Supporting Information

Vertically Aligned Gold Nanomushrooms on Graphene Oxide Sheets as Multifunctional Nanocomposites with Enhanced Catalytic, Photothermal and SERS Properties

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Experimental Section

Materials: All the chemicals were of analytical grade and used without further purification. MBA was purchased from Sigma-Aldrich. Deionized distilled water (DI water) was used throughout. GO was supplied by the XF Nano, INC. (Shanghai, China), ultrasonic dispersion in water. Polyethylenimine (PEI) at molecular weight of 1.8 K was purchased from Aladdin. Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Sinopharm Group Chemical Regent Co., Ltd (Shanghai, China), silver nitrite ($AgNO_3$) was supplied by Shenbo Chemical Co., Ltd (Shanghai, China). L-ascorbic acid was supplied by Dingguochangsheng Biotechnology Co., Ltd (Beijing, China).

Characterization: Scanning electron microscopy (SEM) images were captured using an S-4800 scan electron microscopy (Hitachi, Japan). Transmission electron microscopy (TEM) images were captured using a JEM1200EX transmission electron microscopy (Electronics, Japan). XRD-7000 (Shimadzu, Japan) was used for XRD spectra recorded. XPS Au 4f spectrum was captured by an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA). Raman spectra were recorded using a LabRam HR 800 spectrometer (HORIBA Jobin Yvon, France). UV/vis/NIR spectra were measured on the spectrophotometer (Shimadzu, Japan). The electromagnetic fields of GO/AuNMs were calculated by the commercial software FDTD solutions (Lumerical Solutions, Inc).

Synthesis of GO and Au seeds hybrids: The preparation of GO/PEI complexes is according to our previous work [1]. In details, PEI solution (100 mg mL^{-1}) was slowly added to GO solution (1 mg mL^{-1}) to make the weight ratio of GO: PEI is 2:1 under stirring. Then the mixture was ultrasonicated about 30 min, stirred overnight and washed 3 times with DI water by centrifugation and re-dispersed. For the procedure of

assembling 6.5 nm or 13 nm Au seeds to GO/PEI sheets, 25 μL GO/PEI aqueous was added to 1 mL Au seeds solution for stand with several hours. The precipitate was washed several times and dissolved in 0.5 mL DI water.

Synthesis of GO/AuNMs nanocomposites: Reaction solution containing MBA ethanol solution (667 μM), $HAuCl_4$ (1.7 mM), L-ascorbic acid (4.1 mM) solution was prepared freshly. Then, 5 μL of the synthesized GO/Au seeds was added to 60 μL of reaction solution. The color of the reaction solution was changed from nearly transparent to blue within seconds. The reaction was continued for 30 minutes and washed two times with DI water by centrifugation.

Catalytic reduction of 4-Nitrophenol: 50 μL 3.8 μg/mL GO/AuNMs nanocomposites or GO/Au seeds (with respect to the GO concentration) were mixed with 50 μL $NaBH_4$ and 500 μL 4-nitrophenol, The yellow color of the solution disappeared gradually, indicating the reduction of 4-nitrophenol. The reaction progress was monitored by the measurement of the UV/Vis absorption spectra and the absorbance at the wavelength of 400 nm was used to determine the concentration of 4-nitrophenol.

Bacteria culture: Staphyloccocus aureus (S. aureus) was selected as model bacteria to study the photothermal antibacterial activity of GO/AuNWs nanocomposites. Bacteria were grown in the Luria-Bertani (LB) medium (10 g/L tryptone, 5 g/L yeast extract, and 10 g/L NaCl, pH 7) at 37 °C on a shaker bed at 200 rpm. 1×10^6 CFU/mL S. aureus was incubated with 100 μL 3.8 μg/mL GO/AuNWs nanocomposites or GO/Au seeds, followed by irradiation for 10 min. After that, the bacteria were transferred to the agar plate and colony number was counted after 12 h incubation. Pure water and GO/Au seeds were utilized as controls.

Photothermal treatments: To compare the photothermal effect of GO/Au seeds and GO/AuNMs, 100 μL of the as-prepared nanocomposites solution was irradiated by a NIR laser (808 nm, 175 mW/cm^2) and a thermoindicator was used to test the temperature change. Pure water was utilized as negative control. To test the bacteria killing ability, 100 μL of the as-prepared GO/Au seeds or GO/AuNMs was mixed with 10 μL portion of S. aureussolution, followed by irradiation for 10 min by a NIR laser (808 nm, 175 mW/cm^2). Then, the S. aureus remaining in the mixture were diluted 10^3 times, and 50 μL of the dilution was transferred onto a Petri dish containing LB medium and cultured at 37 °C for 12 h. The control experiments of S. aureus incubated in water by the NIR irradiation, and incubated with water, GO/Au seeds and GO/AuNMs without NIR irradiation were also performed.

