Electronic Supplementary Information

One-step Fabrication of Hollow-channel Gold Nanoflowers with Excellent Catalytic Performance and Large Single-particle SERS Activity

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Preparation of MO-FeCl₃ nanofiber templates

13.5 mg of FeCl₃ was dissolved in 1 ml of 5 mM Methyl orange (MO) aqueous solution to prepare the template dispersions. Following the addition of $FeCl_{3}$ an orange flocculent precipitate appeared immediately, indicating the formation of the nanofiber templates.

MO consists of a planar hydrophobic section with hydrophilic edge groups (SO₃⁻), and can self-associate by stacking like plates in aqueous solutions. In the aqueous solution of 5 mM MO, the average aggregate of MO contains five to seven monomers.^{1, 2}

 Fe^{3+} ions play the role of a flocculant suppressing the electrostatic repulsions between MO aggregations and complex with MO to form a one-dimensional template with nanofiber structures ^{2, 3}, as shown in Fig. S1A and Scheme S1.



Fig. S1 SEM image (A) and the histogram (B) of width distribution of MO-FeCl₃ nanofiber template (by counting 200 nanofibers)



Scheme S1 Schematic illustration of MO–Fe³⁺ nanofiber template



Fig. S2 SEM image of as-prepared HAuNFs before centrifugation

Mechanism of the template auto-degradation

We monitored the UV-vis spectra of the following systems:

- (1) MO-FeCl₃ template and ascorbic acid (AA);
- (2) MO solution, AA, and HAuNFs;
- (3) MO-FeCl₃ template and HAuNFs;
- (4) MO-FeCl₃ template, AA, and HAuNFs.

In systems (1), (2) and (3), the absorption of MO solution or MO-FeCl₃ template dispersions was almost unaltered after 3h.

In system (4), the absorption assigned to MO/ MO-FeCl₃ decreased and then disappeared within 12 mins (Fig. S3B).

As a result, we ascribe the template auto-degradation to the combined effect of $FeCl_3$ in the template, excessive AA, O_2 in the solution, and as-formed nanoflowers.

Following the addition of reducing agent AA to the reaction system containing MO-FeCl₃ template and HAuCl₄, AA first reacts with HAuCl₄ to produce gold nanocrystasl, and then the excess AA reacts with Fe^{3+} in the template, as well as O₂ in the solution.

(Standard reduction potential of $AuCl_4$ /Au: +0.99 V, Fe^{3+}/Fe^{2+} +0.77 V)

The auto-degradation undergoes two steps.

Step (1):

According to Equation (1)-(3), FeCl₃ AA, O_2 in the solution could form Fenton-like system, generating highly reactive hydroxyl radical (HO•). ⁴

$Fe^{3+} + AA \rightarrow Fe^{2+} + AA \bullet + H^+$	(1)
$AA+O_2 \rightarrow dehydroasorbate + H_2O_2$	(2)
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$	(3) (Fenton reaction)

Step (2):

The powerful hydroxyl radical (HO•) destroys MO molecule.⁵

The as-formed Au nanoflowers can act as catalysts in Step (1) or/and (2).^{6,7}



Fig. S3 (A) UV-vis spectrum of the supernatant after centrifugation of the reaction solution; (B)Time-dependent UV-vis absorption spectra of the mixture of the MO-FeCl₃ nanofiber and AA solution, following the addition of HAuNFs.



Fig. S4 X-ray diffraction (XRD) pattern of HAuNFs



Fig. S5 SAED pattern of an individual HAuNF



Fig. S6 (A) SEM image and (B) UV-vis spectrum of the HAgNFs prepared using MO- $Fe(NO_3)_3$ nanofiber templates.

In the fabrication of HAgNFs, the cation-aromatic interactions between Ag+ ions and benzene in the MO molecules, ^{8, 9} lead Ag+ to be absorbed onto the MO-Fe(NO₃)₃ nanofibers.



Fig. S7 TEM image of AuNSs synthesised by adding AA solution into $HAuCl_4$ solution in the absence of template.



Fig. S8 SEM image of the HAuNFs synthesised with 50 mM AA (A) and 150 mM AA (B)



Fig. S9 (A) TEM image of one branch of an HAuNF; (B) HRTEM image from the region indicated within the box in (A), showing the {311} facets made of (111) and (100) sub-facets. (C) The corresponding atomic models of {311} planes projected from the [110] zone axis.



