Supplementary data of

# A $CO_2$-tunable Plasmonic Nanosensor based on Interfacial Assembly of Gold Nanoparticles on Diblock Copolymers Grafted from Gold Surface

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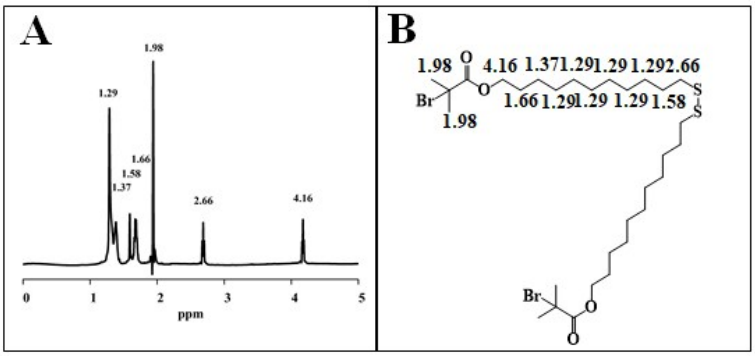


Figure S1. (A) H-NMR spectra of the DTBU initiator; (B) chemical structure of the DTBU initiator.

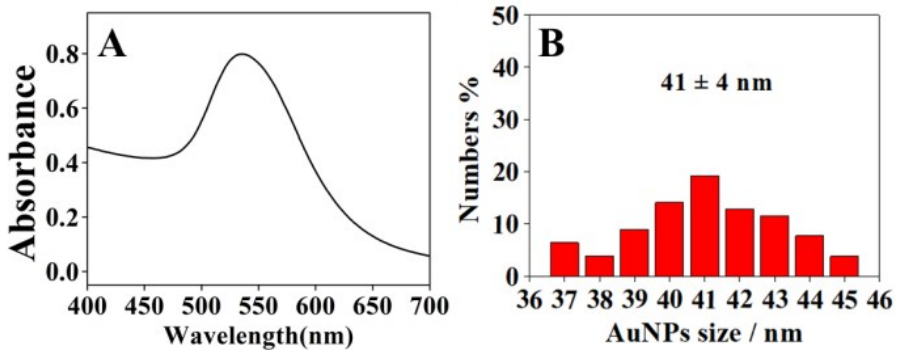


Figure S2. (A) UV-vis spectra of the prepared gold nanoparticles; (B) AuNPs size statistics of SEM images (a) in Figure 2.

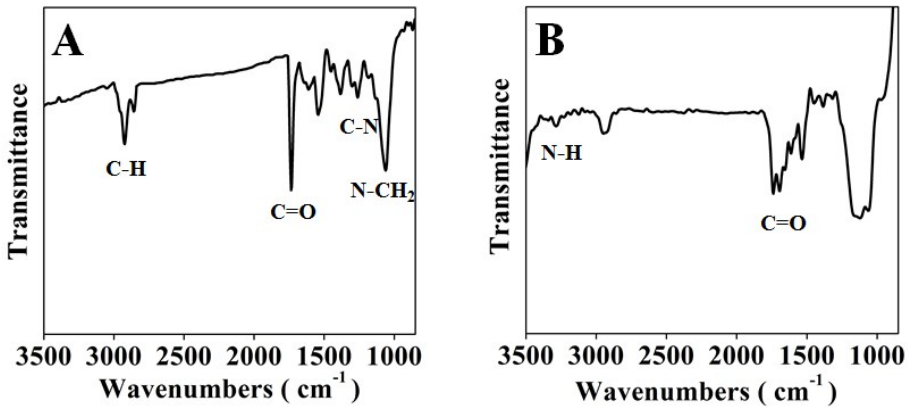


Figure S3. FT-IR spectra of Au film-PDEAEMA (A)and Au film-PDEAEMA-PAAm (B) synthesized by sequential SI-ATRP.