SERS detection of Ag^+: The synthesized AuNMs solution was diluted twice. Then 30 μL 0.05 M L-ascorbic acid and certain concentration of Ag^+ were added to 30 μL of diluted AuNMs solution. After 2 hours, ultrasonic for 10 seconds. 5 μL of the product was drop on silicon wafer and dried in atmosphere for SERS detection. Measurements at different position were carried out for each sample to ensure the reproducibility. Laser wavelength: 532 nm; power: 2.45 mw; lens: 50× objective; acquisition time: 5s.

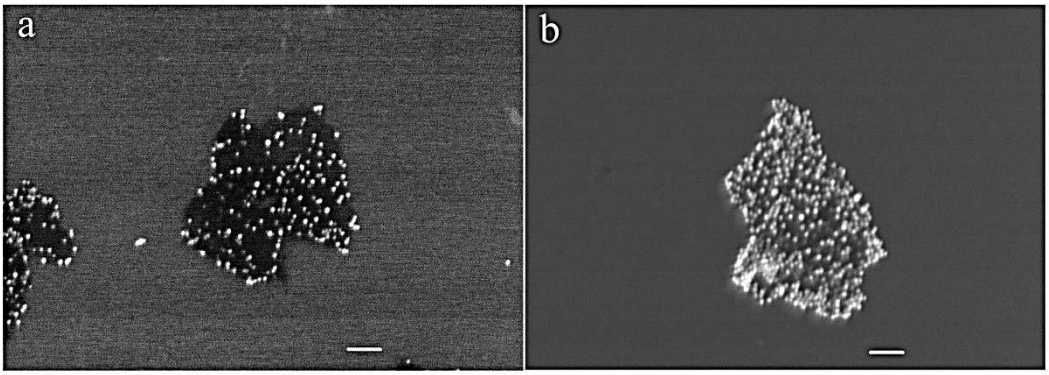

Fig. S1 SEM images of GO/Au seeds hybrids. a, GO/Au seeds (6.5 nm); b, GO/Au seeds (13 nm). The scale bars are equal to 200 nm.

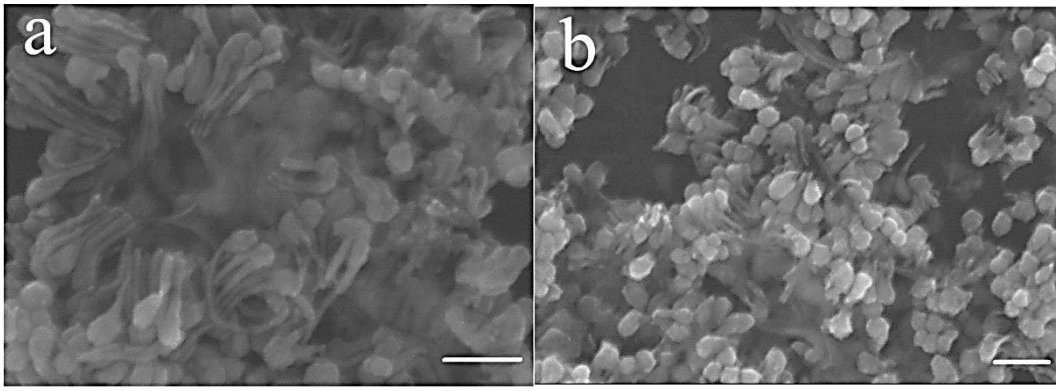

Fig. S2 SEM images of AuNMs grown from 13 nm AuNSs on GO sheets. The scale bars are equal to 100 nm.

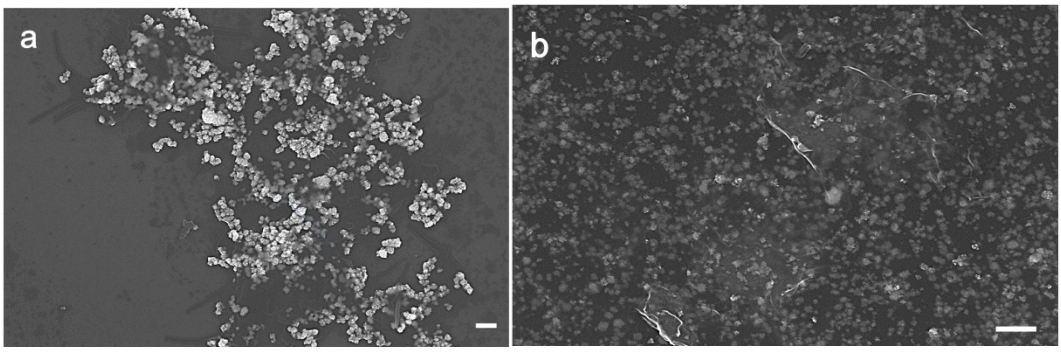

Fig. S3 SEM images of the product in the presence of Au seeds (a) or GO (b). The scale bars are equal to 300 nm.

