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*Supporting Information*

# A Novel 3D Hierarchical Plasmonic Functional Cu@Co3O4@Ag Array as Intelligent SERS Sensing Platform with Trace Droplet Rapid Detection Ability for Pesticide Residue Detection on Fruits and Vegetables

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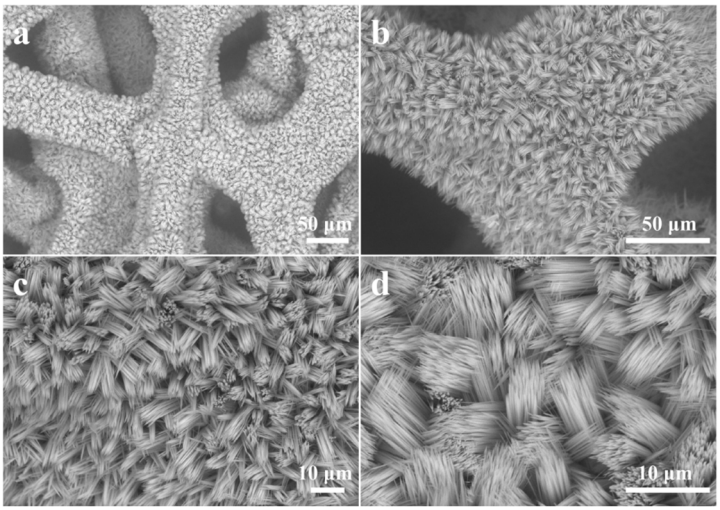