Fig. S10 (A) TEM image of one branch of an HAuNF; (B) HRTEM image from the region indicated within the box in (A), showing the {411} facets made of (111) and (100) sub-facets. (C) The corresponding atomic models of {411} planes projected from the [110] zone axis.

Table 51 110 jection angles between (100) and (111) facets				
{h11}	{111}	{211}	{311}	{411}
Angle with {100}	55°	35°	25°	19°

Table S1 Projection angles between (100) and (h11) facets



Fig. S11 (A-C): HRTEM images of the lateral facets revealing the projection angle between the surface and the {111} facets.



Scheme S2 Mechanism of the methyl orange degradation by $NaBH_4$ using HAuNFs/AuNSs as catalysts.¹⁰



Fig. S12 Catalytic properties of AuNSs towards methyl orange degradation: the extinction spectra recorded at different reaction time points using AuNSs as catalyst.



Fig. S13 Catalytic properties of AuNSs towards the reduction of 4-NP: the extinction spectra recorded at different reaction time points using AuNSs as catalyst.

Conversion calculation

For the reaction of methyl orange (MO) degradation using HAuNFs as catalysts, the conversion (within 100 s) is calculated using the following equation: Conversion = $1-C_{100 \text{ s}}/C_0 = 1-A_{100 \text{ s}}/A_0$

Where $C_{100 s}$ and C_0 are the concentrations of MO at t=100 s and 0 s respectively.

 $A_{100 s}$ and A_0 are peak absorbance at 465 nm of MO at t=100 s and 0 s respectively.

Cycle number	A_0	A _{100 s}	Conversion (%)
1	1.9750	0.0716	96.4
2	1.9491	0.0616	96.8
3	1.9402	0.0566	97.1
4	1.9580	0.0602	96.9
5	1.9225	0.0562	97.1
6	1.9527	0.0709	96.3
7	1.9537	0.0607	96.9
8	1.8808	0.0453	97.6
9	1.8896	0.0586	96.9
10	1.8999	0.0550	97.1

Table S2 A_{100 s}, A₀ and conversion of each cycle in MO degradation using HAuNFs as catalysts

For the reaction of 4-NP reduction using HAuNFs as catalysts, the conversion (within 120 s) is calculated using the following equation:

Conversion = $1 - C_{120} / C_0 = 1 - A_{120} / A_0$

Where $C_{120 s}$ and C_0 are the concentrations of MO at t=120 s and 0 s respectively.

 $A_{120 s}$ and A_{0} are peak absorbance at 400 nm of 4-NP at t=120 s and 0 s respectively.

Cycle number	A_0	A _{120 s}	Conversion (%)
1	1.0706	0.0634	94.1
2	1.1174	0.0523	95.3
3	1.1165	0.0799	92.8
4	1.0935	0.0544	95.0
5	1.1398	0.0557	95.1
6	1.0605	0.0513	95.2
7	1.1057	0.0544	95.1
8	1.1774	0.0549	95.3
9	1.1297	0.0704	93.8
10	1.1285	0.0420	96.3

Table S3 A_{120s} , A_0 and conversion of each cycle in 4-NP reduction using HAuNFs as catalysts

SERS enhancement factor estimation

Surface area:

HAuNFs

The surface area of the HAuNF was estimated by assuming the spikes on the outer surface to be cones.

 $\mathbf{S}_{\mathbf{HAuNF}} = \mathbf{S}_{\mathbf{Outer}} + \mathbf{S}_{\mathbf{Inner}}$



 $D_{HAuNF} = 190 \text{ nm}, h= 25 \text{ nm}, \theta = 22.5^{\circ}$ $D_{core} = D_{HAuNF} - 2h = 140 \text{nm}$

 $r = htan \theta = 10 nm$



d(inter-particle spacing) = 5 nm

r =10 nm

Scheme S3 Schematic model of estimating the outer surface area of HAuNFs (The scheme is not proportionally represented.).