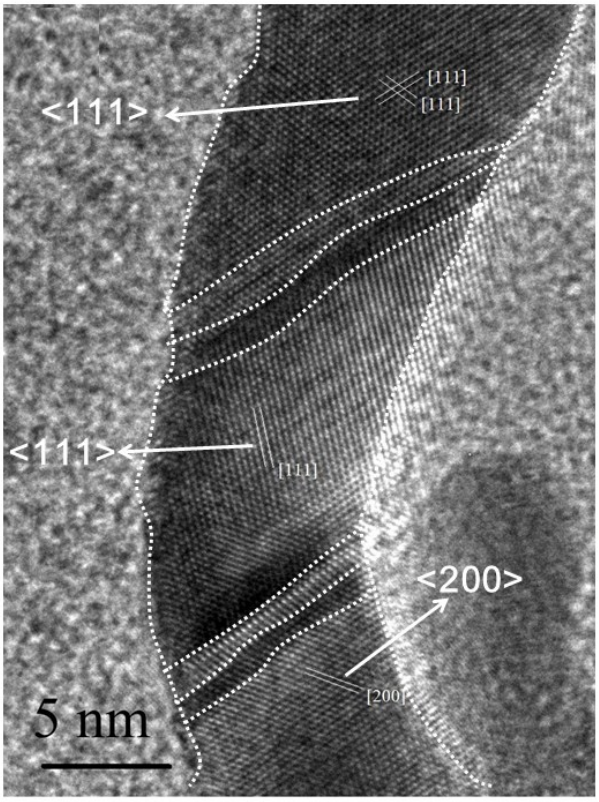

Fig. S4 The magnified HRTEM images of AuNMs,

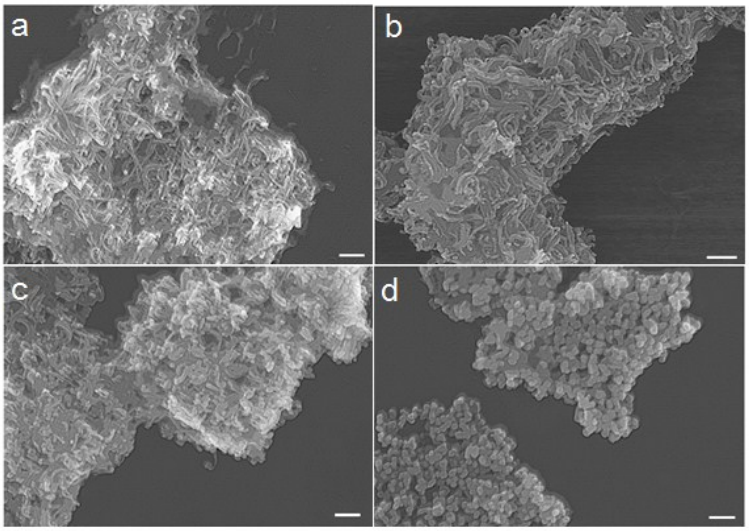

Fig. S5 SEM images of the AuNMs grown on GO at different MBA concentration: (a) 6 mM, (b) 2 mM, (c) 1mM, (d) 0.5mM. Scale bars are equal to 100 nm.

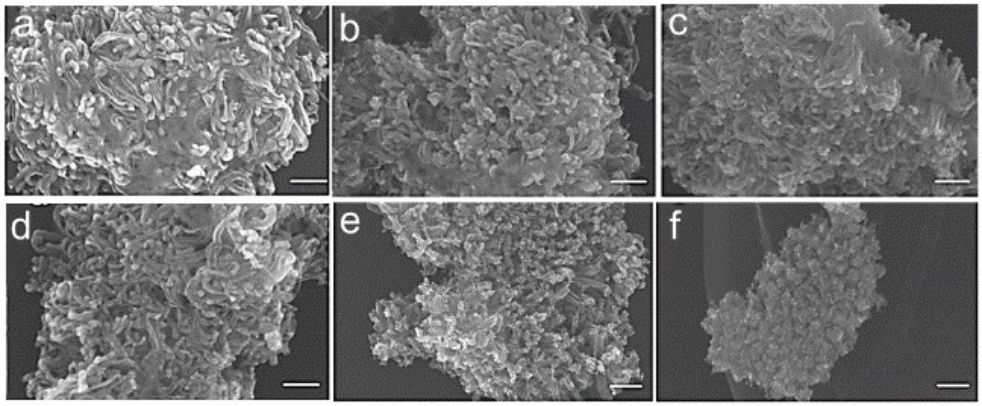

Fig. S6 SEM images of the AuNMs grown on GO at different concentration of ethanol: (a) 88%; (b) 75%; (c) 59%; (d) 50%; (e) 33%; (f) 25%. Scale bars are equal to 100 nm.

