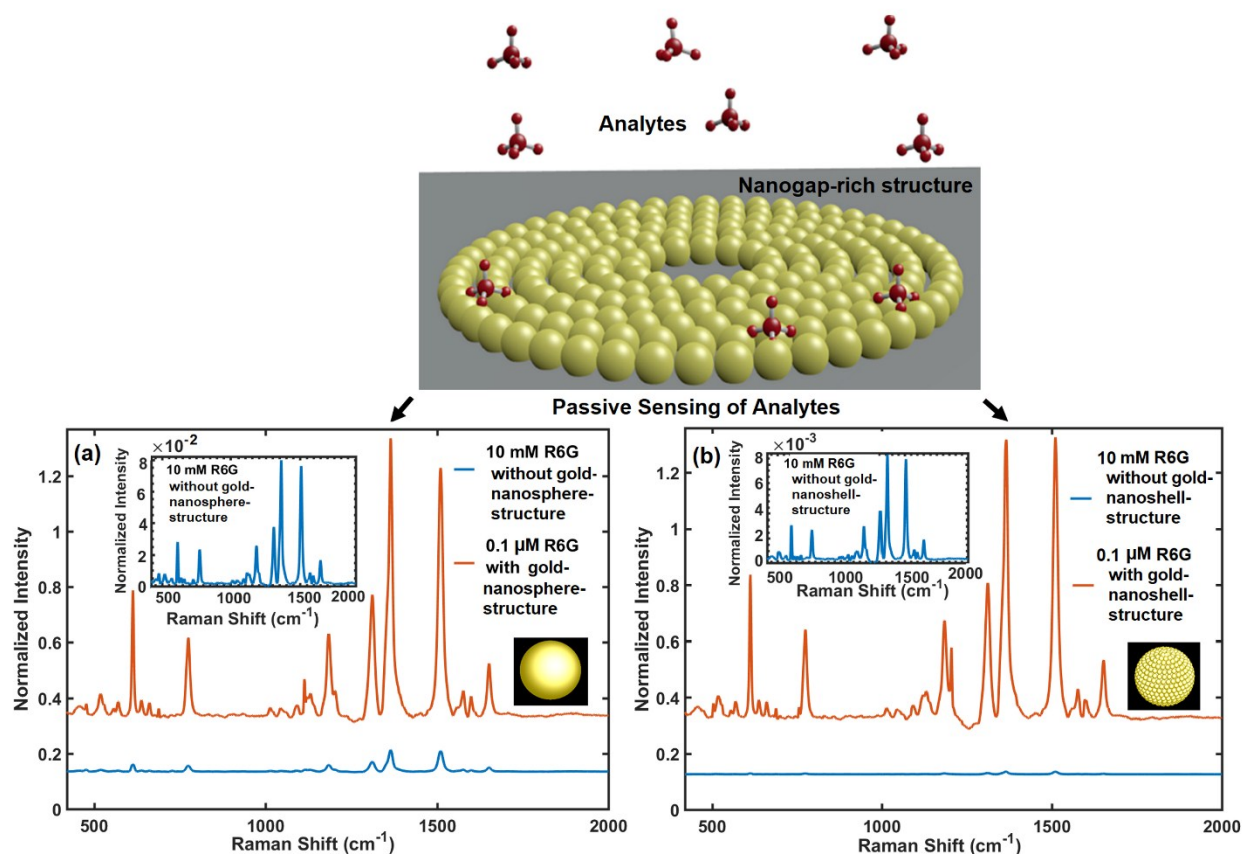


Fig. S3 (a) Normalized Raman intensity of R6G at 1364 cm^{-1} in the absence of gold-nanosphere-structure (blue curve) and on gold-nanosphere-structure (red curve). Inset: Magnified Raman signal for R6G (10 mM) in the absence of gold-nanosphere-structure. (b) Normalized Raman intensity of R6G at 1364 cm^{-1} in the absence of gold-nanoshell-structure (blue curve) and on gold-nanoshell-structure (red curve). Inset: Magnified Raman signal for R6G (10 mM) in the absence of gold-nanoshell-structure. The image on top depicts that passive sensing is used to obtain these data.