**Fig S1.** SEM images of Cu@$Co_3O_4$ NWs under different magnifications.

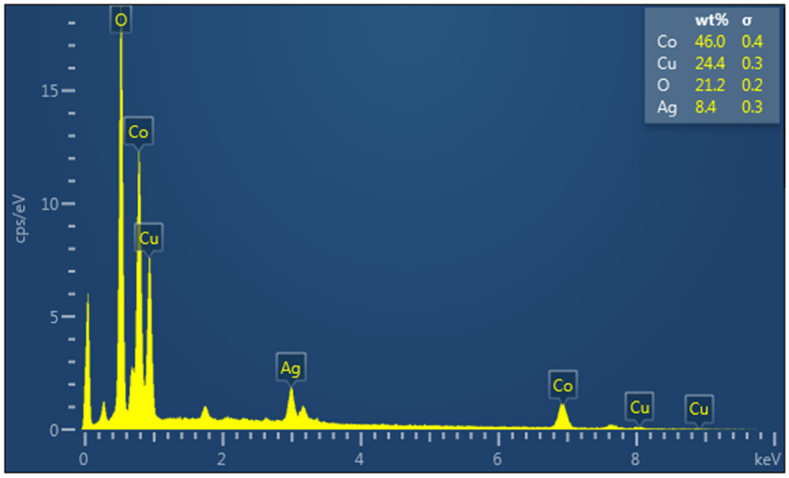


**Fig S2.** EDS spectrum of hierarchical Cu@$Co_3O_4$@Ag-H substrates.

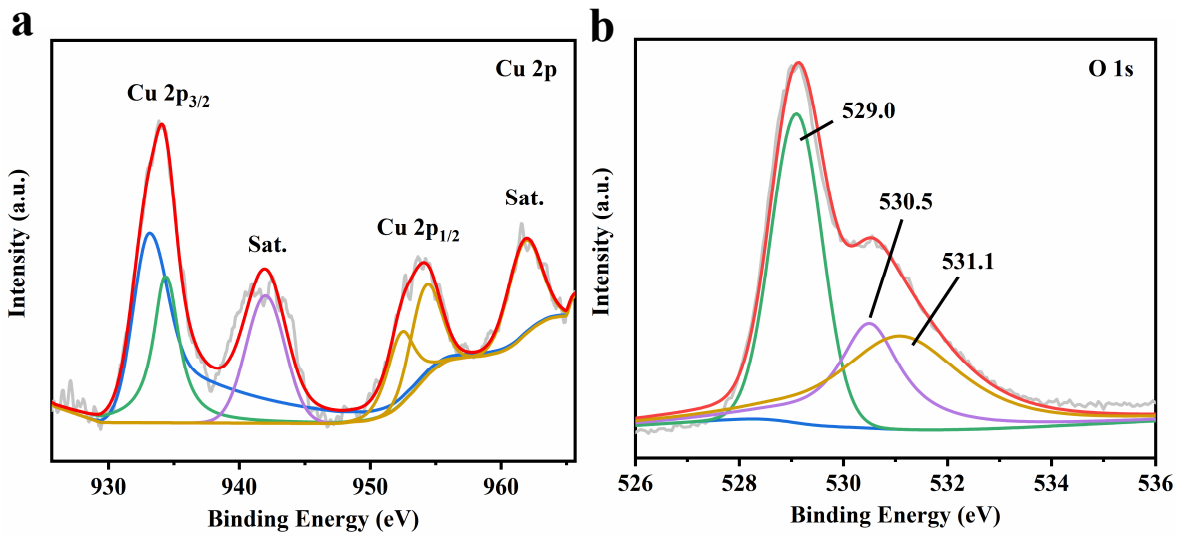


**Fig S3.** High-resolution XPS spectra of (a) Cu 2p and (b) O 1s of Cu@$Co_3O_4$@Ag-H substrates.

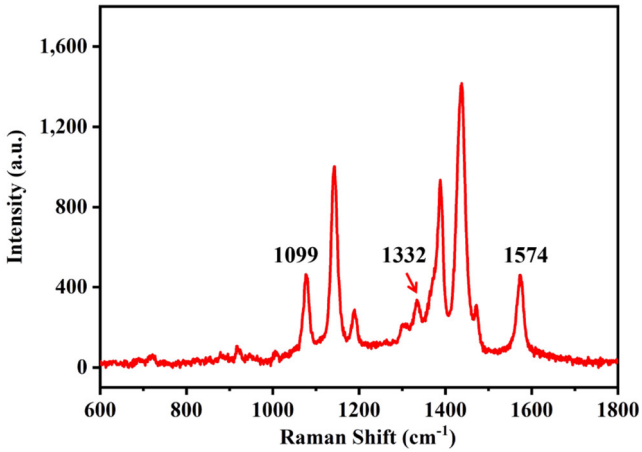


**Fig S4.** Raman spectrum of 4-NBT ($10^{-5}$ M).

**Table S1. The detailed Raman band assignment of 4-NBT.**

| Observed band ($cm^{-1}$) | Vibrational mode |
|---|---|
| 1099 | $CH_3NC$ deformation, C=S stretching |
| 1332 | S-S stretching |
| 1574 | $CH_3N$ stretching, C=S stretching |

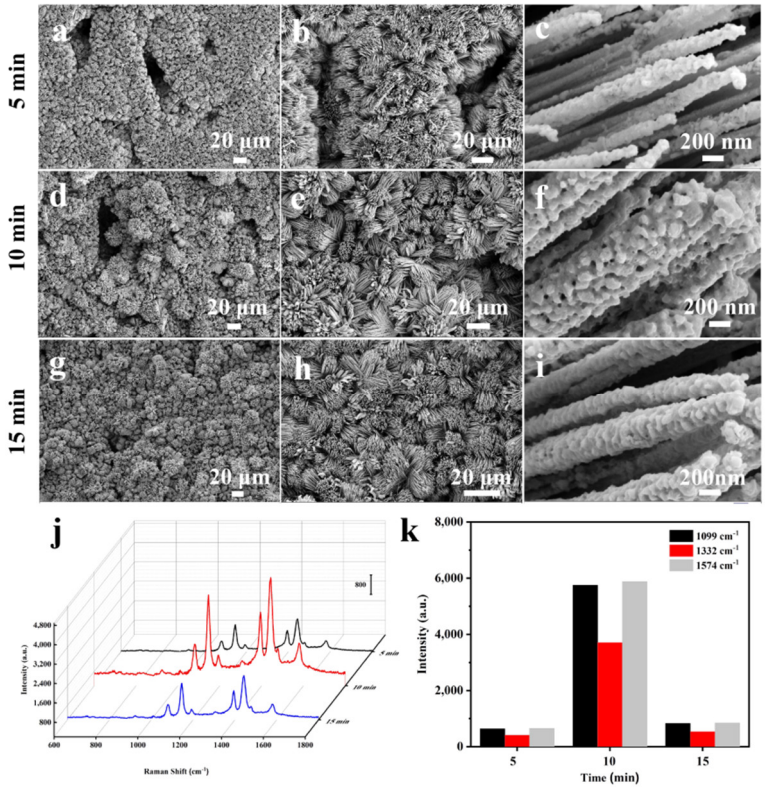


**Fig S5.** (a) SEM images of Cu@$Co_3O_4$ @Ag-S prepared at different deposition times (a-c) 5 min, (d-f) 10 min, (g-i) 15 min. (j) Raman spectra of $10^{-3}$ M 4-NBT ethanol solution on different substrates with deposition times of 5 min, 10 min and 15 min, respectively. and (k) Corresponding intensity distribution of the 1099 $cm^{-1}$, 1332 $cm^{-1}$and 1574 $cm^{-1}$ peaks.