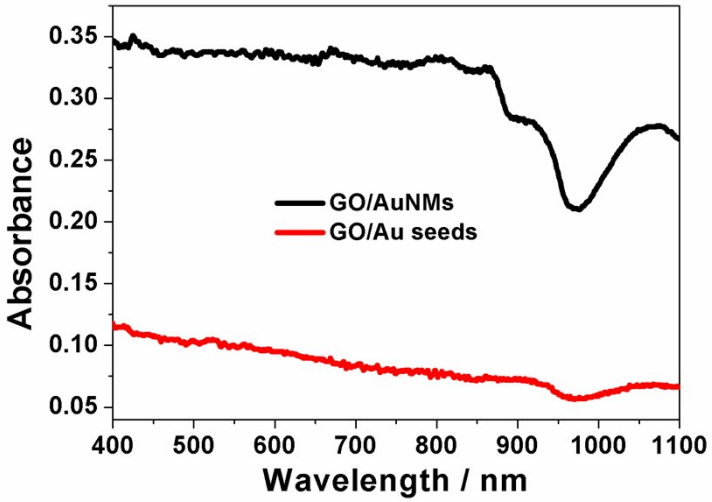

Fig. S7 UV/vis/NIR spectra of GO/AuNMs (black) and GO/Au seeds (red) with the same concentration of GO (3.8 μg/mL).

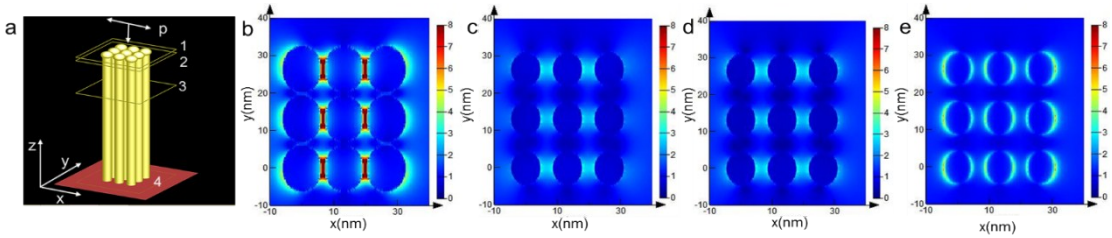

Fig. S8 E-field amplitude patterns obtained from FDTD simulations of the GO/AuNMs at wavelengths from 400 nm to 700 nm. (a) Depiction of GO/AuNMs substrate with four different layers marked (1-4). The polarization direction, p, along the x axis perpendicular to the incident light is given. The lengths and diameters of the simulated AuNM stipes were 233 nm and 9 nm,

respectively, and the diameter of the AuNM caps was 12 nm. (b) E-field amplitude pattern at the flat layer of the caps of AuNMs (layer 1 in a). (c) E-field amplitude pattern at the interface between the stipes and caps of AuNMs (layer 2 in a). (d) E-field amplitude pattern at the flat layer of the stipes of AuNMs (layer 3 in a). (e) E-field amplitude pattern at the interface between GO and the stipes of the AuNMs (layer 4 in a).

Table R1. The reaction rate constants (*k*) of different catalysts for the reduction of 4-NP

Catalyst	[4-NP](M)	[$NaBH_4$] (M)	*k* (min^{-1})	Ref.
GO/AuNMs	3.4×10^{-4}	0.1	1.27	Present work
$Cu_{2-x}Se$/rGO/PVP nanofibers	4NP : $NaBH_4$ = 1 : 500		0.14	2
Ni/SiO_2	1×10^{-4}	0.2	0.068	3
Au/graphene	1×10^{-4}	0.1	0.19	4
Cu_3Ni_2	1×10^{-4}	0.02	0.58	5
Au-PNIPA	1.1×10^{-4}	0.1	0.045	6
AuNSs	8.986×10^{-2}	0.615	0.2221	7
Pt@3DG	4NP : $NaBH_4$=1 : 28		0.389	8
PS/RGO@AuNP composite	4NP : $NaBH_4$=1 : 100		0.2202	9
H40-PEI-PEG-stabilized AuNPs	4NP : $NaBH_4$=1 : 500		0.256	10
$Co_{0.85}Se$–TiO_2 nanofilms	5×10^{-3}	0.03	0.3835	11
Pt–Au pNDs/RGOs	4NP : $NaBH_4$=1 : 2381		0.228	12
Ag/GO nanocomposites	4NP : $NaBH_4$=1 : 83		0.493	13

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