

Supporting Information

Ultrasensitive SERS Detection of Trinitrotoluene through Capillarity-constructed Reversible Hot Spots based on ZnO-Ag Nanorods Hybrids

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Instruments

The as-prepared nanostructures on the substrate were sent to characterizations on a CAMSCAN APOLLO 300 field-emission scanning electron microscopy (FE-SEM) at 15KV. The crystal structure of the products was studied using a Bruker D8 X-ray diffractometer with Cu K α irradiation at $\lambda = 1.5406 \text{ \AA}$. For high-resolution TEM measurements, one drop of the alcohol dispersed suspension of sample was placed on a carbon-coated copper grid and allowed to dry in air. The grid was then observed on a Tecnai GF2 operated at an accelerating voltage of 400 kV. Selected area electron diffraction (SAED) patterns were also obtained. The absorbance spectrum of ZnO and ZnO-Ag hybrids samples were measured using a PerkinElmer Lambda35 fiber-optic UV-vis NIR spectrophotometer.

Experimental Section

Materials:

Chemicals and Reagents. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Advanced Pure 99.998%), rhodamine 6G (R6G Advanced Pure 95%), hexamethylenetetramine (HMT Advanced Pure 95%), 4-aminothiophenol (4-ATP, $4\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$) were all purchased from Aladdin Chemistry Co. Ltd., China. Ethanol (AR) was all purchased from Longke Co., China. And the pH of pure ethanol is 6.94. Ultrapure water from Milli-Q source was used throughout the experiments. All reagents were used as received without further purification. 2, 4, 6-Trinitrotoluene (TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$), picric acid (PA, $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$), 2-nitrotoluene (2-NT, $\text{C}_7\text{H}_7\text{NO}_2$), 2, 4-dinitrotoluene (DNT, $\text{C}_7\text{H}_6\text{N}_2\text{O}_4$), and 1,3-dinitrobenzene(DNB, $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$) was purified from ICM. N-type Si (100) was cleaned sequentially with acetone, ethanol and deionized water for 15min respectively, then dried with nitrogen flow.

Preparation of ZnO NRs

Briefly, the 0.375M $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in the pre-mixed solution of ethanolamine and 1, 2-dimethoxyethane. The proportion of ethanolamine and 1, 2-dimethoxyethane was 1:1. After stirring for 30min, a clear solution was obtained. Then the dip-coating method was used for obtain zinc oxide gel film. The clean silicon substrate was dipped in zinc oxide gel film within 1 min, and then pulled with the speed 0.6 mm/s by gel instrument, dried at 80°C. These processes were repeated three times. And then the substrate coated with a thin film was heat-treated for 2 hours at 550°C to obtain a seed crystal film. After seeding, hydrothermal growth of ZnO

nanorods were performed in a thermal container. 0.025 M solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.025 M solution of HMT in distilled water were prepared and equal volume aliquots of each solution were mixed together. All the chemicals were analytical grade and used without further purification. Before introducing the substrate into the growth solution, the precursor solution was maintained in a laboratory hydrothermal chamber at 93°C for 1 h to stabilize the growth temperature. The Si wafers with ZnO seed were floating into the precursor solution maintained at 93°C for 12h. The as-prepared samples were rinsed in deionized water, and then dried in oven at 70°C .

Preparation of ZnO-Ag NRs hybrids

The ZnO nanostructures were coated with Ag nanoparticles by sputtering (EMITECH K550X sputter coater) at room temperature. Before deposition, the vacuum chamber of pressure was decreased down to 1×10^{-1} mbar. And different deposition times from 4 to 26 min with a current of 30 mA were used for optimized conditions.

SEM Measurements

Figure S1. FE-SEM image of ZnO-Ag hybrids with the different reaction time, (a) 3h, (b) 8h and (c) 12h, respectively.

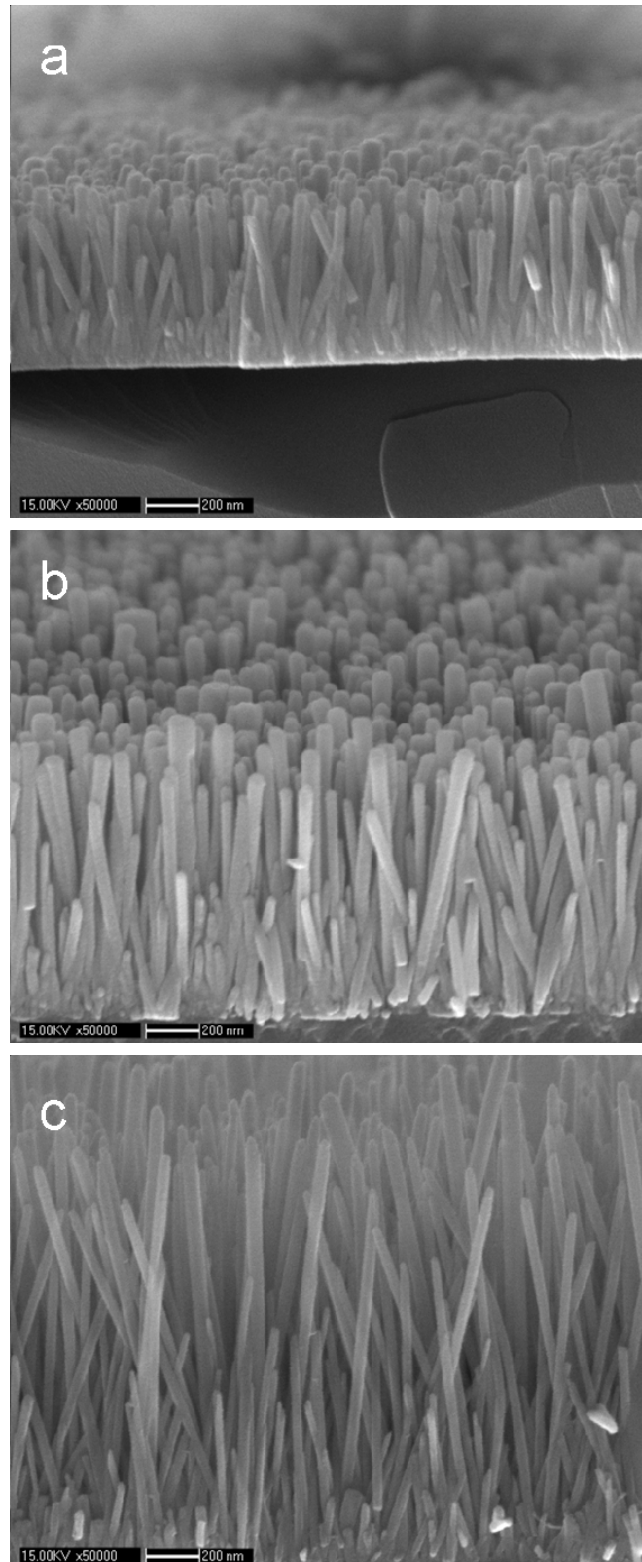


Figure S2. FE-SEM image of ZnO-Ag hybrids with different Ag deposition times, (a-c) 4min, (d-f) 10min, (g-i) 16min, (j-l) 26min.

