Tunable 3D light trapping architectures based on self-assembled SnSe$_2$ nanoplate arrays for ultrasensitive SERS detection

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Figure S1. (a-c) Representative top-view SEM images of the resulting SnSe$_2$ NPAs, corresponds to a certain deposition time (5, 10 and 20 min, respectively). (d-f) Representative top-view SEM images of the resulting SnSe$_2$ NPAs, corresponds to a certain deposition time (5, 10 and 20 min, respectively). The thickness of the SnSe$_2$ NPAs is about 30–40 nm (> 10 layers, bulk).
Figure S2. Height of SnSe$_2$ NPs as a function of deposition time.
Figure S3. Raman spectra of SnSe$_2$ NPA s with different deposition time.
Figure S4. SERS spectra of R6G (10^{-6} M) adsorbed on SnSe₂ NPAs with different deposition time.
Figure S5. SERS spectra of R6G (10^-6 M) adsorbed on SnSe2 NPAs (another batch of samples) with different deposition time. The result indicates the highly reproductive feature, compared with the results shown in Figure 3a.
Charge-transfer process

The valence band (VB) and the conduction band (CB) of SnSe$_2$ were calculated by the following equations (S1) and (S2) [1]

\[ E_v = -(\chi(A)^s \chi(B)^s \chi(C)^s)^{1/(a+b+c)} + 1 / 2E_g \]  
\[ E_c = E_v + E_g \]  

where $E_v$ and $E_c$ are the valence band and conduction band edge, respectively. $\chi$ is the electronegativity of the semiconductor, which is geometric mean of the electronegativity of the constituent atoms. For SnSe$_2$, the value of bandgap $E_g$ was calculated to be 1.2 eV by the following equation (S3)[2]

\[ E_g = 1240 / \lambda_{\text{obs}} \]  

where $\lambda_{\text{obs}}$ is 1028 nm, as required from the photoluminescence spectra shown Figure S6a. Thus, the $E_v$ and $E_c$ of SnSe$_2$ was -4.7 eV and -3.5 eV, respectively. Figure S6b depicts the charge-transfer process at the interface between R6G probe molecule and SnSe$_2$. The valence band (VB) (-4.7 eV) and conduction band (CB) (-3.5 eV) of SnSe$_2$ are located between the HOMO (-5.70 eV) and LUMO (-3.40 eV). The vibronic coupling between SnSe$_2$ (CB state $|S>$ and VB state $|S'>$) and R6G molecule (excited state $|K>$ and ground state $|I>$) leads to the charge transfer process.

Considering of the excitation energy and R6G molecule, when a laser with wavelength of 532 nm was used, the following transfer processes can occur according to the energy level relationship [3]: (1) ($T_{SS}$), (2) ($T_{IK}$), (3) ($T_{SK}$), (4) ($T_{IS}$), (5) ($T_{IS'}$) and (6) ($T_{SK}$), which are shown in Figure S6b. Attributing to enormous enhancement of the polarizability of the R6G molecule, recombination of electrons and holes is increasing, which enhances the peak intensity of R6G molecules.

In additional, for the two dimensional SnSe$_2$ nanomaterials, the large specific surface area will also benefit to the easier combination of surface atoms (Sn, Se) with adsorbed R6G molecules, in turn leading to stronger photoinduced charge-transfer process [4].
Figure S6. (a) Photoluminescence spectra of SnSe$_2$ NPAs. (b) Schematic illustration of the photoinduced charge-transfer process between SnSe$_2$ NPAs and R6G under the excitation of 532 nm.
Calculation of enhancement factor (EF)

The Raman enhancement factor (EF) of as-fabricated SnSe$_2$ NPAs SERS substrate was calculated by the following equation (S4) [5]:

$$EF = \frac{I_{\text{SERS}}}{N_{\text{SERS}}} \cdot \frac{N_{\text{NR}}}{I_{\text{SR}}} \quad (\text{S4})$$

In equation S4, $I_{\text{SERS}}$ and $I_{\text{SR}}$ are the Raman intensity of normal Raman signal collected from probe molecule adsorbed on SnSe$_2$ NPAs (1cm×1cm) and normal Raman signal collected from probe molecule (0.1 M) drop on rectangular glass (1cm×1cm), respectively. $N_{\text{SERS}}$ and $N_{\text{NR}}$ are the amounts of molecules involved in the SERS experiments and estimated for 100 μL of the aqueous solution of probe molecule (0.1 M) dropped on a glass which produced a deposition area about 1cm$^2$ (1cm×1cm), respectively. Here we use R6G probe molecules and 611 cm$^{-1}$ peak to calculate the EF.

