

Quasi Optical Cavity of Hierarchical ZnO Nanosheets@Ag Nanoravines with Synergy of Near- and Far-Field Effects for *In Situ* Raman Detection

Jing Yu,^{†,‡,§} Yu Guo,^{‡,§} Huijie Wang,[§] Shuai Su,[†] Chao Zhang,^{*,‡} Baoyuan Man,[‡] and Fengcai
Lei^{*,†}

[†] College of Chemistry, Chemical Engineering and Materials Science, Institute of Biomedical
Sciences, Shandong Normal University, Jinan, 250014, P.R. China.

[‡] School of Physics and Electronics, Institute of Materials and Clean Energy, Shandong Normal
University, Jinan, 250014, P.R. China.

[§] School of Physics and Information Engineering, Shanxi Normal University, Linfen, 041004, P.
R. China.

[†] College of Animal Science and Technology, Shandong Agricultural University, Taian, 271018,
P. R. China.

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1. Experimental section

1.1 Materials

The zinc oxide (ZnO, AR, $\geq 99.0\%$), sodium hydroxide (NaOH, AR, $\geq 96.0\%$), rhodamine 6G (R6G, BS), malachite green (MG, BS, $\geq 95.0\%$), Sudan I (BS, $\geq 95.0\%$), crystal violet (AR) and silver wire (Ag, $\geq 99.99\%$) were all purchased from Sinopharm Chemical Reagent Co. Ltd.; the polydimethylsiloxane (PDMS) film with thickness of 50 μm and the target of zinc oxide ($\geq 99.9\%$) were obtained from Hangzhou Bald Advanced Materials CO. Ltd. and Deyang ONA new materials Co. Ltd., respectively.

1.2 Preparation of ZnO NSs@Ag NRs

Firstly, the ZnO seed layer was prepared upon the PDMS film via magnetron sputtering with power of 100 W and sputtering time of 300 s. Then, the near-saturated precursor solution was obtained by dissolving 8 g NaOH and 1.8 g ZnO in 20 mL deionized water with continuous stirring for 10 min. After that, the precursor solution was diluted at 40 times to synthesize the ZnO NSs followed by the process of immersing the prepared PDMS film into the diluted solution for several minutes. Finally, the AgNRs were covered on the surface of the ZnO NSs by thermal evaporation: In detail, 0.0015 g Ag wire with the length of 1 cm was put into a molybdenum boat, and the prepared PDMS substrate with ZnO NSs was placed on the top of molybdenum boat (the distance was 15 cm). The pressure was 6×10^{-3} Pa and the current was set as 90 A.

1.3 Raman detections

Raman spectra were recorded by the Horiba HR Evolution 800 Raman microscope system using a 50 \times objective and laser of 532 nm with power of 0.048 mW, and the integration time was 8 s throughout the experiment, where the diffraction grid was selected as 1800 gr/mm. All the data in

the Raman spectra were averages collected from five different points on a same substrate, and the error bars in figures were estimated as the normal ‘measurement uncertainty’.

1.4 Self-cleaning test

The substrate was firstly immersed in the solution of R6G for 3 h to adsorb sufficient molecules, then washed with the deionized water to remove the residual ones on its surface, and the Raman test was subsequently processed. After that, the substrate was immersed in 5 mL water and exposed under the UV light (365 nm, 20 W) for 30 min, and then the Raman test was processed again. To evaluate the reusability, several cycles of this process were done.

2. Theoretical section

2.1 FDTD simulations

Five structures, including ‘ZnO seed layer’, ‘vertical ZnO NSs’, ‘vertical ZnO NSs@Ag NRs’, ‘inverted ZnO NSs@Ag NRs’ and ‘exfoliated ZnO NSs@Ag NRs’, were built in the simulations. The ZnO seed layer consisted of a zinc oxide film (thickness of 30 nm) and a PDMS film (thickness of 50 μm), wherein the former one covered on the later one. The vertical ZnO NSs were built upon the ZnO seed layer with thickness of 30 nm, length and width of 600 nm, angle with the Z axis of 15°, and four of them wrapped around each other to form a QOC. The Ag NRs covered continuously on the surfaces of ZnO seed layer and ZnO NSs to form the vertical ZnO NSs@Ag NRs, composed of a number of adjacent Ag NBs of 5 nm thickness, 30 nm length and width, spaced 2 nm apart. The inverted ZnO NSs@Ag NRs was the same with the vertical one, excepting for the opposite direction of the incident light. The periodic and perfectly matched layer absorbing boundary conditions were respectively used in the XY and Z directions in all above four structures. Three separated ZnO NSs@Ag NRs stacked together to form the structure of exfoliated ZnO

NSs@Ag NRs, and in this simulation the perfectly matched layer absorbing boundary condition was adopted in all directions of XYZ. The refractive index data of Ag, ZnO and PDMS were obtained from Ref. 1-3, respectively,¹⁻³ and the wavelength of both the incident and monitoring lights were set as 532 nm, consisting with the one used in experiment. No particular molecular adsorption was involved in these simulations.