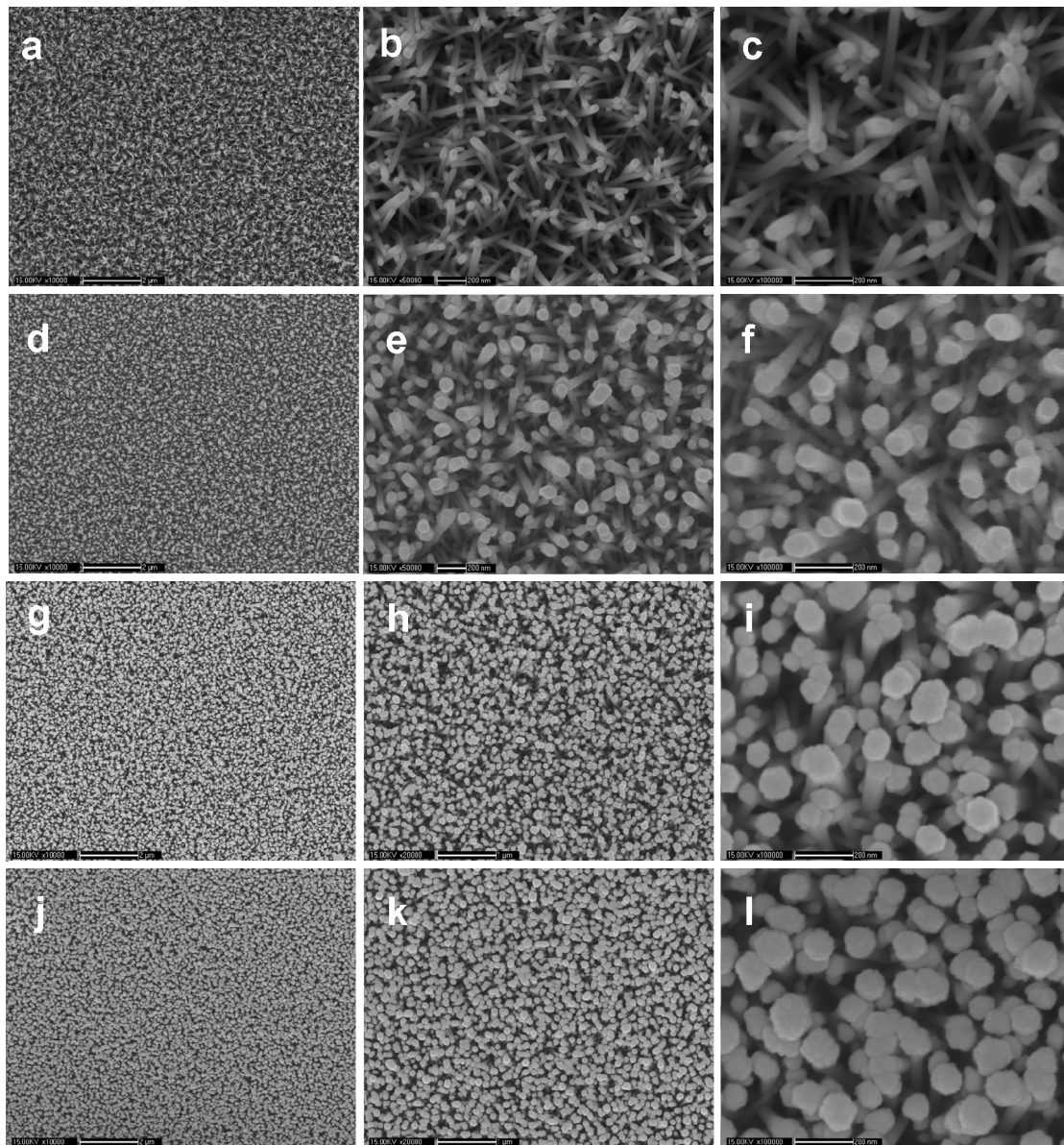


Figure S3. UV-vis analysis of ZnO and ZnO-Ag substrate with 16 min Ag deposition time.

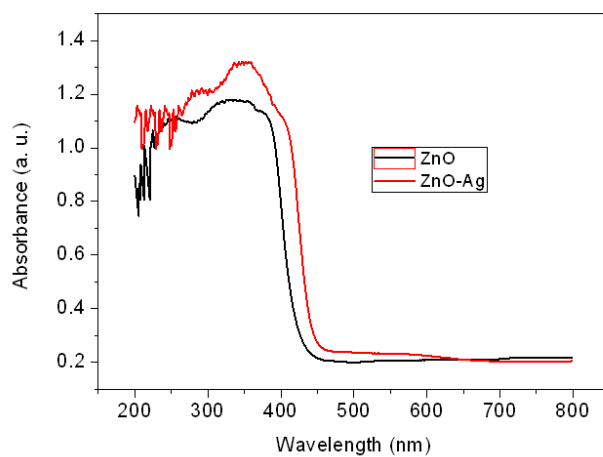


Figure S4. XRD patterns of (a) the ZnO nanorod arrays; and (b) the ZnO-Ag nanorod arrays.

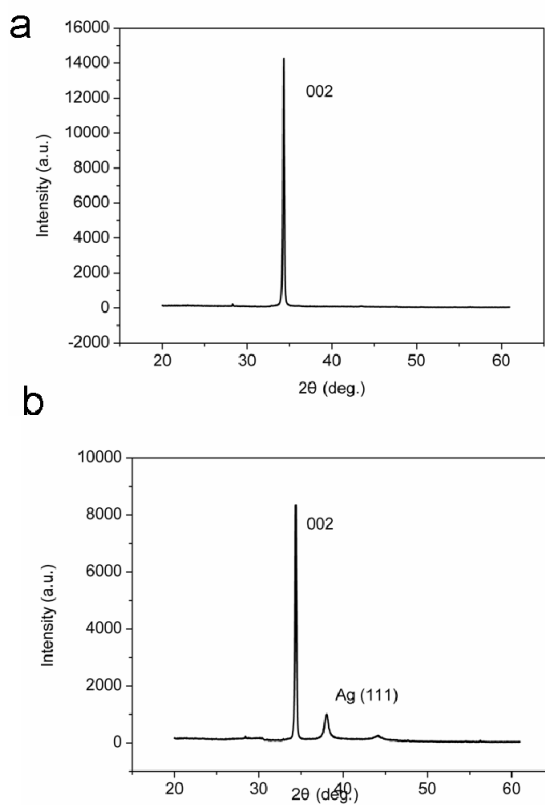


Figure S5. The SERS spectra of R6G collected on the substrates with different Ag-sputtering durations exposed to a 1×10^{-10} M R6G solution with a data acquisition time of 5s, (a) 550 nm length of ZnO nanorods; (b) 960nm length of ZnO nanorods; (c) 1.5 μ m length of ZnO nanorods.