The amounts of the detected molecule $N_{\text{SERS}}$ can be calculated by:

$$N_{\text{SERS}} = C V_{\text{solution}} S_{\text{spot}} N_{\text{A}} / S_{\text{sub}} \quad (\text{S5})$$

where $C$ is the concentration of probe molecule, $V_{\text{solution}}$ is the volume of used probe molecules drop, $S_{\text{spot}}$ and $S_{\text{sub}}$ are the area of laser spot and the area of rectangular glass substrate (1cm$^2$), respectively, $N_{\text{A}}$ is Avogadro constant ($6.22 \times 10^{23}$). The laser spot diameter $d$ ($d = 1.22 \lambda_{\text{laser}} / N_{\text{A}}$), $\lambda_{\text{laser}}$ is the incident wavelength 532 nm, the numerical aperture of the objective lens $N_{\text{A}} = 0.5$ is about 1.3 μm. Thus, the laser spot area $S_{\text{spot}} = \pi (d / 2)^2$ is about 1.33 μm$^2$.

The Raman 611 cm$^{-1}$ intensity of R6G/SnSe$_2$ NPAs (1×10$^{-10}$ M) is 35.6 counts (Figure S7b) with 10 s acquisition time, and that of bulk R6G is 562.5 counts with 1 s acquisition time (Figure S7a). With normalization in case of acquisition time, the Raman intensity ratio is estimated to be $I_{\text{SERS}} / I_{\text{SR}} = (35.6/10)/(562.5) = 6.33 \times 10^{-3}$. Therefore, according to the equation (S4) and (S5), the EF of as-fabricated SnSe$_2$ NPAs SERS substrate was calculated to be $EF = (6.33 \times 10^{-3})(10^{-1} / 10^{-10}) = 6.33 \times 10^6$. 

Figure S7. (a) SERS spectra of R6G (0.1 M) adsorbed on glass substrate (1 s acquisition time). (b) SERS spectra of R6G (1×10^{-10} M) adsorbed on glass substrate (10 s acquisition time).
Figure S8. The Raman intensities of R6G at peak of 1361 cm$^{-1}$ and 1648 cm$^{-1}$, acquired from SERS spectra shown in Figure 4a.
Figure S9. The Raman intensities of R6G at peak of 1361 cm\(^{-1}\) and 1648 cm\(^{-1}\), acquired from SERS spectra shown in Figure 4c.
**Figure S10.** Sample to sample Raman intensity variations. 5 SERS spectra (yellow line) and 5 SERS spectra (red lines) are collected from different samples. A small sample-to-sample RSD of 6.2% was achieved.
Figure S11. (a) Measured reflectivity of SnSe$_2$ NPAs with different deposition time. (b) Measured transmittance of SnSe$_2$ NPAs with different deposition time.
Figure S12. (a-e) Calculated electric field ($|E|/|E_0|_\text{max}$) distributions of SnSe$_2$ NPAs with different heights. (f) Schematic diagram of the modeled structure (symmetric structure, with 85° angle for both nanoplates).
Figure S13. (a-e) Calculated electric field ($|E|/|E_0|$) distributions of SnSe$_2$ NPAs with different heights. (f) Schematic diagram of the modeled structure (symmetric structure, with 75° angle for both nanoplates).
Figure S14. (a-e) Calculated electric field ($|E|/|E_0|$) distributions of SnSe$_2$ NPAs with different heights. (f) Schematic diagram of the modeled structure (asymmetric structure, with 85° angle for the left nanoplate and 75° angle for the right nanoplate).
Figure S15. (a-e) Calculated electric field (|E|/|E_0|) distributions of SnSe_2 NPAs with different heights. (f) Schematic diagram of the modeled structure (asymmetric structure, with 85° angle for the left nanoplate and 80° angle for the right nanoplate).
**Figure S16.** (a-e) Calculated electric field ($|E|/|E_0|_\text{max}$) distributions of SnSe$_2$ NPAs with different heights. (f) Schematic diagram of the modeled structure (asymmetric structure, with 80° angle for the left nanoplate and 75° angle for the right nanoplate).
Figure S17. The calculated maximum intensity $|E|/|E_0|$ of SnSe$_2$ NPAWs with different heights and angles (asymmetric structure)
Figure S18. (a-b) Calculated electric field ($|E|/|E_0|$) distributions for vertical-structured SnSe$_2$ NPAs ($t=5$ min, height=0.25 μm, width=0.3 μm, thickness=35 nm) and tiled SnSe$_2$ nanoplate ($t=1$ min, thickness=35 nm, length=0.25 μm, width=0.3μm), respectively.
Enhanced SERS performance via inserting high reflective layer-Distributed Bragg Reflectors (DBR)

We use Ta$_2$O$_5$/SiO$_2$ DBR as the high reflective layer. The n, k value of Ta$_2$O$_5$ are 2.1469 and 0.00081579 for 532 nm (laser wavelength), respectively. The n value of SiO$_2$ is 1.46 for 532 nm.

