Supporting information

Controllable synthesis of AgNWs@PDA@AgNPs core-shell nanocobs based on a mussel-inspired polydopamine for highly sensitive SERS detection

Zhiliang Zhang ^{a,c*} Tiantian Si^b Jun Liu^a Kehui Han^b and Guowei Zhou^{b*}

^aState Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353, PR China ^bSchool of Chemistry and Pharmaceutical Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China ^cBeijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Science, Beijing 100190, China.

Email: zhzhl@iccas.ac.cn



Fig. S1 (a) the XRD spectrum of AgNWs@PDA in the range of 10-35°, TEM images of (b) AgNWs, (c) AgNWs@PDA and (d) AgNWs@PDA@AgNPs respectively.



Fig. S2 (a) Raman spectra of R6G molecules from 10^{-7} to 10^{-11} M on AgNWs substrate and (b) Raman spectra of R6G molecules from 10^{-7} to 10^{-9} M on AgNWs@PDA substrate.



Fig. S3 (a) SERS spectra of R6G molecules $(1 \times 10^{-6} \text{ M})$ on AgNWs, AgNWs@PDA, AgNWs@PDA@AgNPs and AgNPs, (b) SERS spectra of R6G of concentrations from 10^{-7} to 10^{-11} M collected from the as-prepared AgNPs substrate.



Fig. S4 (a) the correlation between R6G concentration and Raman peak intensity, (b) SERS spectra of R6G solutions on 10 mm² AgNWs@PDA@AgNPs substrate and Raman spectrum of 40 μ L 1×10⁻⁵ M R6G solution on 20 mm² silicon wafer substrate.



Fig. S5 (a) SERS spectra of R6G at different concentrations $(10^{-7} \text{ to } 10^{-10} \text{ M})$ on AgNWs@PDA substrate after regulating the PDA thickness to 10 nm and (b) the respective SERS spectra of R6G molecules from 10^{-7} to 10^{-11} M on AgNWs@PDA@AgNPs substrate with the PDA thickness to 10 nm.



Fig. S6 (a) the typical SERS spectra of R6G collected over an area of 20 μ m × 20 μ m at 2 μ m intervals, and (b) the SERS spectra of an R6G aqueous solution (10⁻⁸ M) on AgNWs@PDA@AgNPs substrate.

Part 2. Calculation of enhancement factor

The average SERS enhancement factor (EF) of the AgNWs@PDA@AgNPs core-shell nanocobs was determined by computing the ratio of SERS to normal Raman scattering (NRS) of R6G, where the detailed distribution of singular molecules EF was not considered. EF could be defined using the following expression:

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

where I_{SERS} and I_{RS} represented the intensities of the same band of the SERS spectra and the Raman spectra (non-SERS)respectively, and N_{SERS} and N_{RS} represented the number of molecules on the substrates within the laser spot.

During the SERS examination, a certain concentration C_{SERS} and volume V_{SERS} R6G aqueous solution was dispersed to an area S_{SERS} on the AgNWs@PDA@AgNPs substrates. For normal Raman experiment, dispersed a certain volume V_{RS} and concentration C_{RS} R6G ethanol solution to an area of S_{RS} on cleaned silicon wafer and dried in the air. The above equation becomes:

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{S_{SERS}V_{RS}C_{RS}}{S_{RS}V_{SERS}C_{SERS}}$$

Raman measurements were conducted under identical experimental conditions (laser wavelength, laser power, microscope objective/lenses, accumulation time). In the experiments, 10 μ L 10⁻¹² M R6G (detection limit) solution was dispersed to an area of about 10 mm² for the AgNWs@PDA@AgNPs nanocobs and 40 μ L 1×10⁻⁵ M R6G ethanol solution was dispersed to an area of about 20 mm² on a silicon wafer substrate. Fig.S4 shows the SERS spectrum and the Raman spectrum of R6G from the above-mentioned substrates. The intensities for the C–C–C in-plane bend mode at 612 cm⁻¹ are 262 units for solid R6G and 1361 units for AgNWs@PDA@AgNPs nanocobs. According to the above equation, the average EF is calculated to be 6.49×10⁷ for the AgNWs@PDA@AgNPs nanocobs.