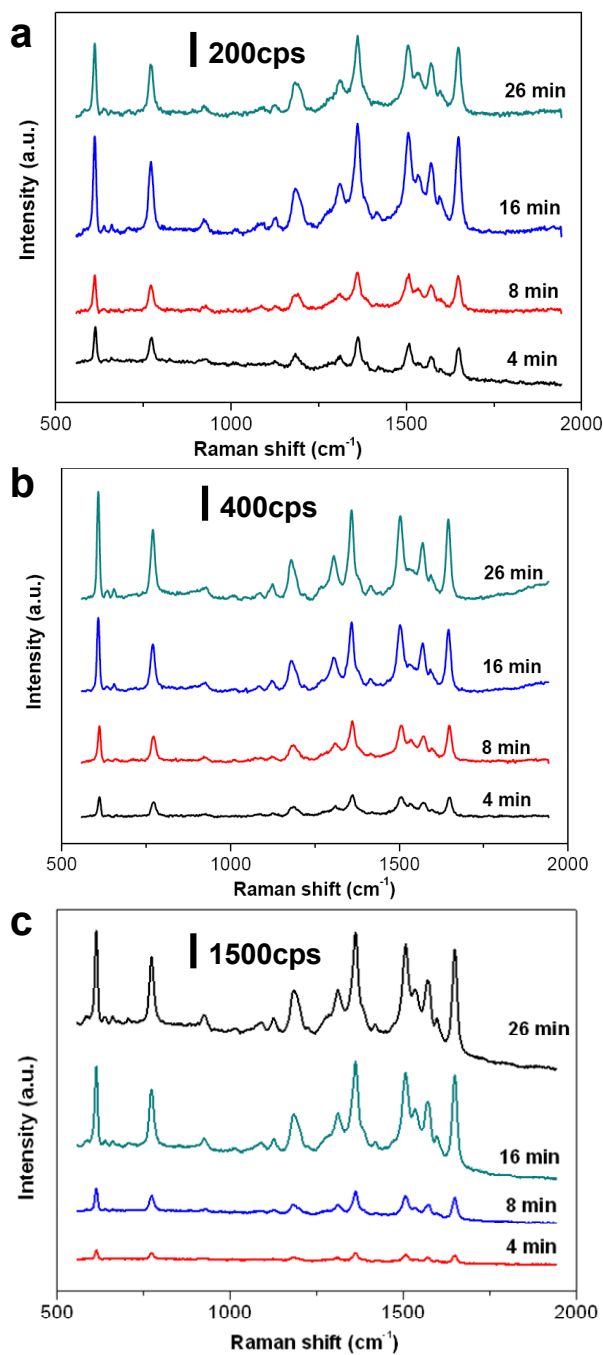


Figure S6. The SERS spectra of R6G collected on the ZnO-Ag substrates with different concentration of R6G (a) concentration from 1×10^{-9} M to 1×10^{-14} M; (b) the enlarge figure of SERS spectra of R6G with the concentration of 1×10^{-13} M and 1×10^{-14} M.

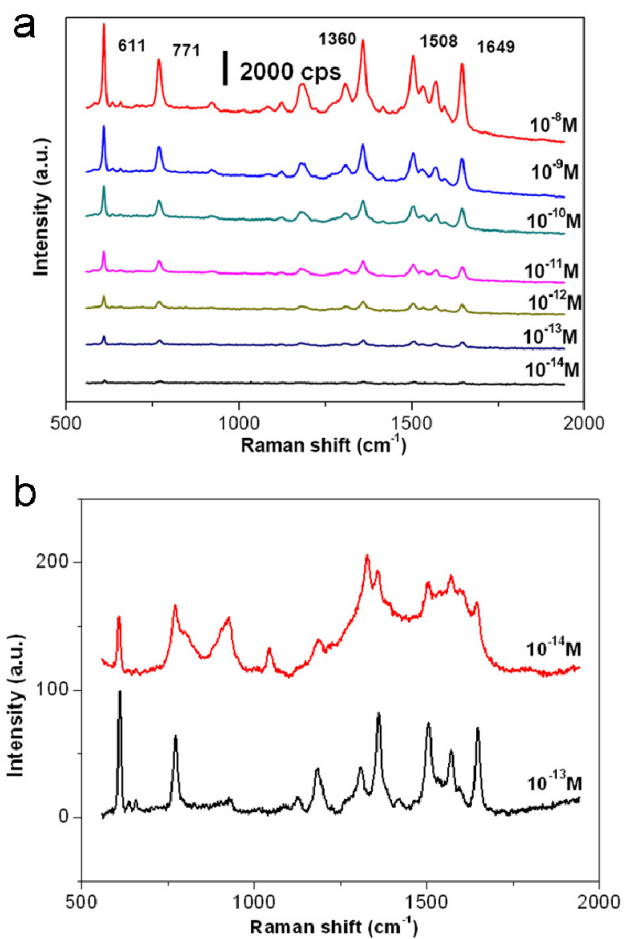


Figure S7. The SERS spectra of R6G collected on the ZnO-Ag substrates with concentration of R6G 1×10^{-11} M (blank line), the Raman spectra collected on the Si-wafer with concentration of R6G 1×10^{-3} M for comparison (red line).

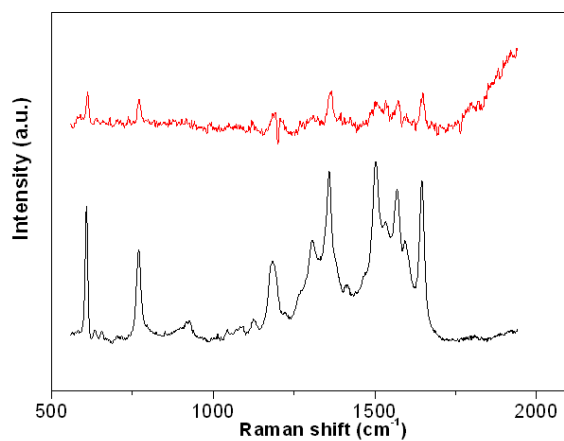
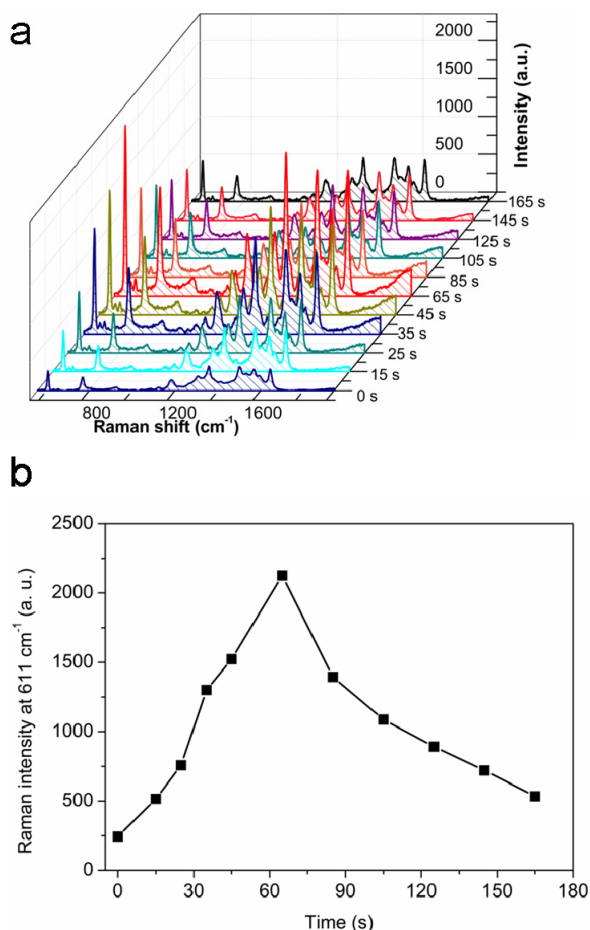


Figure S8. (a) The time-resolved Raman spectra of R6G was collected after dropping 5 μL of ethanol on ZnO-Ag nanorod array hybrids (the length of rod was 1.5 μm); (b) The temporal evolution of corresponding Raman intensity at 1430 cm^{-1} of (a).