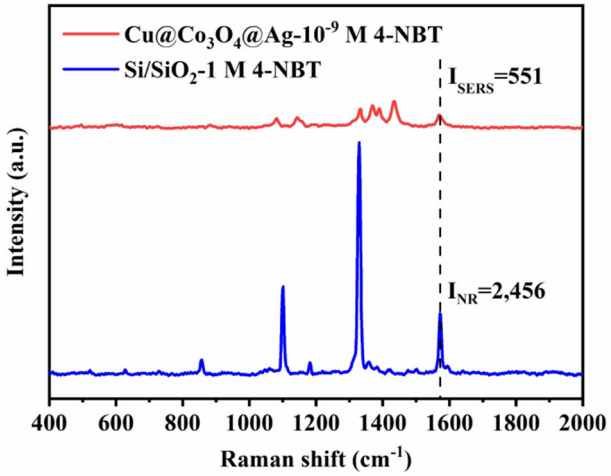


**Fig S6. Raman spectra of 4-NBT for EF measurement:** red line presents SERS spectrum of $10^{-9}$ M 4-NBT absorbed on the SERS substrate (multiplied by 5); blue line presents Raman spectrum of 1 M 4-NBT absorbed on the blank non-SERS platform ($Si/SiO_2$ wafer).

The enhancement factor (EF) of the as-prepared SERS substrate was estimated according to the widely accepted formula:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NR}/N_{NR}}$$

The $I_{SERS}$ and $I_{NR}$ are the intensities of the selected band in the SERS and normal Raman spectra, respectively. $N_{SERS}$ and $N_{NR}$ are the estimated molecule number under laser excitation for SERS, and the molecule number for the reference sample (solid), respectively.

We take the intensity at the characteristic peak 1574 $cm^{-1}$ of 4-NBT as the value of $I_{SERS}$ and $I_{NR}$. We can see $I_{SERS}$ =551 (multiplied by 5), $I_{NR}$ =2513 (multiplied by 5) from the **Fig S6**, and simplify $N_{SERS}$ and $N_{NR}$ to the concentration of 4-NBT solution dripping on SERS substrate and $Si/SiO_2$ wafer substrate. EF=$2.24\times10^8$ can be obtained by calculation.

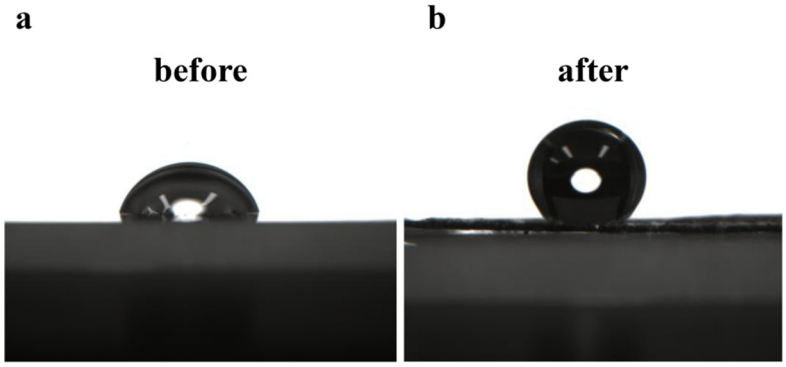


**Fig S7.** Water contact angle on Cu@$Co_3O_4$@Ag-F substrate (a) Before superhydrophobic treatment; (b) After superhydrophobic treatment.

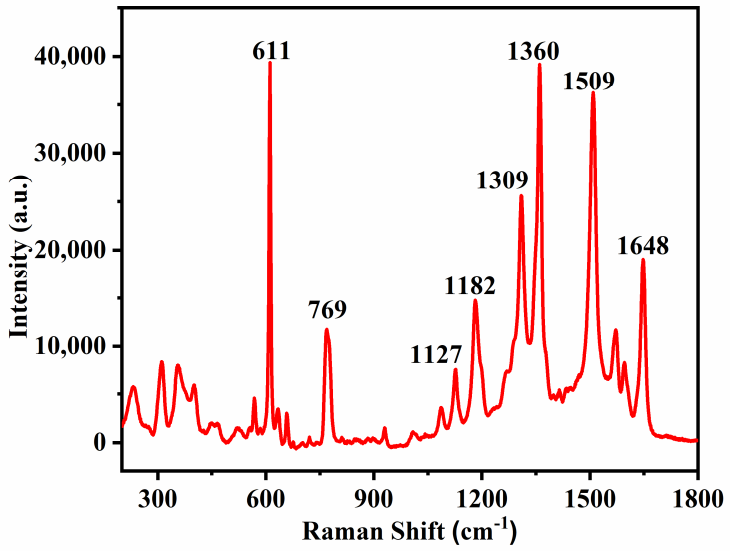


**Fig S8.** Raman spectrum of R6G ($10^{-4}$ M).

**Table S2. The detailed Raman band assignment of R6G.**

| Observed band ($cm^{-1}$) | Vibrational mode |
|---|---|
| 612 | C-C in plane deformation modes δ(C-C) $_{ring}$ |
| 769 | C-H out of plane deformation modes δ (C-H) $_{ring}$ |
| 1182 | C-H and N-H bending modes β(C-H) $_{xanthene}$ and β(C-H) $_{xanthene}$ |

| | |
|---|---|
| **1309** | **C=C stretching modes ν(C=C) xanthene** |
| **1509** | **C-C stretching modes ν(C-C) xanthene** |
| **1648** | **C=O stretching modes ν(C=O)** |

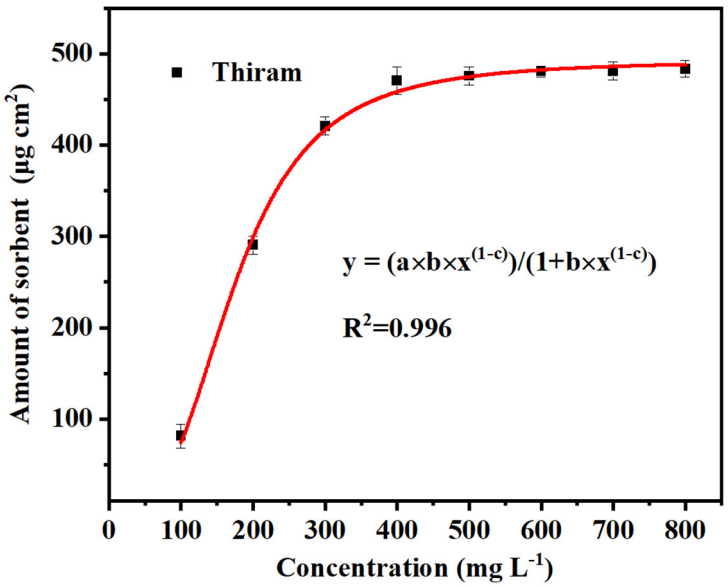


**Fig S9.** Adsorption curves of thiram at different concentrations on the superhydrophobic Cu@$Co_3O_4$@Ag-H substrates.

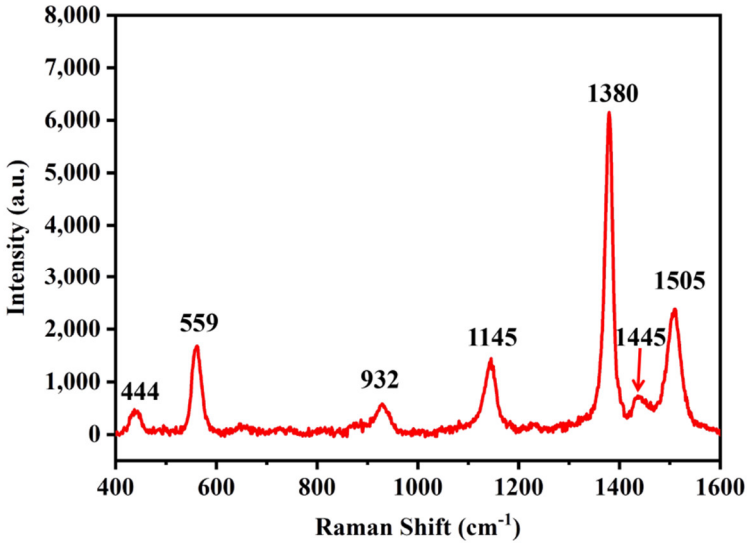


**Fig S10.** Raman spectrum of thiram (100 ppm).

**Table S3. The detailed Raman band assignment of thiram.**

| Observed band ($cm^{-1}$) | Vibrational mode |
|---|---|
| 444 | $CH_3NC$ deformation, C=S stretching |
| 559 | S-S stretching |
| 932 | $CH_3N$ stretching, C=S stretching |
| 1145 | $CH_3$ rocking, C-N stretching |
| 1380 | $CH_3$ symmetric rocking, C-N stretching |
| 1445 | $CH_3$ antisymmetric deformation |
| 1505 | $CH_3$ rocking, C-N stretching |