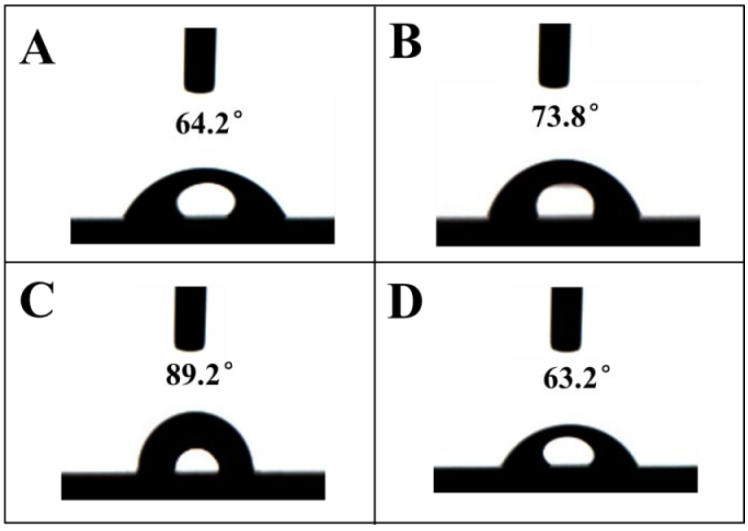


Figure S4. Micrographs of water droplets on gold surface (A), gold surface coated with initiator (B), Au film-PDEAEMA (C) and Au film-PDEAEMA-PAAm(D).

Samples were dried in $N_2$ flow.

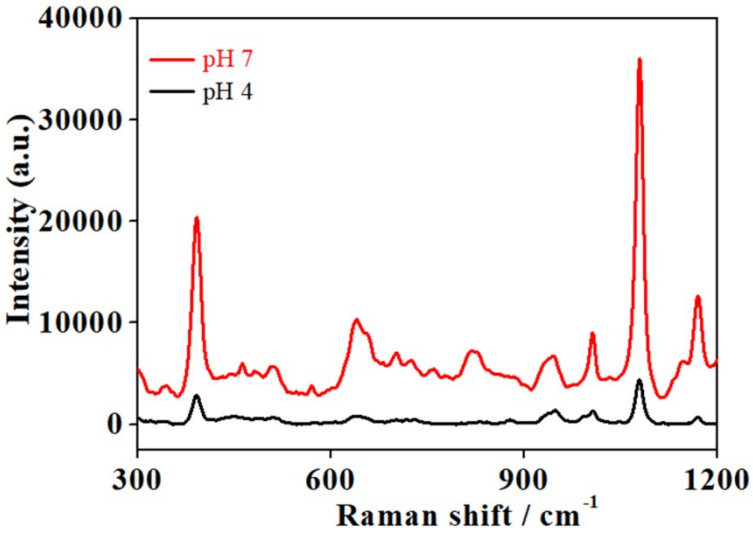


Figure S5. SERS spectrum of $10^{-5}$ M 4MPh adsorbed on the optimal SERS substrates, alternating pH to 4 and 7 by HCl and NaOH in water solution. The acquisition time was 2s.

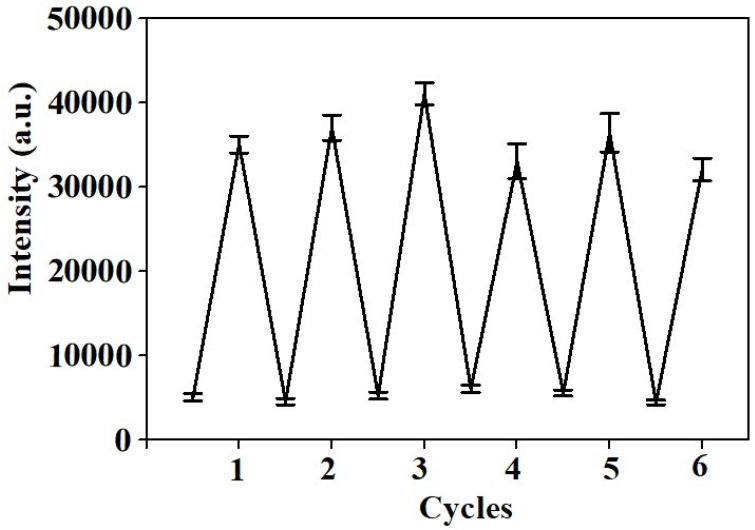


Figure S6. SERS spectrum of $10^{-5}$ M 4MPh adsorbed on the optimal SERS substrates, alternating bubbling with $CO_2$ and $N_2$ in water solution. Error bar is calculated with 5 repeats. The acquisition time was 2s.