When 1×10^{-9} M R6G ethanol was directly added onto the hybrids array 1.5 μm length, the Raman signals of R6G could clearly be detected and the huge enhancement appeared at ~ 65 s. This huge enhancement was due to the formation of Raman hot spot through capillary force of solvent evaporation by the self-approaching of flexible ZnO-Ag nanorods.

Estimation of enhancement factor

We used the peak at 611 cm^{-1} (for R6G) to estimate the enhancement factor (EF). The SERS EF is a quantitative measure of the Raman signal amplification of an analyte. We calculated this value using the reported protocol.^[1] The EF can be calculated by:

$$EF = \frac{I_{SERS} N_{Ref}}{I_{Ref} N_{SERS}}$$

Where N_{SERS} and N_{Ref} are the number of molecules probed on the nanoflower and on the reference sample, respectively. I_{SERS} and I_{Ref} correspond to SERS signal and the un-enhanced normal signals intensities, respectively. Herein, a certain volume (V_{SERS}) and concentration (C_{SERS}) R6G aqueous solution was dispersed to an area of Raman concentration for non-SERS Raman spectra certain S_{SERS} at the ZnO-Ag hybrid substrate. For non-SERS Raman spectra, a certain volume (V_{Ref}) and concentration (C_{Ref}) R6G aqueous solution was dispersed to an area of S_{Ref} at a clean Si substrate. Both the substrates were dried in the air. Considering the area of laser spot is the same, the foregoing equation thus becomes:

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

In our experiment, 1 μL of 1×10^{-11} M R6G solution was dispersed to an area of 10 mm^2 for the ZnO-Ag hybrid substrate shown in Figure S6 and 1 μL of 1×10^{-3} M R6G ethanol solution was dispersed to an area of $\pi \text{ mm}^2$ for the silicon wafer. For the band at 611 cm^{-1} , I_{SERS} / I_{Ref} was $243/18=13.5$. Therefore average enhancement factor for the band at 611 cm^{-1} is calculated to be 4.3×10^8 . With the same method, the Efs for the SERS substrates shown in Figure S6, S7 was estimated to be 4.3×10^8 .

Figure S9. (a) the SERS spectra of R6G collected on the ZnO-Ag substrates (the length of rod was 960 nm) with different concentration of R6G from 1×10^{-8} M to 1×10^{-14} M; (b) The time-resolved Raman spectra of R6G was collected after dropping 5 μ L of ethanol on ZnO-Ag nanorod array hybrids (the length of rod was 960 nm).

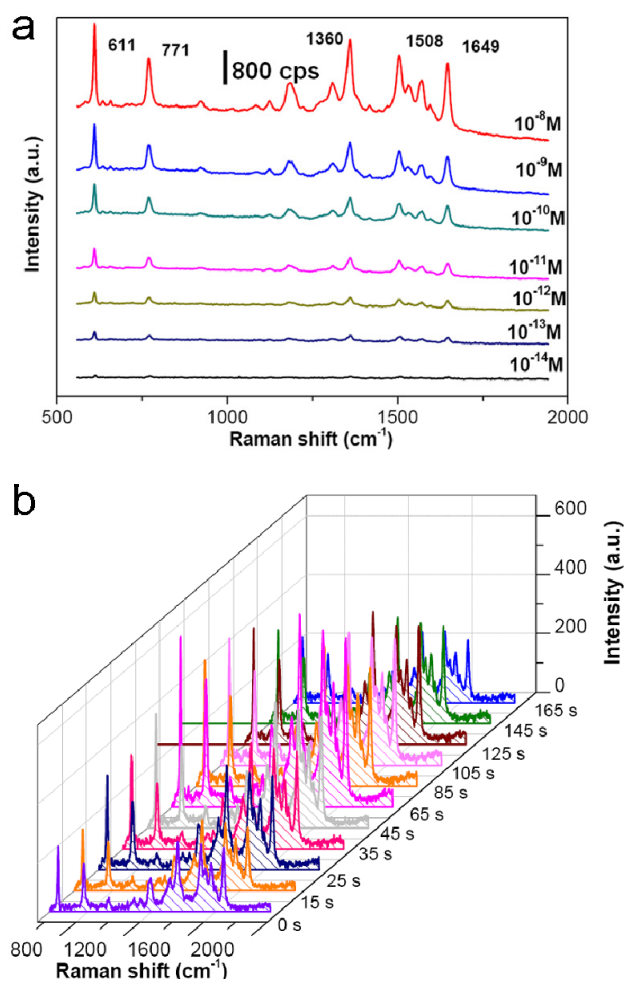


Figure S10. (a) the SERS spectra of R6G collected on the ZnO-Ag substrates (the length of rod was 550nm) with different concentration of R6G from 1×10^{-7} M to 1×10^{-13} M; (b) The time-resolved Raman spectra of R6G was collected after dropping 5 μ L of ethanol on ZnO-Ag nanorod array hybrids (the length of rod was 550 nm).

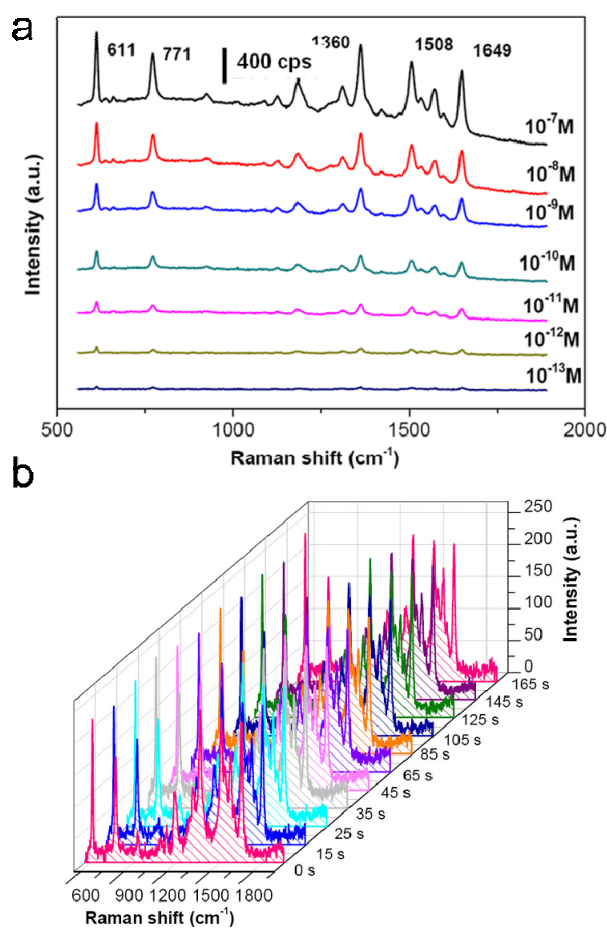


Figure S11. The time-resolved Raman spectra of 4-ATP was collected at the interval of 20 s after dropping 5 μL of acetone on the length of 1.5 μm nanorod array ZnO-Ag hybrids.