2.2 Enhancement factor

According to the standard equation of the EF:

$$EF = \frac{\left(\frac{I_{ERS}}{N_{ERS}} \right)}{\left(\frac{I_{RS}}{N_{RS}} \right)} = \frac{N_{RS}}{N_{ERS}} \times \frac{I_{ERS}}{I_{RS}} \quad (1)$$

where N_{ERS} and N_{RS} are the numbers of probe molecules contributing to the inelastic scattering intensity, respectively, evaluated by enhanced and normal Raman scattering measurements and I_{ERS} and I_{RS} are the corresponding intensities. In our experiments, the Raman signals are *in situ* collected from the substrates immersed in solution. Thus, the N_{RS}/N_{SERS} can be calculated as:

$$\frac{N_{RS}}{N_{ERS}} = \frac{C_{RS} \times V_{RS} \times N_A}{C_{ERS} \times V_{ERS} \times N_A} \quad (2)$$

where C (C_{RS} and C_{ERS}) is the molarity of the probe molecules, V (V_{RS} and V_{ERS}) is the corresponding volume irradiated by the laser spot, and N_A is Avogadro's constant. In our experiments, the V_{RS} equals to the V_{ERS} . Thus, the EF can be further estimated as:

$$EF = \frac{I_{ERS}}{I_{RS}} \times \frac{C_{RS}}{C_{ERS}} \quad (3)$$

In this paper, the substrate with vertical ZnO NSs is selected as the reference, and its corresponding Raman performance is shown in Figure 2b (R6G of 10^{-2} M). Choose intensity of peaks of 613 cm^{-1} , 774 cm^{-1} and 1364 cm^{-1} as the standard values (ZnO NSs@Ag NRs, R6G of 10^{-12} M), the EFs

can be obtained as ca. 5.76×10^9 , 3.43×10^9 and 2.30×10^9 , respectively, and thus the average EF can be estimated as 3.83×10^9 . This value is an average collected from the irradiation area, contributed by both the LHSs and the SHSs.

3. Discussions on other Raman tests

3.1 Reproducibility, uniformity and stability

Figure S3a shows the intensity changes of some characteristic peaks of R6G (10^{-8} M) collected from ZnO NSs@Ag NRs which are prepared by twenty different batches. No significant changes are observed in this figure except for slight fluctuations, indicating good reproducibility of the preparation process. To evaluate the uniformity of this substrate, Raman mapping of R6G (10^{-8} M, peak of 613 cm^{-1}) over an area of $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ is tested in our experiment, with results shown in Figure S3b, where the relatively uniform colour distribution implies that the base is highly homogeneous. In addition, the storage time does not affect the Raman performance of the substrate when it is stored in the air without any protective measures. Figure S4 shows that the Raman spectra of R6G remain unchanged after 12-days storage of substrate, indicating that the substrate possesses fine stability.

3.2 Erasable property

According to previous reports, both the ZnO and the Ag are highly efficient photocatalysts,^{4, 5} and the combination of them will lead to well co-catalytic effect. On one hand, the LSPR effect of Ag NR can concentrate the incident lights around them, and on the other hand the excited hot electrons by Ag NR can be transferred to the surface of ZnO NS to enhance its catalytic activity. In the experiment, R6G molecules can be completely degraded if the ZnO NSs@Ag NRs is exposed on UV light (with residual R6G on its surface) for 30 mins in water, and the subsequent

Raman tests show that the irradiation don't change the Raman performance of the substrate (Figure S6a). Figure S6a shows that after 5 exposures, the substrate can still maintain the original Raman enhancement, indicating that the substrate has excellent rewritability, which is very important for practical applications. Figure S6b is a schematic of the co-catalytic reaction of ZnO and Ag.