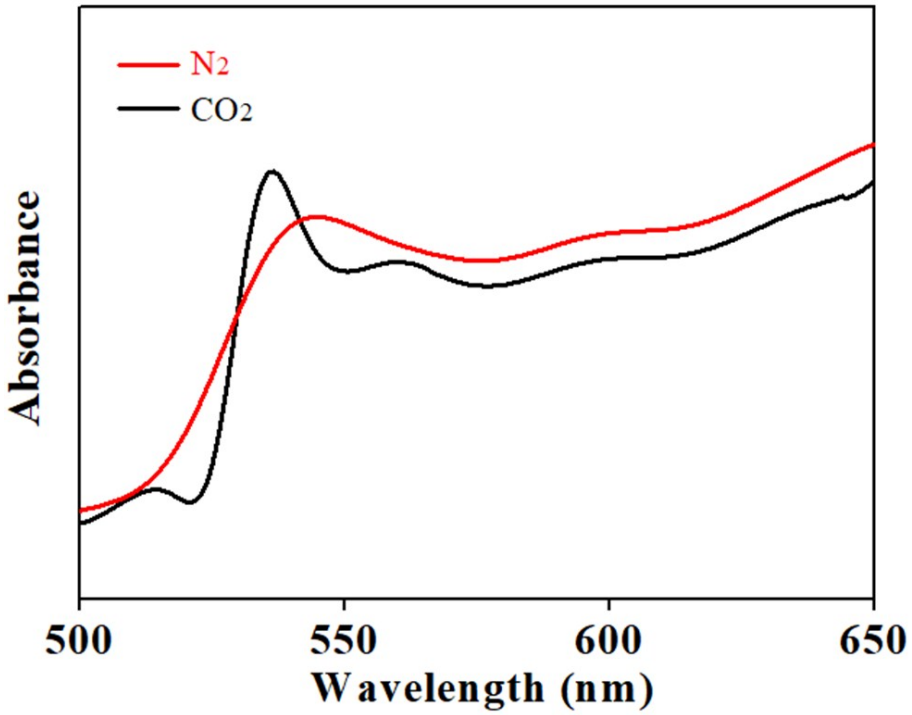


Figure S7. UV-vis spectra of Au film-PDEAEMA-PAAm-AuNPs with immersion times of 10 h in $N_2$ saturated water solution or $CO_2$ saturated water solution.