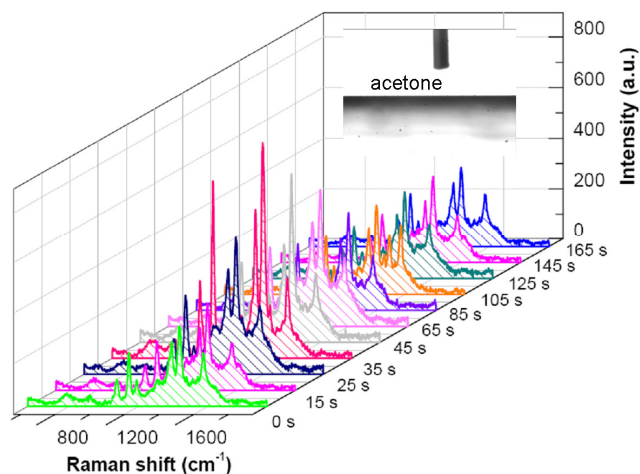


Figure S12. The time-resolved Raman spectra of 4-ATP was collected at the interval of 20 s after dropping 5 μL of methyl alcohol on the length of 1.5 μm nanorod array ZnO-Ag hybrids.

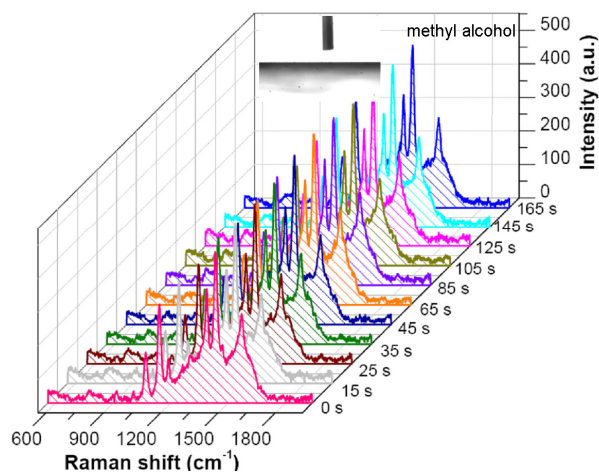


Figure S13. The time-resolved Raman spectra of 4-ATP was collected at the interval of 20 s after dropping 5 μL of isopropanol on the length of 1.5 μm nanorod array ZnO-Ag hybrids.

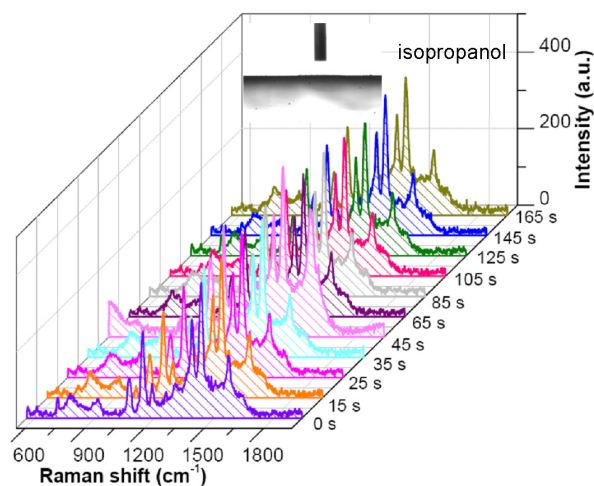


Figure S14. The time-resolved Raman spectra of 4-ATP was collected at the interval of 20 s after dropping 5 μL of ethyl acetate on the length of 1.5 μm nanorod array ZnO-Ag hybrids.

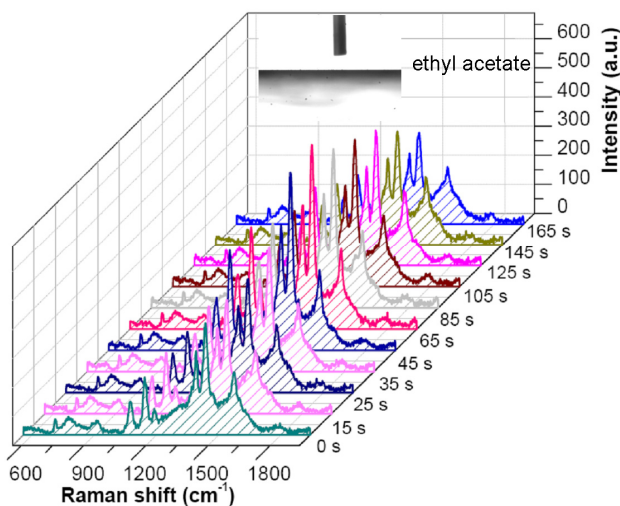


Figure S15. The time-resolved Raman spectra of 4-ATP was collected at the interval of 20 s after dropping 5 μL of water on the length of 1.5 μm nanorod array ZnO-Ag hybrids.

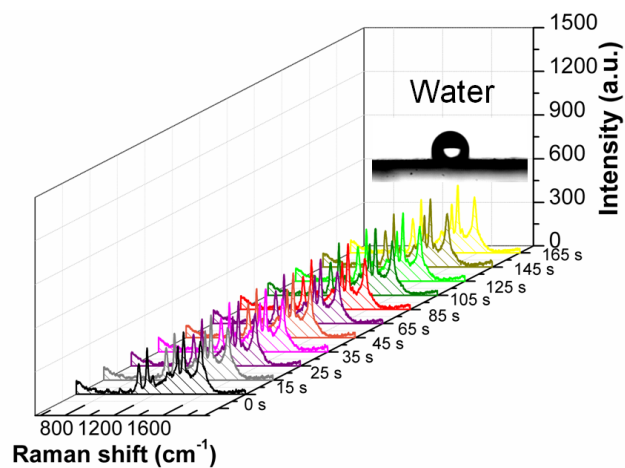


Figure S16. A series of SERS spectra of R6G molecules collected on randomly selected 15 places of the ZnO-Ag hybrids substrate.

