Supporting Information

SERS and OWGS detection of dynamic trapping TNT molecular based on functional self-assembly Au monolayer film

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S1. The reproducibility of the SERS substrate about our technique

The reproducibility of the SERS enhancement about our technique from the same batch 8 spots has been mentioned in the paper (*The sensitivity, selectivity and reproducibility of SERS substrate*). To further assess the reproducibility of SERS substrates, the intensity of the main vibration of TNT from the 45 spots on the same substrate and 20 spots from the different batches SERS spectra are shown in Figure S1a and Figure S2a.

To get a statistically meaningful result, the relative standard deviation (RSD) of the Raman intensity of the carbon skeleton stretching modes was calculated. We choose two prominent TNT peaks, strong Raman band at 1364 cm^{-1} and weak band at 1542 cm^{-1} and the formation peak of Meisenheimer complex at 2930 cm^{-1} to calculate the RSD of the Raman intensity. Figure S1b, c, d show that the RSD of the Raman vibrations at 1364, 1542, 2930 cm^{-1} are 12.27, 10.32 and 11.23%, respectively. And Figure S2b, c, d show that the RSD of these Raman vibrations are 11.66, 10.93 and 12.74%, respectively. Therefore, the less than 20% RSD variation of the same and different batches further demonstrates the as-prepared assembly as a promising substrate for high reproducibility SERS detection.

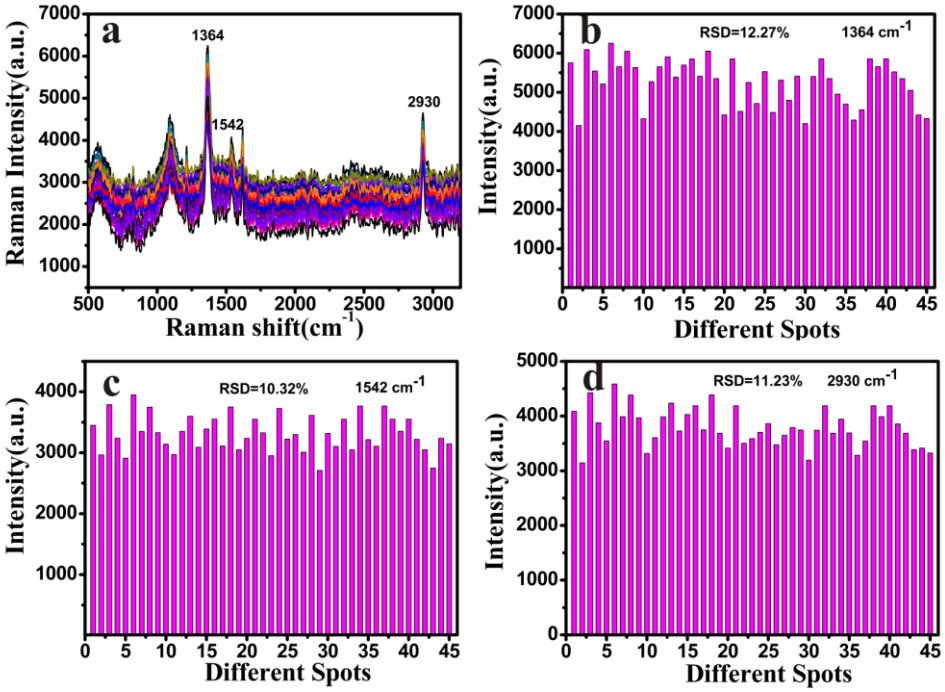

Figure S1. (a) The SERS spectra of the main vibration of TNT (1×10^{-7} M) from the same substrate. The intensities of the main vibrations at (b)1364 cm^{-1}, (c)1542 cm^{-1}, (d) 2930 cm^{-1} in the 45 spots SERS line-scan spectra collected on the same substrate.

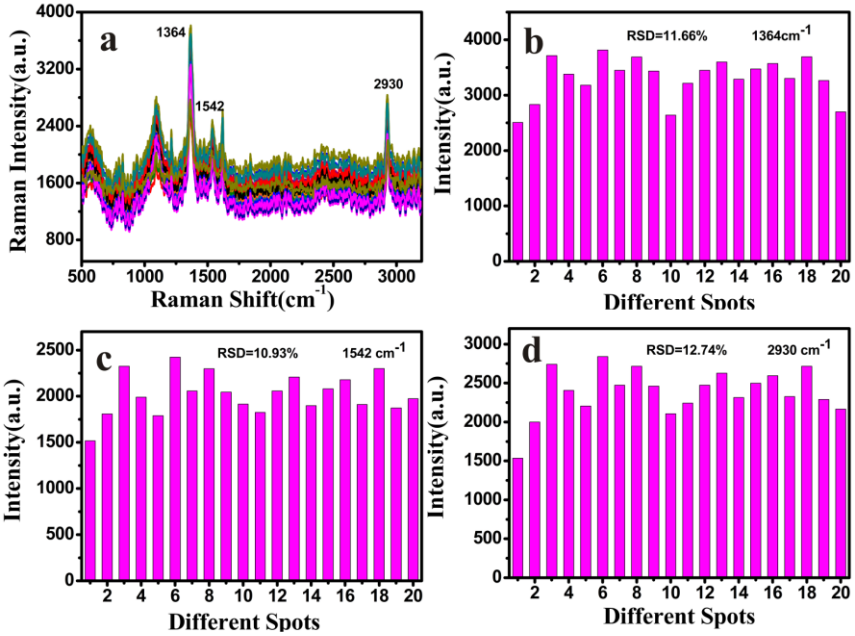

Figure S2. (a) The SERS spectra of the main vibration of TNT (1×10^{-7} M) from different batches. The intensities of the main vibrations at (b) 1364 cm^{-1}, (c) 1542 cm^{-1}, (d) 2930 cm^{-1} in the 20 spots SERS line-scan spectra collected on the different batches substrates.