4. Figures

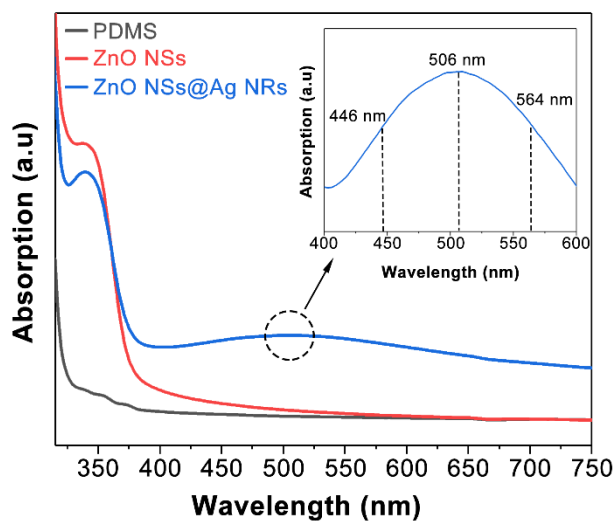


Figure S1 Absorption spectra of the PDMS, ZnO NSs and ZnO NSs@Ag NRs, respectively.

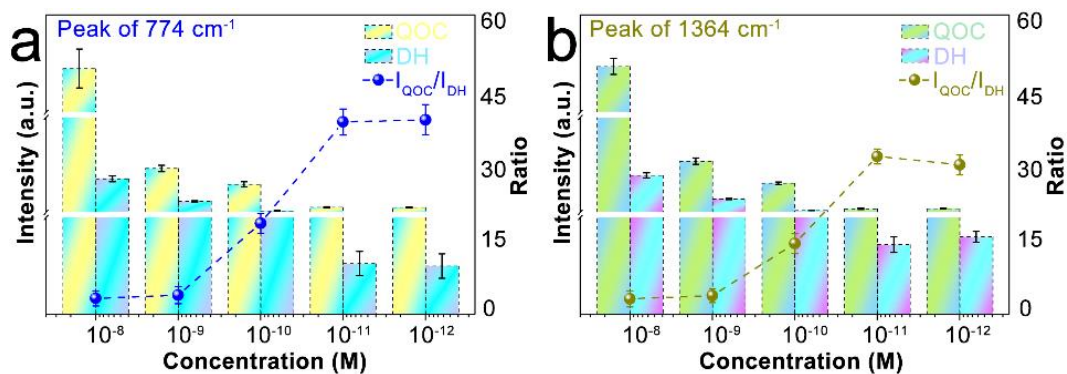


Figure S2. Intensity comparisons of peak 774 cm^{-1} (a) and 1364 cm^{-1} (b) of R6G detected by vertical and exfoliated ZnO NSs@Ag NRs, respectively.

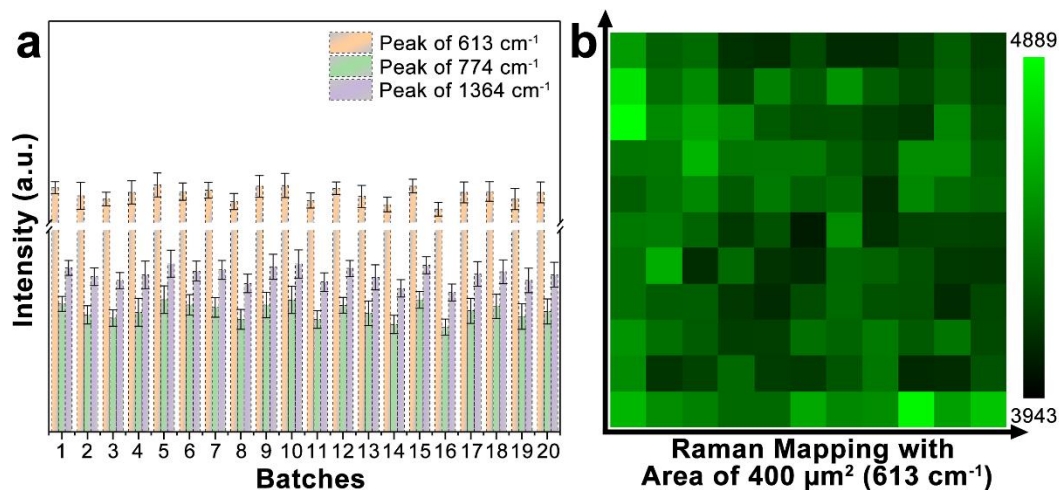


Figure S3. (a) intensity changes of some characteristic peaks of R6G (10⁻⁸ M) detected by ZnO NSs@Ag NRs with twenty different batches, (b) Raman mapping with area of 400 μm² for peak 613 cm⁻¹ (R6G, 10⁻⁸ M).