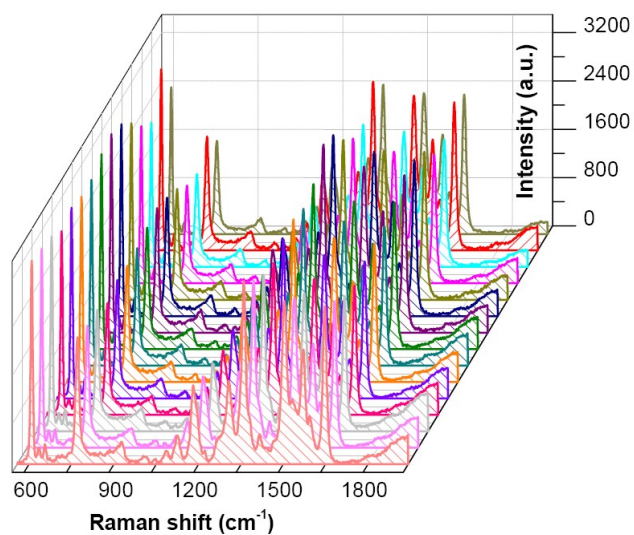
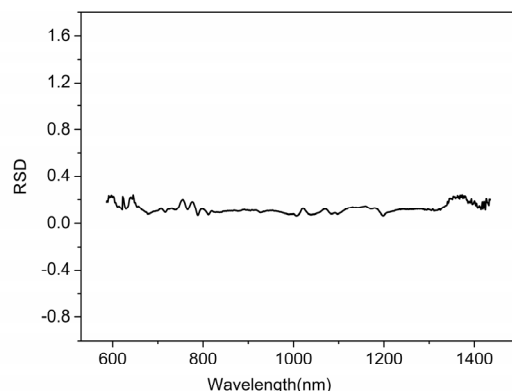


Figure S17. The corresponding RSD value curve.



The SERS spectra of R6G at 15 random sites on the substrate showed good uniform in intensity (Figure S16, S17). Moreover, the relative standard deviation (RSD) of major R6G characteristic SERS peaks was calculated to evaluate the reproducibility of SERS signals. As shown in Figure S17, it was revealing almost the same intensity for each characteristic band of R6G. The maximal RSD value of signal intensities of major SERS peaks was observed to be below 0.25, indicating that ZnO-Ag NRs hybrid SERS substrates had a good reproducibility across the entire area. The experimental results indicated that the ZnO-Ag NRs have high sensitivity, good reproducibility and reliability as the substrate for Raman applications.

Figure S18. Raman spectra of (a) 1×10^{-6} M TNT ethanol on the unmodified ZnO-Ag hybrids nanorod arrays, (b) 4-ATP powder and (c) TNT powder and (d) 1×10^{-8} M TNT ethanol on the 4-ATP-modified ZnO-Ag hybrids nanorod array. By the comparison of the above Raman spectra, there was not any the Raman signals of TNT detected on the unmodified ZnO-Ag nanorod array even if TNT concentration was as high as 1×10^{-6} M. Only were the Raman signals of 4-ATP detected after adding 1×10^{-8} M TNT ethanol to the 4-ATP modified ZnO-Ag hybrid nanorod array.

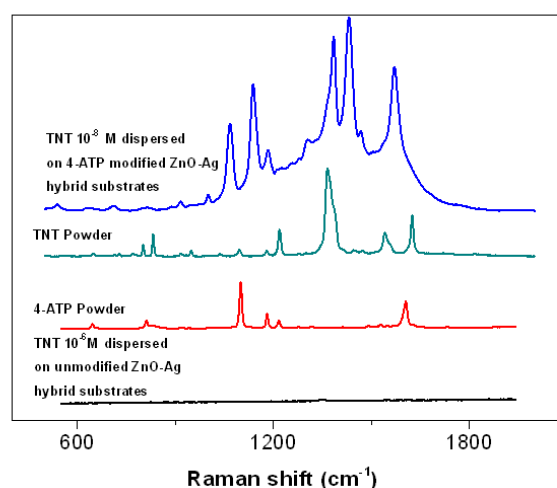


Figure S19. UV-vis absorption spectra of TNT, 4-ATP, TNT and 4-ATP complex. The inset images show the colours with the addition of 0 and 1.5 μL of 0.01 M 4-ATP into 4 mL of 0.1 mM TNT solution, respectively. And the inset structures showed the interaction between π -acceptor and π -donor. The UV-vis spectra in solution were obtained using ethanol as the solvent at room temperature with a path-length of 1 cm.

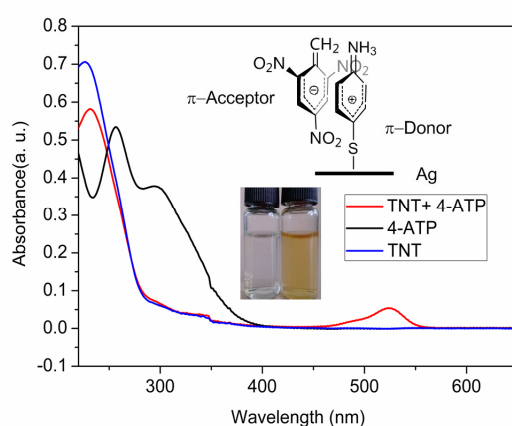


Figure S20. The Raman enhancement (I/I_0) of 4-ATP at 1430 cm^{-1} with the logarithm of TNT concentrations. I and I_0 represent the Raman intensities at 1430 cm^{-1} after the addition of TNT analyte and 4-ATP ethanol solution.

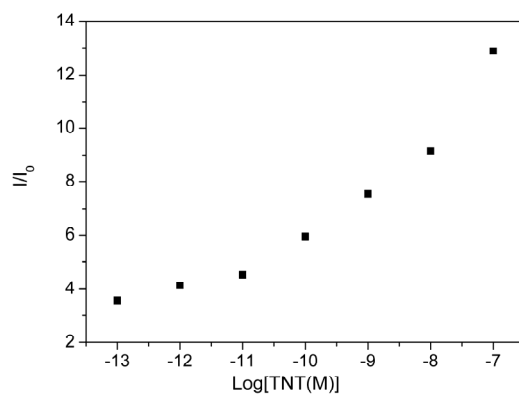


Figure 21. a) The enlarge figure of SERS spectra of DMAB-TNT with the concentration of $1 \times 10^{-13}\text{M}$ and $4 \times 10^{-14}\text{M}$; b) The SERS enhancement comparison data before and after adding $1 \times 10^{-13}\text{mol/L}$ TNT.