Fig. S3 (a) and Fig. S3 (b) show the normalized Raman intensity of $0.1\text{ }\mu\text{M}$ R6G at 1364 cm^{-1} on the gold-nanosphere-structure and gold-nanoshell-structure, respectively (red curve). The corresponding Raman signal of 10 mM of R6G in the absence of nanogap-rich structures are also shown (blue curve). According to the above formula the average SERS enhancement factor (EF) was calculated from four sets of experimental data and average SERS EF are 1.2×10^6 and 1.1×10^7 for gold-nanosphere-structure and gold nanoshell-structure, respectively. These are the enhancement factors of nanogap-rich structures due to the effect of passive sensing of analytes which is also depicted in Fig. S3. These SERS enhancement factors for gold nanospheres and gold nanoshells are comparable to previously reported SERS EF for many conventional SERS substrates that have been reported in the literature.¹⁻⁴

R6G concentration with an OGMB

A droplet of R6G solution with a concentration of $1\ \mu\text{M}$ is placed on a gold film. An OGMB is then generated from R6G solution on the gold film to concentrate R6G as schematically shown in Fig. S4(a).

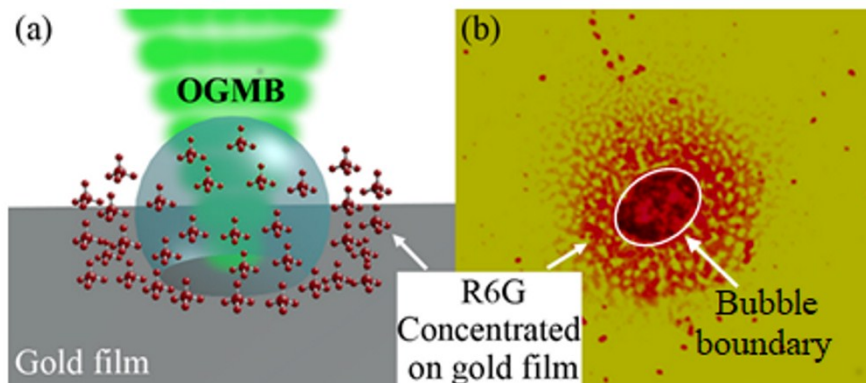


Fig. S4 (a) Schematic of R6G concentration on a gold film with an OGMB. (b) Optical image of R6G molecules concentrated on a gold film through an OGMB.

Due to the strong Marangoni convective flow associated with the OGMB, R6G molecules are attracted towards OGMB and eventually concentrated on the gold film where the OGMB is located. Fig. S4(b) shows the optical image of R6G molecules which are concentrated on the gold film with an OGMB. The black spots in Fig S4 (b) is a result of R6G damage from laser heating. The damage only happens inside the OGMB, because R6G outside of the OGMB are isolated by OGMB as schematically shown in Fig. S4(a). The Raman data in this work were collected from the undamaged areas of the concentrated R6G, which are the outside areas of the bubble boundary as shown in Fig S4 (b).

Active sensing of malachite green (MG)

Malachite Green (MG) is an organic dye and widely used in aquaculture industry, fish farms, and fresh water aquaria due to its effective fungicide effect. However, the use of MG is controversial and banned in some countries due to its hazardous and genotoxic nature.²

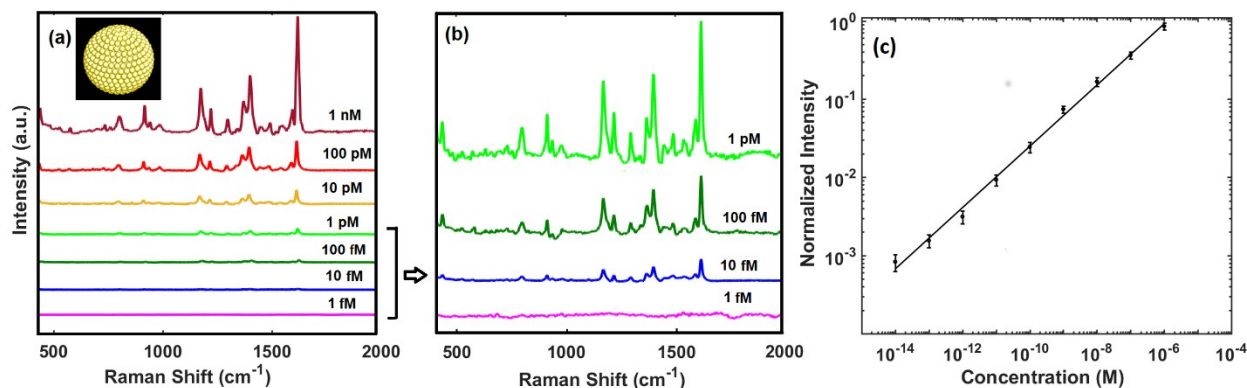


Fig. S5 (a) SERS spectra of MG at different concentrations (1 nM to 1 fM) collected from gold-nanoshell-structure by applying the active sensing method. (b) Magnified spectra of MG corresponding to lower

concentrations (1 pM to 1 fM) of MG indicated in (a) by an arrow. (c) Normalized SERS intensity of MG at $1,619\text{ cm}^{-1}$ versus MG concentration due to active sensing of MG.