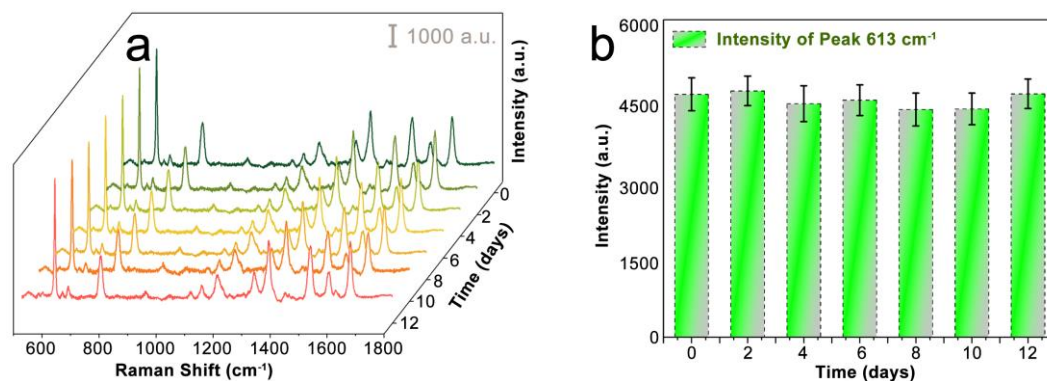


Figure S4. (a) Raman spectra of R6G (10⁻⁸ M) detected by ZnO NSs@Ag NRs after long-time storage, (b) intensity changes of peak 613 cm⁻¹ in (a).

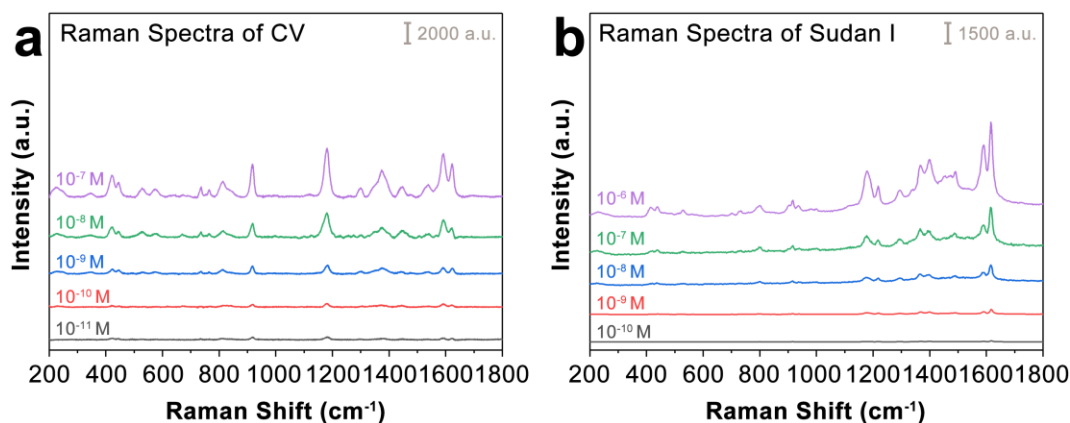


Figure S5. (a) *in situ* detections of CV (10^{-7} M to 10^{-11} M) and (b) Sudan I (10^{-6} M to 10^{-10} M), respectively.

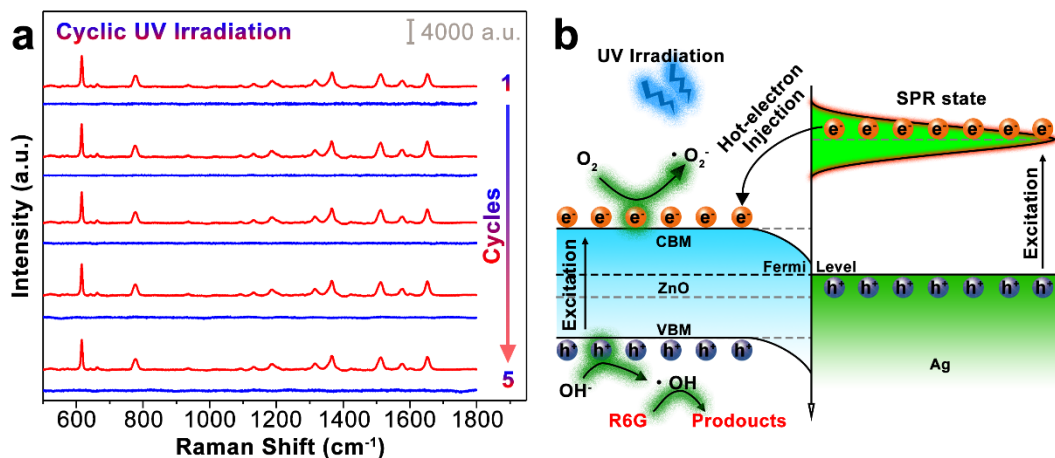


Figure S6. (a) cyclic Raman detections of R6G (10^{-8} M) after the UV irradiation (365 nm) in water, (b) the photodegradation of R6G by the co-catalytic reaction of ZnO NSs@Ag NRs.

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