S2. The influence of pH and Au deposition time for SERS response of Meisenheimer complex

In addition, the intensity of SERS not only relates to the concentration of the TNT but also the pH of TNT solution and the amount of gold nanoparticles. So, in order to obtain the optimum

condition, we study the influence about pH of the TNT solution (10^{-7} M) and the amount of gold nanoparticles.

Some groups have studied the pH measurement. [1,2] In our experiment, we find that the pH of TNT ethanol solution is about 6, combine with the above conditions of literature, so we add the NaOH to control the pH of TNT ethanol solution, adjust pH to 6, 9 and 13, respectively. From the intensity of around 2930 cm^{-1}, we can conclude that the pH=9 is the optimum pH of maximum SERS (Figure S3). We speculate the reason may be that in alkaline condition, hydroxyl is electronic group, TNT accepts electronic more easily to form Meisenheimer complexes. However, when pH is too high, it will destroy basement, so enhancing effect is not the best.

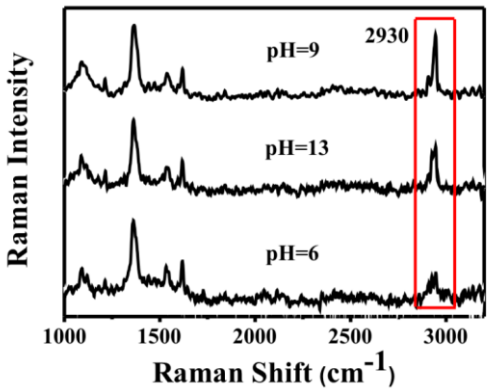

Figure S3. Raman spectra from different pH of the TNT solution, pH=6, 9, 13

Besides, in order to gain the different amount of gold nanoparticles, we study different time of Au nanoparticles immersed (figure S4). Through the SEM, we can see that 1 hour gold shows that gold deposition is low density with well disperse, 3 hours shows a higher density of Au NPs and close arrange, 5 hours exhibits the highest density and close approach, and the corresponding Raman spectra shows constantly enhance (figure S4D). This is attributed to plasmonic coupling between nanoparticles in close proximity, which results in huge local electromagnetic field enhancements in these confined junctions or SERS "hot spots". [3-6] Our results also show that the time exceed the 5 h, the Au NPs appear multilayer reunion phenomenon, is not a single-layer film, so we no longer research the longer time deposition. On the basis of the experiment results, the best measuring conditions for the detection of TNT are thus setting at pH=9 of the TNT solution and the immersed time of gold nanoparticles is 5 hours.

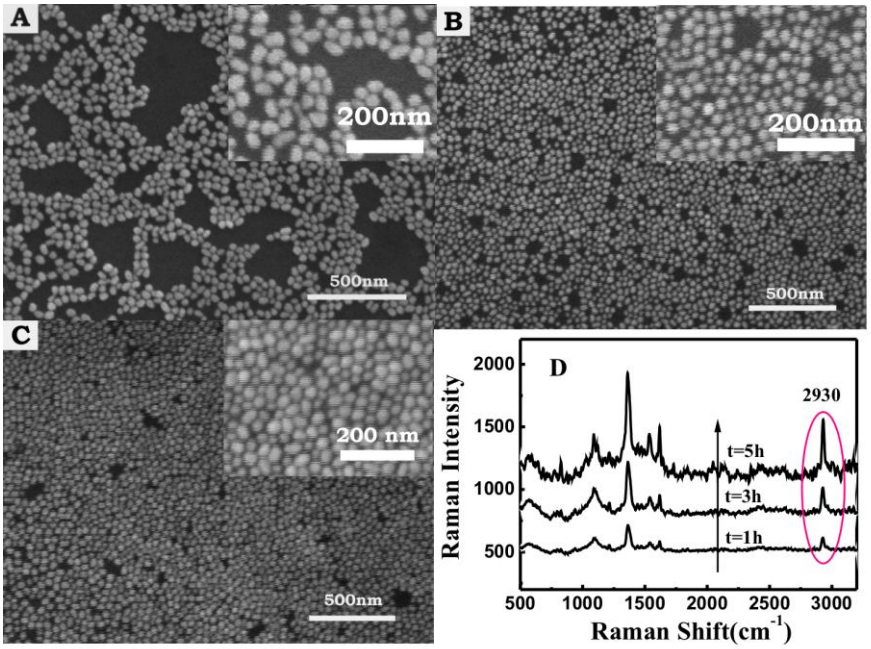

Figure S4. SEM images of different deposition time of gold nanoparticles (A: 1h, B: 3h, C: 5h), demonstrate the formation of hot pots. (D)Raman spectra from different deposition time of gold nanoparticles, time=1 h, 3 h, 5 h (pH=9).

References:

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