Fig. S5 (a) shows the SERS spectra of MG on a gold-nanoshell-structure at different concentrations by applying the active sensing method. Fig. S5 (b) shows the SERS spectra of MG at lower concentrations. MG is detectable at a concentration of 10 fM through the active sensing method. The following characteristic Raman peaks of MG are observed, which corresponds to N-C bonding and C-C stretching at 1619 cm^{-1} , N-phenyl stretching at 1402 cm^{-1} , C-H in-plane bending at 1174 cm^{-1} and 1298 cm^{-1} , N-C stretching at 1369 cm^{-1} and C-H out-of-plane bending at 918 cm^{-1} and these peaks are closely coincide with the reported Raman peaks of MG.^{2,5} Fig. S5 (c) shows the normalized SERS intensity of MG at 1619 cm^{-1} as a function of MG concentration. The experimental data (circles) are fitted by the equation of $\log_{10}(y) = 0.39 \log_{10}(x) + 2.31$ with $R^2=0.996$. Here, x is the concentration of MG and y is the normalized SERS intensity of MG at 1619 cm^{-1} .

Effect of gold-coating on glass substrate for OGMB generation

As mentioned in the text of main article, gold coating on cover glass is not a pre-requirement for generating OGMB. As discussed in our previous publication,⁶ OGMB can also be generated on a glass substrate without gold film. However, gold coating can enhance laser heating effect and reduce the required laser intensity to generate OGMB.

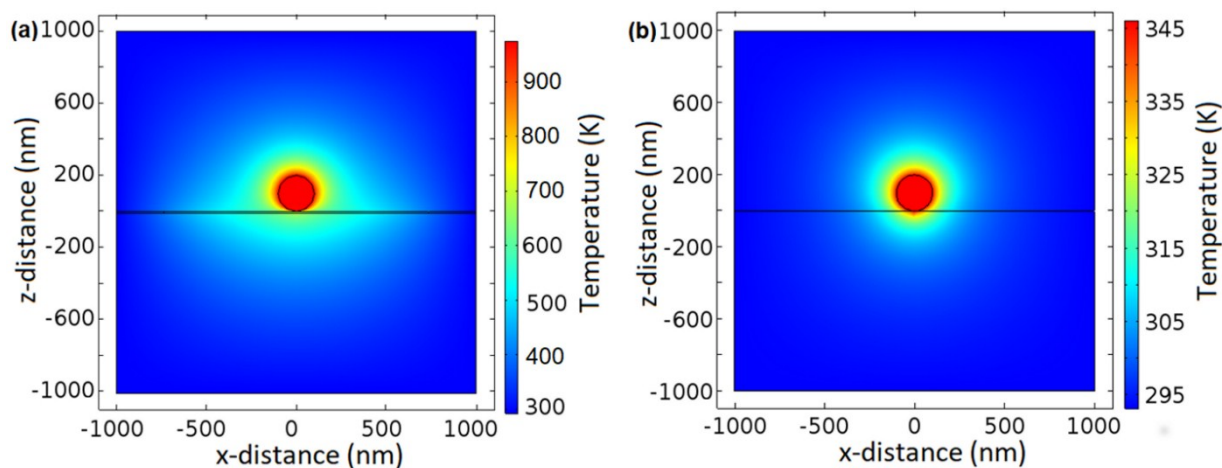


Fig. S6 COMSOL Multiphysics simulated profile of temperature distribution of 200 nm gold-nanosphere on (a) gold-coated cover glass (b) cover glass without gold-coating.

