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Supporting Information

Instruments

- 5 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 Kα irradiation at λ = 1.5406 Å. For high-resolution TEM measurements, one drop of the alcohol dispersed suspension of sample was placed on a 10 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 MNSs samples were measured using a PerkinElmer Lambda35 fiber-optic UV-vis NIR spectrophotometer.
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Method for ZnO seeds preparation by atomic layer deposition (ALD)

Clean (111)p-Si slide were put into the reaction chamber of ALD equipment. Diethyl Zinc(DEZn) and water supplied the Zn and O sources for the growth of ZnO 20 respectively. DEZn pulse time was 0.1s. Cleaning time was 2s. Hydrogen peroxide pulse time was 0.1s. Cleaning time was 3s. The carrier gas was N₂. Substrate temperature was 250°C. Cyclic growth lasted 50 cycles.

SEM experiments

Figure S1 High-quality Si pillar arrays as template.



5 Figure S2. FE-SEM image of ZnO-Ag MNSs hybrids with different Ag deposition times, (a) 4min, (b) 8min, (c) 12min, (d) 16min



XRD experiments

Figure S3. XRD patterns of the flower-like ZnO MNSs (the black line) and the flower-like ZnO-Ag MNSs hybrids (the red line).



Scheme S1. Schematic for (a) the prepared ZnO MNSs grafted on Si pillar arrays by two-step solvent method; (b) the growth of ZnO MNSs grafted on Si pillar arrays directly.



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10 The deposition of ZnO seeds experiments were completed in Institute of Microelectronics, Beijing. Detailed descriptions of the preparation have been added to the Supporting Information. The main steps are as follows:

Clean (111)p-Si slide were put into the reaction chamber of ALD equipment. Diethyl Zinc(DE) and water supply the Zn and O sources for the growth of ZnO respectively. DEZn pulse time was 0.1s.

15 Cleaning time was 2s. Hydrogen peroxide pulse time was 0.1s. Cleaning time was 3s. Carrier gas was N₂. Substrate temperature was 250°C. Cyclic growth lasted 50 cycles.

Figure S4. FE-SEM image of ZnO nanosheets by growth of 1.5h before adding the same volume of solvent (deionized water).



Figure S5. FE-SEM image of ZnO nanosheets by growth of 1.5h after adding the same volume of solvent (deionized water).



Based on the methods of secondary solvent addition, the sparse ZnO that had grown before was partially dissolved. Fine crystal nuclei appeared on the silicon column template. Figure S6. FE-SEM image of ZnO nanosheets growth of 5.5h directly by a one-step method with the precursors of the diluted concentration 0.01 M zinc nitrate and 0.05M urea mixture.



Figure S7. FE-SEM image of ZnO nanosheets growth of 5.5h directly by a one-step method with the precursors of the concentration 0.02 M zinc nitrate and 0.1M urea mixture.



Figure S8 FE-SEM image of ZnO nanosheets before the subsequent pyrolysis at 350 °C.



Figure S9 FE-SEM image of ZnO nanosheets after the subsequent pyrolysis at 350 °C, and it became ZnO MNSs.



UV-vis experiments

Figure S10. UV-vis analysis of ZnO and ZnO-Ag substrate.



The UV/Vis spectrum of ZnO and ZnO-Ag substrate revealed the broad plasmon absorption band peaking at 385 nm.

SERS experiments

Figure S11. The SERS spectra of R6G collected on the substrates with different Agsputtering durations exposed to a 1×10^{-7} M R6G solution.



Figure S12. The SERS spectra of R6G collected on the substrates with different ZnO MNSs grown time exposed to a 1×10^{-7} M R6G solution.



Figure S13. The superhydrophobic property of ZnO-Ag MNSs with water CA of 150°



Figure S14. The SERS spectra of R6G collected on the ZnO-Ag MNSs substrates with different concentration of R6G 1×10^{-12} M to 1×10^{-13} M.



Figure S15. The SERS spectra of R6G collected on the ZnO-Ag MNSs substrates with concentration of R6G 1×10^{-11} M and collected on the Si-wafer with concentration of R6G 1×10^{-3} M for comparison.



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:

$$EF = \frac{I_{SERS} N_{\text{Re}f}}{I_{\text{Re}f} N_{SERS}}$$

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 unenhanced 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 MNSs hybird substrate. For non-SERS Raman spectra, a certain volume(V_{Ref}) and concentration (C_{Ref}) R6G aqueous solution was dispersed to an area, the substrates were dried in the air. Considering the area of laser spot is the same, the foregoing equation thus becomes:

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

In our experiment, 1 μ L of 1×10⁻¹⁰ M R6G solution was dispersed to an area of 10 mm² for the ZnO-Ag MNSs hybird substrate shown in Figure 2a and 1 μ L of 1×10⁻³ M R6G ethanol solution was dispersed to an area of π mm² for the silicon wafer. For the band at 611 cm⁻¹, I _{SERS} /I _{Ref} were 1156.3245/104.2971=11.08683. With the same method, the EF for the SERS substrates shown in Figure 2a was estimated to be 3.5292×10^8 .

Figure S16. a) The SERS spectra of R6G collected on the ZnO-Ag MNSs arrays substrates with Ag-sputtering for 12 min after being exposed to different concentrations of R6G in alcohol solution.



