## **Supporting Information**

for

Sandwich-like layer-by-layer assembly of gold nanoparticles with tunable SERS properties

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## Additional experimental data

## Calculation of the EF value:

 $EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})$ 

 $N_{\rm bulk}$  is the number of molecules of the solid 4-ATP in the laser illumination volume. In our work, the laser spot of 100 µm in diameter and the penetration depth (ca. 180 µm) of the focused laser beam are used. Taking the density of the solid 4-ATP (1.18 g/cm<sup>3</sup>) into account,  $N_{\rm bulk}$  was calculated to be about 8 × 10<sup>15</sup> molecules within the illuminated laser light.

 $N_{\rm abs}$  can be obtained according to the method proposed by Murphy and co-workers [1]. According to the report by Kim et al., each 4-ATP molecule occupies ca.  $0.20~{\rm nm}^2$  on the surface of Au nanoparticles [2]. Because the laser spot is about  $7.85\times 10^{-5}~{\rm cm}^2$ , the number of the molecules on the BBB thin film within the laser spot is assumed to be  $1.8\times 10^{11}$ . This is estimated by counting the number of the big Au nanoparticles on the spot and calculating the surface area of those Au nanoparticles.

Taking account of the intensity ratio of the 1587 cm $^{-1}$  band, the the EF value for the BBB thin films are calculated to be ca.  $3.6 \times 10^4$ . Other EF values could be obtained similarly.

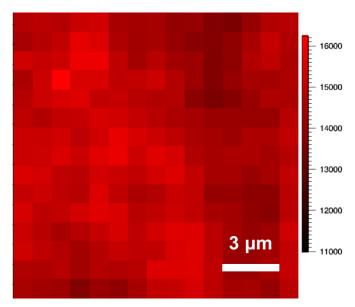


Figure S1: SERS mapping ( $15 \times 15 \ \mu m^2$ , step 1  $\mu m$ ) of the 1078 cm<sup>-1</sup> band of 4-ATP on the BBB thin film. The spectra were measured using a laser scanning confocal spectrometer (Renishaw inVia) with a 785 nm laser excitation.

## References

- [1] Orendorff, C. J.; Gole, A.; Sau, T. K.; Murphy, C. J. *Anal. Chem.* **2005**, *77*, 3261. doi:10.1021/ac048176x
- [2] Kim, K.; Yoon, J. K. J. Phys. Chem. B. 2005, 109, 20731. doi:10.1021/jp052829b