Fig. S6 (a) shows temperature distribution of a 200-nm gold nanosphere on a cover glass coated with a 10-nm thick gold film simulated with finite element method (COMSOL Multiphysics). Fig. S6 (b) shows the temperature distribution of same gold nanosphere on a glass substrate without gold film. According to Fig. S6, under the same laser intensity, temperature of gold nanosphere on gold-coated substrate is around three times higher than that on the glass substrate without gold film. So, higher temperature of nanosphere on gold-coated substrate allows us to generate an OGMB at a lower laser intensity. Fig. S7

(a) and Fig. S7 (b) illustrate two gold-nanosphere-structures that are fabricated on a gold-coated cover glass and a cover glass without gold coating at a laser intensity of $34 \text{ mW}/\mu\text{m}^2$ and $171 \text{ mW}/\mu\text{m}^2$, respectively for 2 minutes of laser exposure time. Therefore, the required laser intensity for gold-coated cover glass is five times lower than that for the cover glass without gold coating.

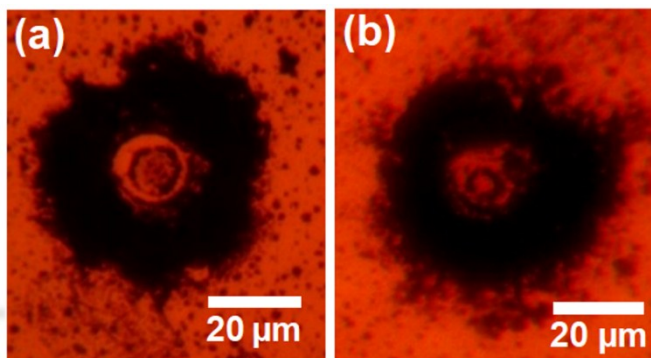


Fig. S7 Nanogap-rich structure fabricated from gold-nanosphere on (a) gold-coated cover glass (b) cover glass without gold coating.

Effect of OGMB duration on active sensing

Fig. S8 (a) shows the optical image of an OGMB with $175 \pm 2 \mu\text{m}$ size which was generated on a gold-nanoshell structure during the active sensing of R6G. The time duration of OGMB generation was 2 minutes. Fig. S8 (b) shows the experimental results of the SERS intensity of R6G at 1364 cm^{-1} on a gold-nanoshell structure as a function of the duration of an OGMB. The concentration of the R6G was 1 nM ($1 \times 10^{-9} \text{ M}$). Fig. S8 (b) shows that, the sensitivity of SERS intensity increases with increasing the OGMB duration until it saturates at around 3.5 minutes. The SERS intensity has been normalized to the maximum SERS intensity at 3.5 minutes. Therefore, the sensitivity of the detection increases with increasing the OGMB duration until this saturation happens.

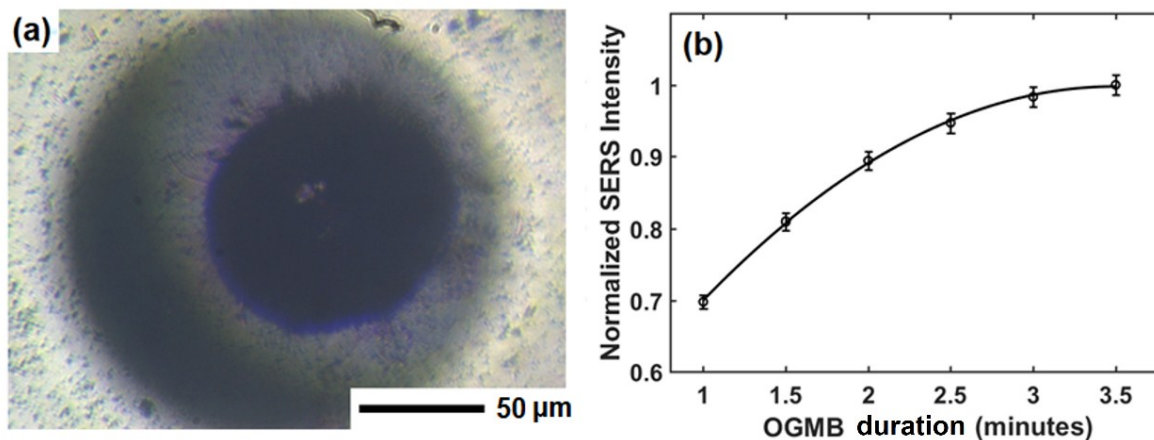


Fig. S8 (a) An OGMB generated on a gold-nanoshell structure for active sensing of R6G. (b) Normalized SERS intensity of R6G as a function of OGMB duration in active sensing.

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