Then the thickness of the Ta$_2$O$_5$ and SiO$_2$ layer can be obtained by the following equation[6]:

$$L = \frac{\lambda_{\text{Bragg}}}{4n}$$  \hspace{1cm} (S6)

where $L$ is the thickness of the layer, $\lambda_{\text{Bragg}}$ is the Bragg central wavelength (532 nm). The calculated thickness of of the Ta$_2$O$_5$ and SiO$_2$ layer are 62 nm and 91 nm, respectively. The reflectivity $R$ of the DBR can then be obtained by the following equation[6]:

$$R = \frac{1-(n_{\text{Ta}_2\text{O}_5}/n_{\text{SiO}_2})^{2m}}{1+(n_{\text{Ta}_2\text{O}_5}/n_{\text{SiO}_2})^{2m})^2}$$  \hspace{1cm} (S7)

where $m$ is the pairs of Ta$_2$O$_5$/SiO$_2$. The result is shown in Figure S18a, the reflectivity of the Ta$_2$O$_5$/SiO$_2$ DBR (10 pairs) is 0.998 (close to 100%).
**Figure S19.** (a) Calculated reflectivity of Ta$_2$O$_5$/SiO$_2$ DBR as a function of DBR pairs. (b-c) The electric field ($|E|/|E_0|$) distributions of Glass/Ta$_2$O$_5$-SiO$_2$ DBR/SnSe$_2$ NPAs scheme and Ta$_2$O$_5$-SiO$_2$ DBR/Glass/SnSe$_2$ NPAs scheme (10 pairs DBR symmetric structure, length of SnSe$_2$ NPAs=1 μm, angle=85°, thickness of Glass=50 nm). Compared to the results shown in Figure S12c, the maximum intensity $|E|/|E_0|$ increases from 3.32 to 5.35 (5.44), which can promote the coupling between the incident light and SnSe$_2$ NPAs, in turn enhance the SERS performance.
Table S1: Summary of semiconductors and noble metals SERS activity

<table>
<thead>
<tr>
<th>Material</th>
<th>Analyte</th>
<th>EF</th>
<th>LOD(M)</th>
<th>Laser</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>SnSe$_2$ NPAs</td>
<td>R6G</td>
<td>6.33x10$^6$</td>
<td>1x10$^{-12}$</td>
<td>532nm</td>
<td>This work</td>
</tr>
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<td>SnSe$_2$ Nanoflakes (isolated flakes)</td>
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<td>-</td>
<td>1x10$^{-8}$</td>
<td>532nm</td>
<td>[3]</td>
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<td>Cu$_2$O Concave Sphere (single particle)</td>
<td>CV and R6G</td>
<td>2.8x10$^5$ (CV), 2.5x10$^5$ (R6G), 2x10$^{-8}$</td>
<td>647nm</td>
<td>[7]</td>
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<td>TiO$_2$ microarrays</td>
<td>Methylen Blue</td>
<td>2x10$^4$</td>
<td>6x10$^{-6}$</td>
<td>532nm</td>
<td>[8]</td>
</tr>
<tr>
<td>SiO$_2$@TiO$_2$ core-shell spheres</td>
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<td>-</td>
<td>1x10$^{-5}$</td>
<td>633nm</td>
<td>[9]</td>
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<tr>
<td>Au@SiO$_2$</td>
<td>R6G</td>
<td>1x10$^6$</td>
<td>1x10$^{-9}$</td>
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<td>Bulk MoS$_2$</td>
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<td>1x10$^{-8}$</td>
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<td>[12]</td>
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<td>3D-stacked Ag NWs</td>
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<td>1.5x10$^{-9}$</td>
<td>632.8nm</td>
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<td>AuNPs@MoS$_2$</td>
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<td>[14]</td>
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<td>3D TiO$_2$ nanofibers</td>
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<td>-</td>
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References: