Supporting Information

Controlled assembly of one-dimensional MoO$_3$@Au hybrid nanostructures as SERS substrate for sensitive melamine detection

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Content

1.

Fig S1. (a) FESEM images of MoO$_3$-NW@Au-NPs for EDX spectrum (e) of Mo (b) O (c) and Au (d) elements, respectively.

2.

Fig S2. SEM images of the produced MoO_3-NW@Au-NPs with (a) and without ATES (b).

3.

Fig. S3. UV-Vis spectra of pure MoO3-NWs (a) and MoO_3-NW@Au-NPs with different m_{MoO3}: m_{Au} ratio (~14 nm Au-NPs): (b) 83.6:1 (c) 20.9:1 (d) 8.4:1 (e) 7.0:1 (f) 5.2:1 (g) 4.2:1, respectively. The insert is the corresponding intensity at the Au absorbance peak of 520 nm from a to g.

ZnO-NR@Au-NPs.

Preparation of ZnO-NR@Au-NPs. ZnO-NRs were synthesized according to our previous work.[1] Briefly, Zn (CH$_3$COO)$_2$·2H$_2$O (0.55 g) and CTAB powder (0.1 g) were dissolved in 60 ml of ethylene glycol at 25 °C. After the solution had been stirred for 1h at room temperature, 20 ml of 80% hydrazine hydrate was added and stirred for another 1 h, and then the solution was placed in an autoclave and heated at 160 ℃ for 6 h, then cooled down to room temperature naturally. The precipitate was washed several times with ethanol and then dried at 70 °C.

The synthesis route of ZnO-NR@Au-NPs is similar to MoO$_3$-NW@Au-NPs. In brief, mix 10 mL of 0.001g/mL homogeneous ZnO nanorods aqueous solution with 1mL ATES (1%) for 1h at room temperature, and drop 5 mL of Au-NPs (27.7 nm) slowly, transonic for 2 h at 25°C.

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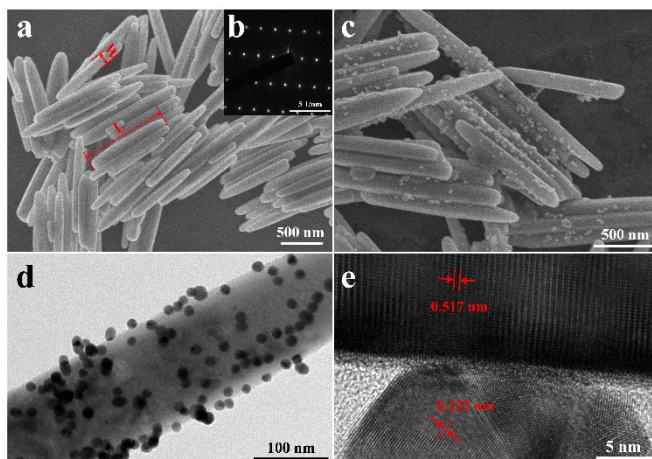
Fig. S4. (a) SEM images of the pure ZnO-NRs and the corresponding SAED pattern (b) in (a); The SEM (c) and magnified TEM images (d) of ZnO-NR@Au-NPs hybrids and HRTEM lattice image (e) of Au nanoparticle on ZnO-NR adjacent surface.

5.

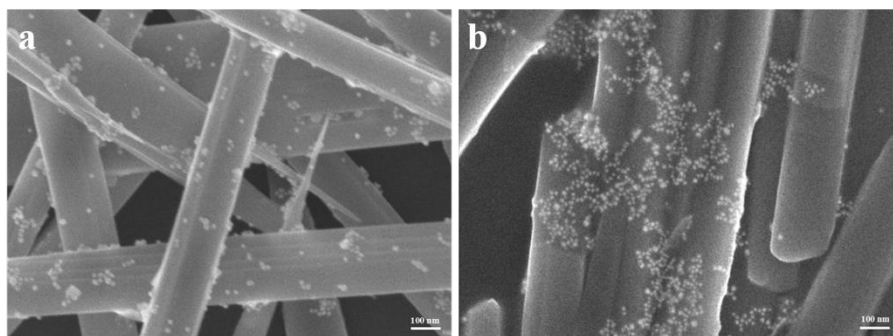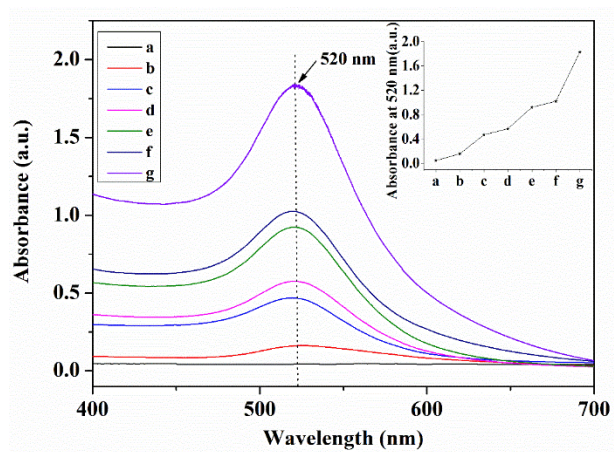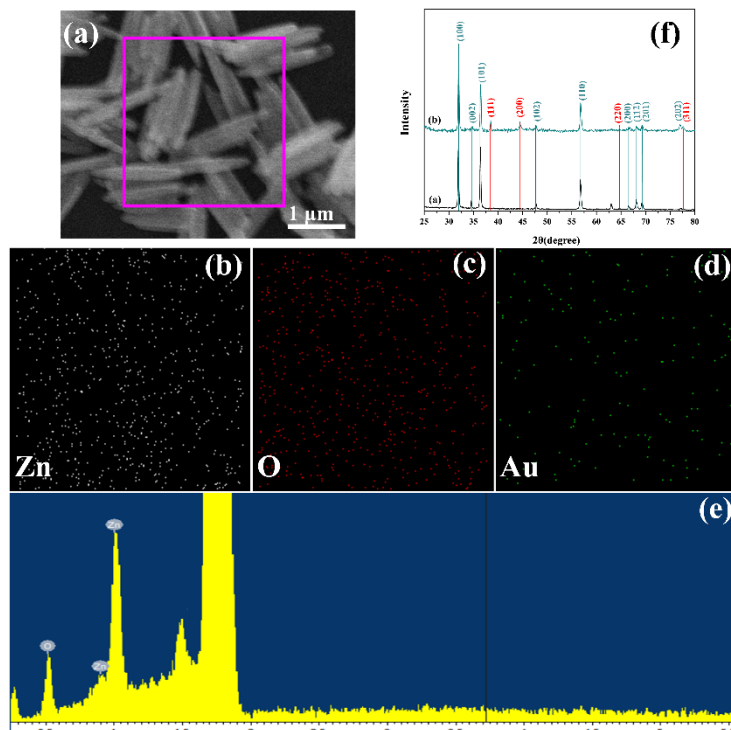**Fig S5.** (a) SEM image of ZnO-NR@Au-NPs hybrid for (e) EDX spectrum of (b) Zn, (c) O and (d) Au elements, respectively; (f) The XRD spectra of ZnO (black, a) and ZnO-NR@Au-NPs (green, b) phases, respectively.

The morphologies of ZnO-NR@Au-NPs. In order to evaluate the feasibly of the synthesis route in other metallic oxide (MO) and noble metal nanoparticle (NMP) systems, we take a widely used ZnO-NRs as an example to synthesize ZnO-NRs@Au-NPs. Fig S4a shows the SEM images of the pure ZnO-NRs micrograph prepared by hydrothermal method (see experimental for details). The well-aligned homogeneous NRs were found to have a length of (1.1± 0.15) μm, a width of (159.3 ± 17.9) nm and an aspect ratio of nearly seven. Fig. S4b shows the corresponding SAED pattern of it, which is characterized that a single NR is a single crystal with a hexagonal structure as proved by Wang[1]. For the self-assembly process, we choose (27.7±3.2) nm Au-NPs (see experimental for details) as decoration, and the morphology after hybridization was shown in Fig. S4c and S4d. Evidently, a large quantity of Au-NPs was present on the surfaces of ZnO-NRs successfully. As it can be observed, the decorating process does not seem to affect the morphology of the preformed ZnO-NR microstructures. The corresponding EDX spectrum of the ZnO-NR@Au-NPs was shown in Fig. S5a-e, implies the presence of Au, Zn and O elements, respectively.

It clearly evidences the successful decoration with Au-NPs on ZnO-NRs, indicating that the ATES self-assembly process have good reliability and flexibility. To further conform the Au-NPs were decorated on the ZnO-NRs, we conducted HRTEM characterization. In Fig. S4e, HRTEM image taken at the interface of NBs and NPs regions clearly reveals two distinct sets of lattice fringes. HRTEM image which is taken at the interface of ZnO-NR and Au NP region obvious reveals two different sets of lattice fringes. In the Au NP region, a lattice fringes of 0.232 nm was observed, coincided with the lattice spacing of (111) planes of the fcc Au.[2] An interlayer spacing of 0.517 nm was observed in the NR region, complying with the d spacing of the (001) lattice planes of ZnO microstructures, as determined from their corresponding XRD analysis in Fig. S5f (ZnO: PDF#36-1451; Au: PDF#04-0784).[3, 4]
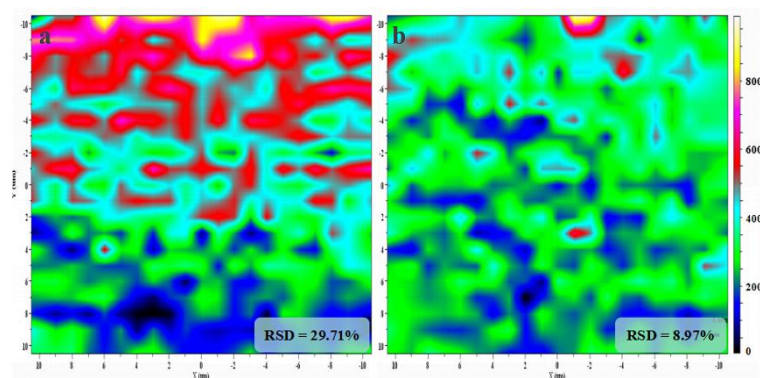
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Fig S6. Raman mapping spectra at 1080 cm^{-1} of 5 mM 4-MPH absorbed on MoO$_3$-NW@Au-NPs hybrids with different Au contents (a) 10 mL (b) 5 mL, respectively.
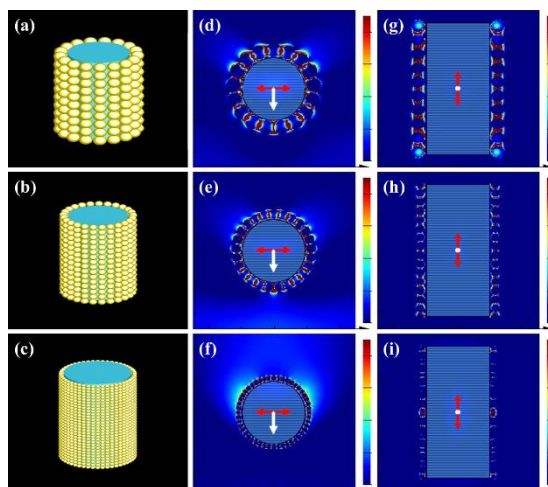
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Fig S7. (a-c) 3D FDTD models(closest packing) for MoO$_3$-NW@Au-NP. The diameter of gold nanoparticles adsorbed on MoO$_3$-NW was 44 (a), 28 (b) and 14 (c) nm, respectively. (d-i) 2D patterns of E-field intensity amplitude ($|E|^2$) around the corresponding models with polarization along x axis (d-f) and z axis (g-i). XY (d-f) and XZ (g-i) planes containing geometric centers of body structure were plotted. The scale bar is 10. The propagation and polarization direction of illumination source is plotted as white arrow and red arrow, respectively.
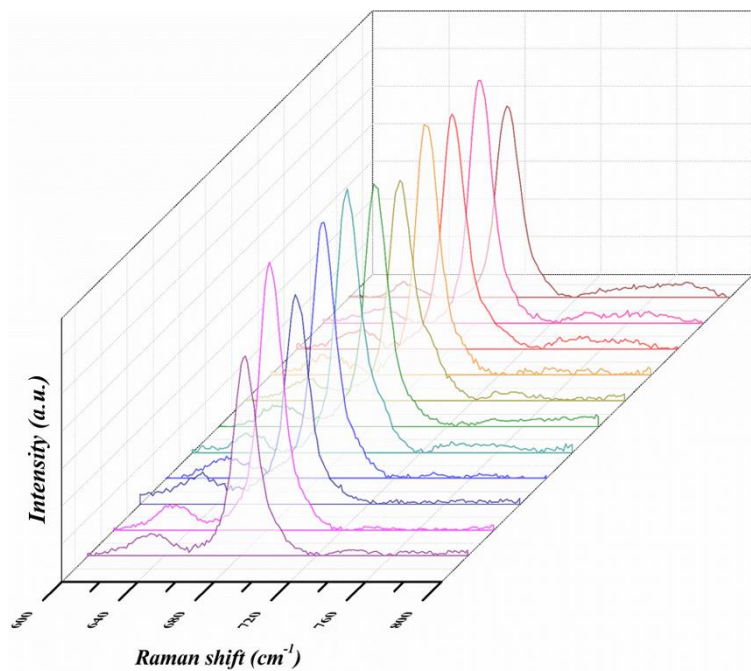
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Fig S8. SERS spectra of 1 ppb melamine at different spots (11 random spots) on MoO$_3$-NW@Au-NPs substrate

9.

In order to calculate the EF of MoO_3-NW@Au-NPs SERS substrate, new experiments were conducted to obtain the Raman spectra of both 0.01M 4-MPH adsorbed on blank Si substrate and 10^{-6} M 4-MPH absorbed on MoO_3-NW@Au-NPs hybrids as shown in Fig S8. The main Raman peaks at 1080 cm^{-1} of 4-MPH on both substrates were used for EF evaluation, which based on the method as following:

$$EF = \frac{I_{SERS}}{I_{bulk}} \times \frac{N_{bulk}}{N_{surface}}$$

where I_{SERS} and I_{bulk} are the SERS intensities of 10^{-6} M 4-MPH on the enhanced substrates and normal Raman spectra of 0.01 M 4-MPH on the substrate at the 1080 cm^{-1} band, respectively; N_{bulk} and $N_{surface}$ are the number of 4-MPH molecules under the same laser illumination conditions for the bulk Raman and SERS experiments, respectively. By substituting values into above equation, EF for the SERS enhancement of 4-MPH adsorbed on MoO_3-NW@Au-NPs was calculated as 8×10^5.
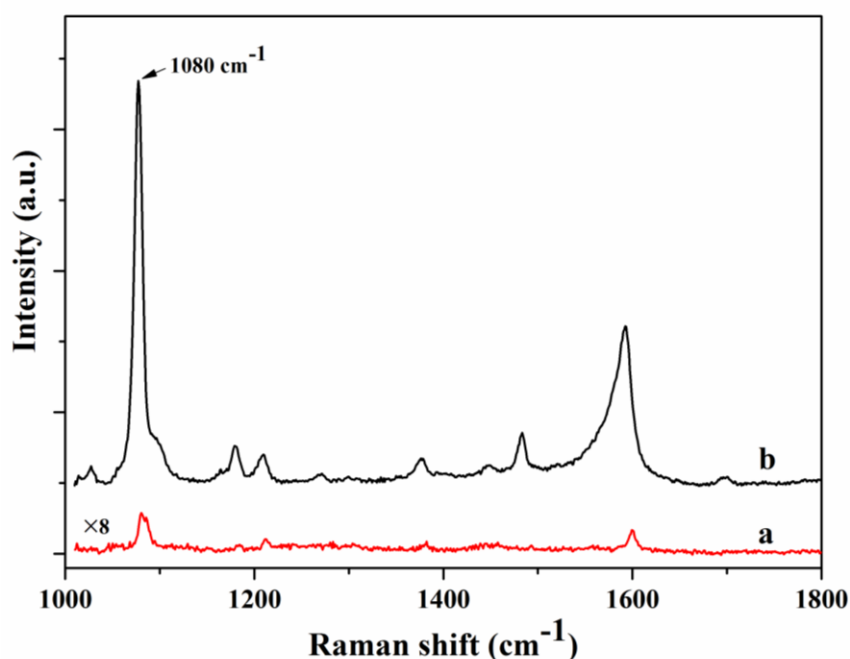

Fig S9. (a) Normalized Raman spectrum of 0.01M 4-MPH adsorbed on blank Si substrate. (b) SERS spectra of 10^{-6} M 4-MPH absorbed on MoO_3-NW@Au-NPs hybrids.
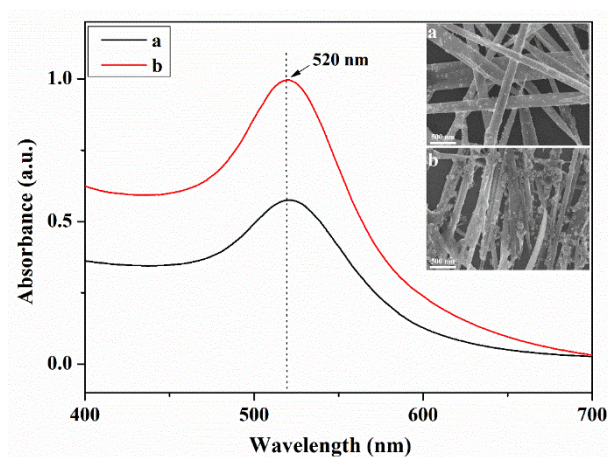
10.

Fig S10. UV-Vis spectra of MoO$_3$-NW@Au-NPs with different conditions as solid SERS substrates: (a) uniform dispersion condition with m$_{MoO3}$: m$_{Au}$ ratio (~14 nm Au-NPs) of 20.9:1; (b) aggregate condition with m$_{MoO3}$: m$_{Au}$ ratio of 5.2:1, respectively. The insert is the corresponding SEM images.

Reference

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