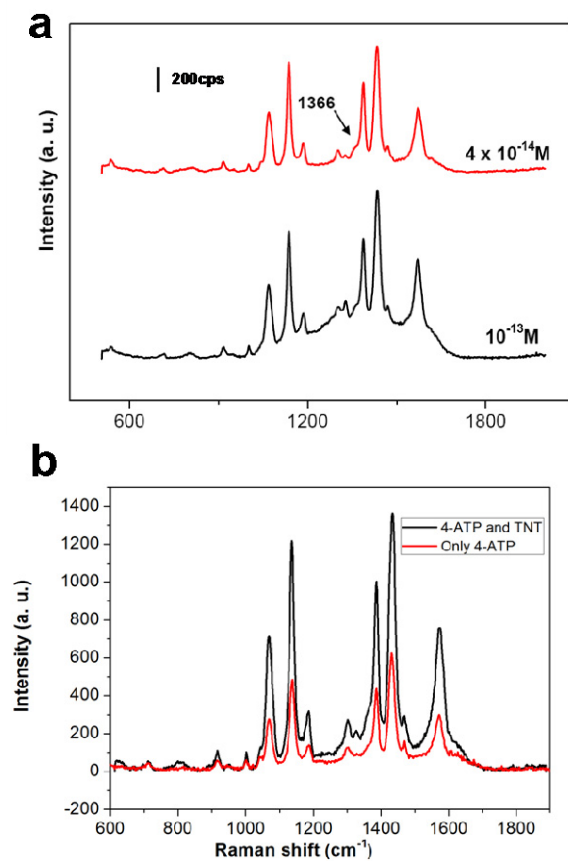
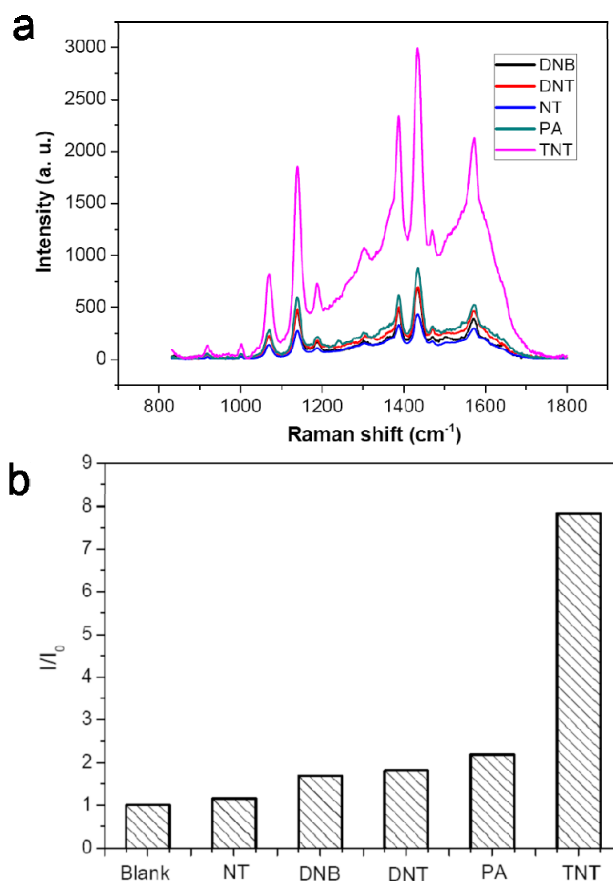


Figure 22 a) Raman spectra of ZnO-Ag with the presence of various TNT structure-like molecules: 2-nitrotoluene (NT), 2, 4-dinitrotoluene (DNT), m-dinitrobenzene (DNB), picric acid (PA) and 2, 4, 6-trinitrobenzene (TNT), with the same concentration of 10^{-9} M in ethanol; b) Comparison of the SERS intensity (1430 cm^{-1}) of different explosives with the same concentration of 10^{-9} M in ethanol. (I was SERS intensity of 4-ATP interacted with explosives, and I_0 was SERS intensity of 4-ATP).



Scheme S1 the flow chart of self-reviving by UV light of this ZnO-Ag NRs hybrids substrate.

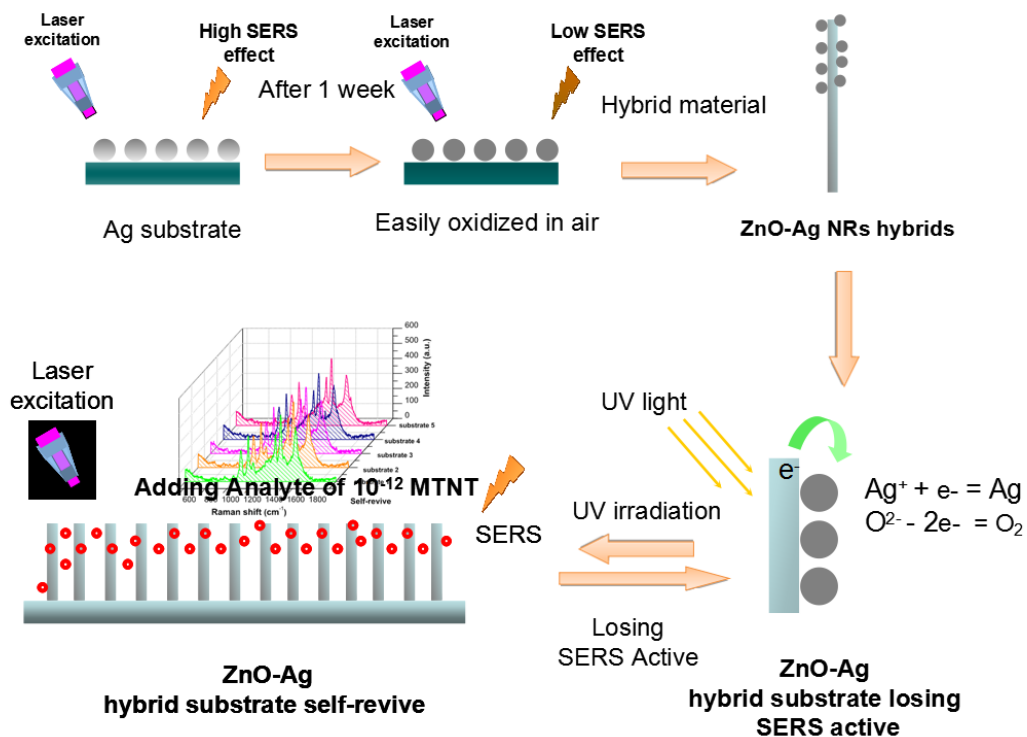


Figure S23. SERS spectra of R6G over ZnO-Ag hybrids substrate of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after irradiation with UV light for 5min for the substrate in curve (2). The integration time is 5s.

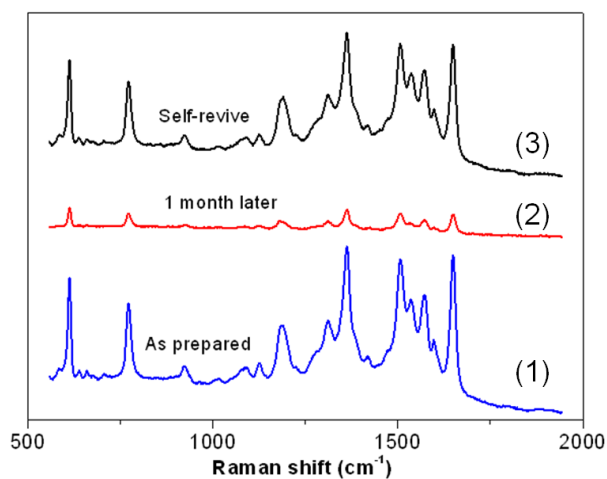


Figure S24. SERS spectra of 4-ATP over five ZnO-Ag hybrids substrates of kept in dark air for a month and after irradiation with UV light for 5min for the substrates achieving self-revive. The integration time is 5s.