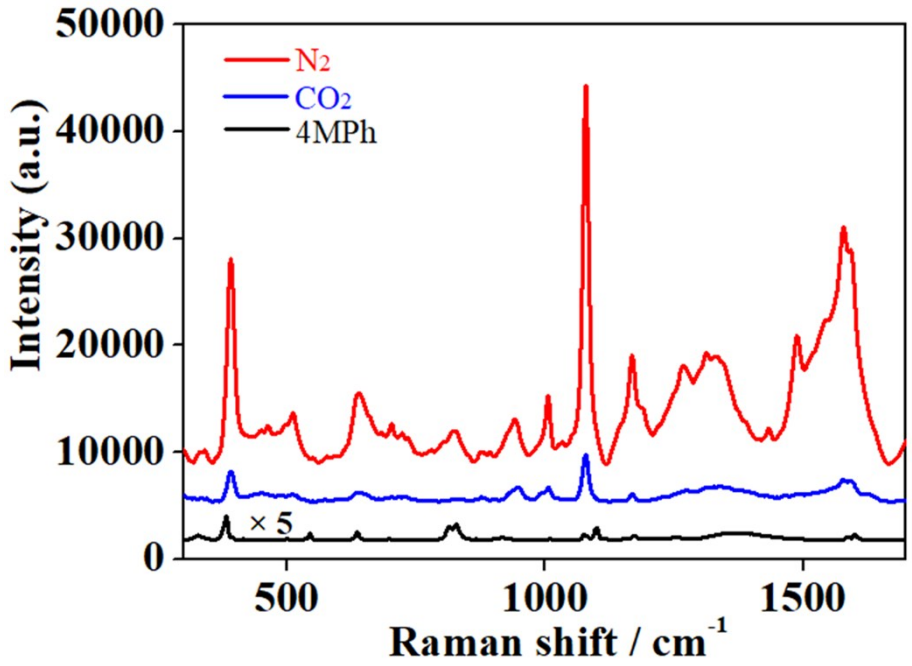


Figure S8. SERS spectrum of $10^{-5}$M 4MPh adsorbed on the optimal SERS substrates, detected after bubbling with $CO_2$ or $N_2$ in water solution; Normal Raman spectrum of solid 4MPh; The acquisition time was 2 s.

Table S1. Experimental Frequencies ($cm^{-1}$) and Assignments of Vibrations of Solid 4MPh and 4MPh on the optimal SERS substrates

| solid 4MPh | SERS | vibrational assignments |
|---|---|---|
| 382 | 392 | 7a |
| 636 | 638 | 12 |
| 828 | 825 | 17b |
| 1010 | 1009 | 18a |
| 1101 | 1080 | 1 |
| 1171 | 1173 | 9a |
| 1601 | 1578 | 8a |

In SERS, the peak at 1080 $cm^{-1}$ is assigned to its aromatic ring breathing vibration $\nu_1$, the other peaks at 392, 638, 825, 1009, 1173, 1587 $cm^{-1}$ are correspond to the ring vibration of of 7a, 12, 17b, 18a, 9a, and 8a of 4MPh,respectively.

(1) EF Calculation

To evaluate the enhancement factor (EF) of SERS, Raman shift of 1080$cm^{-1}$ was chosen to compare the measured SERS intensity and the solid 4MPh Raman intensity by using the following equation (1):

$$EF = \frac{I_{SERS} / N_{ads}}{I_{bulk} / N_{bulk}} \qquad (1)$$

In eq 1, measured intensity was divided by the number of 4MPh molecules under laser illumination for SERS and bulk sample to fairly compare the intensity of single molecule in both situations. $I_{SERS}$ and $I_{bulk}$, which represent measured SERS and bulk Raman intensities, could be obtained from experiments.

The solid sample, $N_{bulk}$, which represents the number of 4MPh molecules under laser illumination in bulk sample, was inferred from bulk density, mass of 4MPh, and illuminated volume:

$$N_{bulk} = Ahn_{bulk} = Ah \frac{\rho_{bulk}}{M_{bulk}} N_A \qquad (2)$$

The illuminated volume was calculated as the product of the area of the laser spot A (~2.88 $\mu m^2$) and the penetration depth h of the focused laser which was estimated by the microscope feature (~19.8 μm). On the basis of the density (1.255 $g/cm^3$) and

mass (126.18 g/mol) of bulk 4MPh, $N_{bulk}$ was calculated as $3.4\times10^{11}$. As for SERS samples, *N*ads could be obtained via:

$$N_{ads} = \frac{A\varphi}{\sigma} \qquad (3)$$

A is the area of the focal laser spot (~2.88 μm$^2$). $\varphi$ is the surface coverage of AuNPs. σ represents the surface area occupied by one adsorbed 4MPh molecule, which was about 0.3 nm$^2$ according to the literature. On the basis of the parameters above, $N_{ads}$ was finally estimated as $3.36\times10^6$ (in $N_2$ saturated water) and $2.59\times10^6$ (in $CO_2$ saturated water).

By substituting measured and calculated values into eq 1, and by averaging over three predominant bands, enhancement factor (EF) of 4MPh adsorbed on the optimal SERS substrates was as estimated to be about $4\times10^7$ (in $N_2$ saturated water) and $6\times10^6$ (in $CO_2$ saturated water).