Figure S17. The SERS spectra of R6G collected on the ZnO-Ag MNSs hybrid substrates and ZnO seeds with Ag NPs substrate with Ag-sputtering for 12min, respectively; the data acquisition time was 5s.



Figure S18. Pure solid K^+ (NTO)⁻ salt and SERS of K^+ (NTO)⁻ salt (10-⁶M) The data acquisition time was 5s.



Figure S19. The corresponding calibration curve for SERS intensity at 850 cm⁻¹ versus - log [NTO].



Figure S20. Vibrational mode of FOX-7



Table S1 Assignment of SERS and the vibrational description for FOX-7^[4]

Vibrational description	SERS assignment	
$v(NO_2)[a]$	858	
$\delta(CH)$ ring [b]	1109	
$\delta(CH)$ ring [b]	1205	
$v_{\rm s}(\rm NO_2)$	1429	
v(C-C)	1607	

[a] v, stretching; [b] δ , bending.

Figure S21. The corresponding calibration curve for SERS intensity at 1607cm⁻¹ versus - log [FOX-7].



Figure S22. The SERS spectra of 4-ATP collected on the ZnO-Ag hybrid substrates with Ag-sputtering for 12 min after being exposed to different concentrations of 4-ATP alcohol solution; the data acquisition time was 5s.



Figure S23. Pure TNT and pure 4-ATP on a blank substrate (Si wafer), and 10⁻⁶ M TNT (dissolved in ethanol) dispersed on unmodified or 4-ATP-modified ZnO–Ag MNSs hybrid substrates. The data acquisition time was 5s.



Figure S24. Curve (1) the as-prepared ZnO-Ag MNSs arrays substrate 1 of SERS spectra of K⁺ (NTO)⁻ salt (1 ×10⁻⁸ M); curve (2) kept substrate 1 in dark air for 49 days; curve (3) after irradiating with UV light for 5 min for the substrate 1 in curve (2), then used this self-reviving substrate 1 to detect K⁺ (NTO)⁻ salt in water;



Figure S25. (a) SERS spectra of self-reviving substrates to detect TNT (1×10^{-8} M); (b) curve (1) the as-prepared ZnO-Ag MNSs arrays substrate 1 of SERS spectra of probe 4-ATP; curve (2) kept substrate 1 in dark air for 49 days; curve (3) after irradiating with UV light for 5 min for the substrate 1 in curve (2), then used this self-reviving substrate 1 to detect TNT (1×10^{-8} M) in water.



Figure S26. (c) Comparison of the SERS intensity (1430 cm⁻¹) of five self-revive substrates and new as-prepared substrate with the same TNT detection condition of 1 $\times 10^{-8}$ M in water.



Figure S27. comparison of the SERS intensity (1109 cm⁻¹) of five self-revive substrates and new as-prepared substrate with the same K⁺ (FOX-7)⁻ salt detection condition of 1 $\times 10^{-6}$ M in water.



Figure S28. (a) SERS spectra of self-reviving substrates to detect K^+ (FOX-7)⁻ salt (1 ×10⁻⁶ M); (b) curve (1) the as-prepared ZnO-Ag MNSs arrays substrate 1 of SERS spectra of K^+ (FOX-7)⁻ salt; curve (2) kept substrate 1 in dark air for 49 days; curve (3) after irradiating with UV light for 5 min for the substrate 1 in curve (2), then used this self-reviving substrate 1 to detect K^+ (FOX-7)⁻ salt (1 ×10⁻⁶ M) in water.



Figure S29 SERS intensity comparison of new as-prepared ZnO-Ag MNSs hybrids arrays substrates and five self-revive substrates of SERS spectra of K^+ (FOX-7)⁻ salt.



Table S2. ICP-OES data of natural water samples.

Sample	Na (mg/L)	Mg(mg/L)	P (mg/L)	S (mg/L)	K (mg/L)	Ca (mg/L)
River	14.175	14.392	0.005	0	13.614	14.557
Tap	6.095	12.864	0	0	1.156	18.990

Table S3. IC data of natural water samples.

Sample	Cl ⁻ (mM)	SO_4^{2-} (mM)
River	0.286	0.112
Tap	0.355	0.167

Calculation of Limit of Detection (LOD)

The LOD was estimated without TNT giving SERS signal at least 1.5 times higher than background (only 4-ATP). The standard curve of TNT was plotted as:

$$Y = A + B \times Log_{10}X$$

where, A and B are the variable obtained via least-square root linear regression for the signal-concentration curve and variable Y represents the normalized SERS signal (I_{with} _{TNT}/ I _{blank}) at TNT concentration of X(C_{TNT}). where, SD is the standard deviation and Y_{blank} is the SERS signal of blank sample (only 4-ATP).

The LOD was calculated as $LOD=10^{\left[\frac{Y_{blank}+3SD}{Y_{blank}}-A\right]/B}$

SD was calculated according to the well-known formula:

$$SD = \sqrt{\frac{1}{n-1} \times \sum_{i=1}^{n} (X_i - X_{average})^2}$$

where, n is the total number of the TNT standard sample. X_i is the "i" sample of the series of measurements. $X_{average}$ is the average value of the SERS signals obtained for the specific series of identical samples repeated n times.

Reference

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