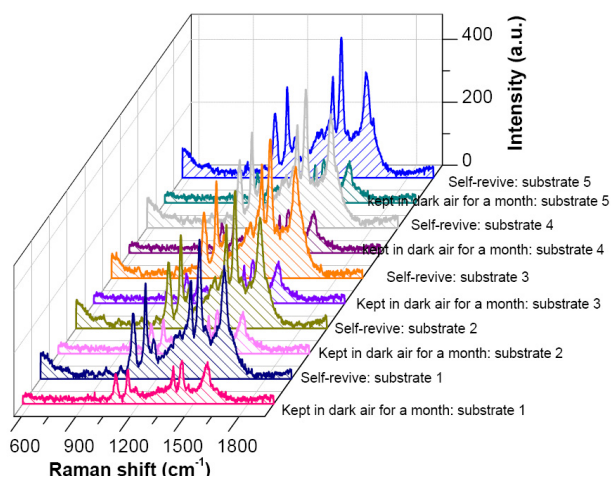


Figure S25. SERS spectra of 4-ATP over ZnO-Ag hybrids substrate 1 of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after self-revive then used this substrate to detect TNT (1×10^{-12} M). The integration time is 5s.

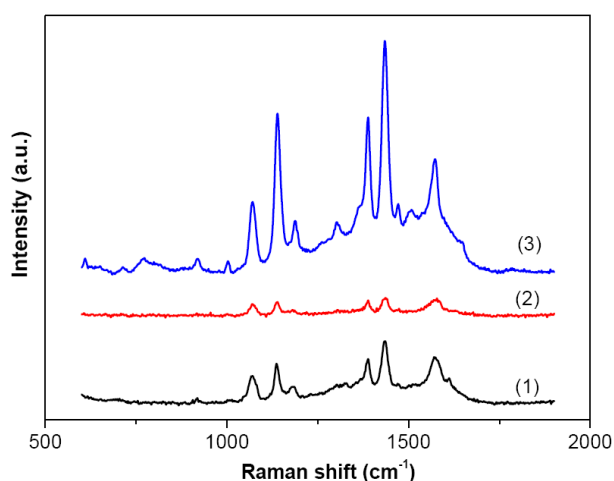


Figure S26. SERS spectra of 4-ATP over ZnO-Ag hybrids substrate 2 of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after self-revive then used this substrate to detect TNT (1×10^{-12} M). The integration time is 5s.

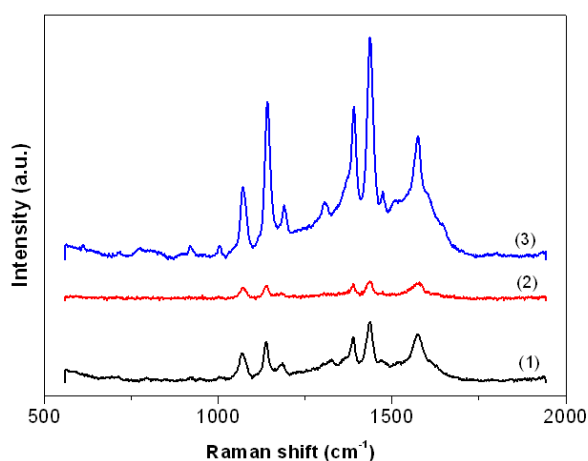


Figure S27. SERS spectra of 4-ATP over ZnO-Ag hybrids substrate 3 of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after self-revive then used this substrate to detect TNT (1×10^{-12} M). The integration time is 5s.

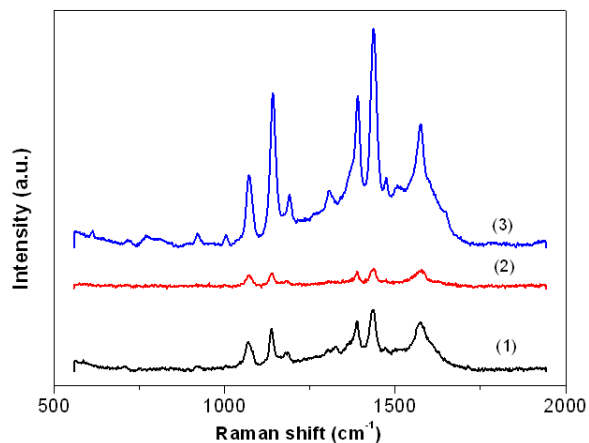


Figure S28. SERS spectra of 4-ATP over ZnO-Ag hybrids substrate 4 of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after self-revive then used this substrate to detect TNT (1×10^{-12} M). The integration time is 5s.

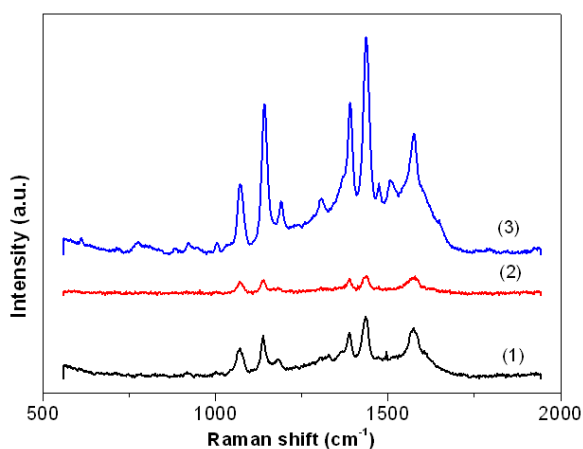
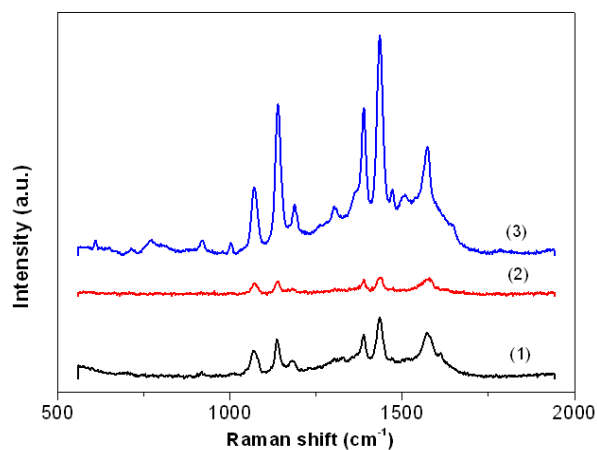


Figure S29. SERS spectra of 4-ATP over ZnO-Ag hybrids substrate 5 of curve (1) the as-prepared, curve (2) kept in dark air for a month and curve (3) after self-revive then used this substrate to detect TNT (1×10^{-12} M). The integration time is 5s.



Reference

- [1] Z. Huang, G. Meng, Q. Huang, Y. Yang, C. Zhu and C. Tang, *Adv. Mater.* 2010, **22**, 4136.