We denote the core radius as $R_c \simeq 70$ nm. The circular footprints of the spikes have average radius $r_s \simeq 10$ nm. The separation between neighboring spike bases are $d_s \simeq 5$ nm, i.e. $(r_s+d_s/2)$ radii patches would touch each other. Since $r_s \ll R_c$, locally the spike bases can be well described with Euclidean approximation. Assuming hexagonal close packing, $(r_s+d_s/2)$ Radii patches occupy $\frac{\pi}{2}$

 $\overline{\sqrt{12}}$ fraction of the core surface. With the total core surface being $4\pi R_c^2$, the number of spikes can be estimated as

$$N_{\rm spike} \simeq \frac{\frac{\pi}{\sqrt{12}} 4\pi R_c^2}{\pi \left(r_s + \frac{d_s}{2}\right)^2},$$
$$= \frac{2}{\sqrt{3}} \pi \frac{R_c^2}{\left(r_s + \frac{d_s}{2}\right)^2},$$
$$\simeq 114.$$

With the Euclidean assumption, the fraction of core surface covered by the spikes is given by

$$\begin{split} \Phi_{\rm spike} &= \frac{N_{\rm spike}\pi r_s^2}{4\pi R_c^2}, \\ &= \frac{\pi}{2\sqrt{3}} \frac{r_s^2}{\left(r_s + \frac{d_s}{2}\right)^2}, \\ &\simeq 0.58. \end{split}$$

With the height of the spikes $h_s \simeq 25$ nm, the lateral height of the spikes (described as right circular cones) is

$$l_s = \sqrt{r_s^2 + h_s^2} \simeq 27 \mathrm{nm}.$$

The outer surface area is given by the sum of lateral surfaces of the spikes and the exposed core surface:

$$\begin{split} S_{\text{Outer}} &= S_{\text{spikes}} + S_{\text{uncovered core}}, \\ &= N_{\text{spike}} \pi r_s l_s + \left(1 - \Phi_{\text{spike}}\right) 4\pi R_c^2 \\ &\simeq 96495 + 25816 \simeq 1.22 \times 10^5 \text{nm}^2. \end{split}$$



Scheme S4 Schematic model of estimating the inner surface area of HAuNFs (The scheme is not proportionally represented.).

$$S_{Inner} = 2DW + 2DT = 2.24 \times 10^4 \text{ nm}^2$$
$$S_{HAuNF} = S_{Outer} + S_{Inner} = 1.44 \times 10^5 \text{ nm}^2$$

AuNSs:

$$D_{AuNSs} = 210 \text{nm}$$
$$S_{AuNSs} = \pi D_{AuNSs}^2 = 1.38 \times 10^5 \text{ nm}^2$$

Enhancement factor

The enhancement factors (EFs) of Raman signals were estimated using the following equation: ¹¹

$$\mathbf{EF} = (I_{SERS} \times N_{normal}) / (I_{normal} \times N_{SERS}),$$

where

*I*_{SERS}: the intensity of a specific band in the SERS spectra of BPT;

 I_{normal} : the intensity of the same band in the normal Raman spectra of BPT under the same condition;

 N_{normal} : the number of probe molecules in the excitation volume for the normal Raman measurements;

 N_{SERS} : the number of adsorbed molecules on an individual particle.

Two Raman modes of BPT at 1100 cm⁻¹ and 1589 cm⁻¹ were chosen for the EF calculations.

To estimate the N_{normal} , we calculated the effective excitation volume by using the following equation:

 $V = \pi \times (d/2)^2 \times H$,

Where

D: the diameter of the beam size $(d = 1 \mu m)$

H: the effective depth of focus (H= 1 μ m, which was estimated by finely controlling the height of the stage during the Raman measurement).

The effective excitation volume was estimated to be of 7.85×10^{-19} m³ for our Raman microscopy with 633 nm excitation using the 100× objective.

 N_{normal} was calculated by using the following equation:

 $N_{normal} = (V \times D/M) \times N_A = 2.83 \times 10^9$ molecules,

where

D: the density of BPT (1.173 g/ml),

M: the molar mass of BPT (1.113 g/mol) and

NA: the Avogadro constant $(6.02 \times 10^{23} \text{ mol}^{-1})$.

To determine N_{SERS} , a self-assembled monolayer of molecules (molecular footprint size of 0.235 nm²)¹² was assumed to be closely packed on the surface of each Au particle.

$$N_{\rm SERS} = {\rm S} / 0.235$$

 $N_{\text{sersHauNF}} = S_{\text{HAuNF}}/0.235 = 6.1 \times 10^5$ molecules.

 $N_{\text{SERSAUNS}} = S_{\text{AuNS}}/0.235 = 5.9 \times 10^5$ molecules.



Fig. S14 Normal Raman spectrum of biphenyl-4-thiol (powder).

Peak assignment:

991 and 1100 cm⁻¹ δ (C-H), 1276, 1589 and 1593 cm⁻¹ ring v (C=C).¹²

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