Supplemental information

A spontaneously formed plasmonic-MoTe$_2$ hybrid platform for ultrasensitive Raman enhancement

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Supplemental figures

Figure S1. Additional characterization of the 1T’ MoTe₂ atomic layers. (a) Raman spectrum of the 1T’ MoTe₂ flake (3L thickness). (b) AFM height image taken at the edge of the 1T’ MoTe₂ flake. (c) Step height profile of the 1T’ MoTe₂ flake along the dashed line labeled in (b), showing a typical 3L thickness of 2.9 nm. (d) High-resolution TEM image of the 1T’ MoTe₂ showing the monoclinic lattice structure. Inset is the fast Fourier transform pattern.
Figure S2. Additional characterization of the AuNPs-MoTe$_2$ structure. (a, b) Additional TEM images of the AuNPs-MoTe$_2$ structure. (c-g) XPS spectra of 1T’ MoTe$_2$ flakes before (c, d) and after (e-g) HAuCl$_4$ treatment for 30 s.
Figure S3. Simulated extinction spectrum of the AuNPs-MoTe$_2$ structure.

Figure S4. SERS spectra of R6G ($4 \times 10^{-7}$ M) coated on 2H MoTe$_2$ before and after HAuCl$_4$ treatment for 30 s.
Figure S5. SERS performance on AuNPs-WTe₂ hybrid structure. (a) Typical Raman spectrum of 1T’ WTe₂ atomic layers (3L). (b) SERS signals of R6G (4×10⁻⁷ M) on bare 1T’ WTe₂ and AuNPs-WTe₂ hybrid structure (after 30 s treatment in HAuCl₄ solution).
Figure S6. Impact of the HAuCl₄ treatment time. (a) SERS spectra of R6G (4×10⁻⁷ M) coated on 1T’ MoTe₂ with various treatment times in HAuCl₄ solution. (b) Raman intensity of R6G 609 cm⁻¹ feature peak as function of HAuCl₄ treatment time extracted from (a). (c-d) SEM images of 1T’ MoTe₂ after immersing in HAuCl₄ solution with various treatment times. Scale bars: 200 nm.
Figure S7. SERS spectra of $10^{-7}$ M R6G (a) and methylene blue (MB) (b) coated on AuNPs-MoTe$_2$ hybrid structure with different Raman excitation wavelengths (532 and 633 nm). The molecular resonance wavelengths of R6G and MB are near 532 and 633 nm, respectively.\textsuperscript{1,2}

Figure S8. SERS intensity of R6G 609 cm$^{-1}$ peak as function of R6G concentration. Data are extracted from Figure 2c.
Figure S9. Uniformity of the SERS signals. (a) Optical image of AuNPs-MoTe$_2$ and the corresponding Raman intensity map of R6G 609 cm$^{-1}$ peak ($4\times10^{-7}$ M R6G coated). Scare bar: 10 µm. (b) SERS spectra collected from 20 randomly selected spots on the R6G ($4\times10^{-7}$ M) coated AuNPs-MoTe$_2$ hybrid structure.
Figure S10. SERS signals of additional analytes. SERS signals of (a) CV and (b) Sudan III analytes coated on AuNPs-MoTe₂ hybrid structure with various concentrations. SERS intensities of (c) CV 1617 cm⁻¹ and (d) Sudan III 1596 cm⁻¹ peaks as functions of analyte concentration.
Figure S11. Characterization of the MoTe$_2$ continuous film. (a) Typical Raman spectrum of the 1T’ MoTe$_2$ continuous film derived from tellurization of Mo film. (b) Raman intensity map of 161 cm$^{-1}$ peak of the 1T’ MoTe$_2$ continuous film, showing the high uniformity of the obtained film.

Note S1. Discussion on the coupling effects of EM and CM

According to the theory proposed by J. R. Lombardi et al., the total SERS effect is caused by coupled contributions of resonances including surface plasmon, charge transfer and molecular resonances.$^{3,4}$ The molecular polarizability can be written as:

$$R_{\text{mol-CT}}(\omega) = \frac{(\mu^0_{\text{mol}} \cdot E^0)(\mu^0_{\text{CT}} \cdot E^0) h_{\text{mol-CT}} \langle Q \rangle}{[(\omega^2_{\text{Mie}} - \omega^2) + \gamma^2_{\text{Mie}}][(\omega^2_{\text{CT}} - \omega^2) + \gamma^2_{\text{CT}}][(\omega^2_{\text{mol}} - \omega^2) + \gamma^2_{\text{mol}}]}$$

where the subscripts Mie, CT and mol represent Mie scattering, charge transfer and molecular resonances, respectively. These three resonances are involved in the denominator of the expression, which is known as the “unified resonance”. From the numerator of the expression, it is clear that the resonances of $\mu_{\text{mol}}$ and $\mu_{\text{CT}}$ are coupled with each other through vibronic coupling with Herzberg-Teller constant $h_{\text{mol-CT}}$. Further, the electric filed $E$, which is enhanced by EM, is coupled with $\mu_{\text{mol}}$ and $\mu_{\text{CT}}$. 
Table S1. Summary of the plasmonic-2D material hybrid structures for SERS sensing.

| SERS structure       | Fabrication method                                  | Analyte | Excitation | Limit of detection | Mechanism | Ref. |
|----------------------|------------------------------------------------------|---------|------------|--------------------|-----------|------|
| AuNPs-1T′ MoTe₂      | In-situ spontaneous AuNP formation                   | R6G     | 532 nm     | 4×10⁻¹⁷ M          | CM + EM   | This work |
| Ag nanostructures-MoS₂ | Femtosecond pulse irradiation                        | R6G     | 532 nm     | 10⁻¹¹ M            | CM + EM   | 5    |
| MoS₂-CuNPs           | Coating & annealing                                  | R6G     | 532 nm     | 10⁻⁹ M             | CM + EM   | 6    |
| Ag nanostructures-MoS₂ | Solution-processed                                    | R6G     | 633 nm     | 10⁻¹¹ M            | CM + EM   | 7    |
| AuNPs-1T/2H MoS₂     | Solution-processed                                   | R6G     | 514 nm     | 10⁻¹⁰ M            | CM + EM   | 8    |
| Graphene-Au nanopyramid | Templating deposition of Au & transfer of graphene | R6G     | 633 nm     | 10⁻¹⁴ M            | CM + EM   | 9    |
| Graphene-Au triangular nanoarrays | Transferring graphene on deposited Au nanorarrays | R6G     | 532 nm     | 10⁻⁷ M             | CM + EM   | 10   |
| AuNPs-MoS₂-graphene  | Evaporation of AuNPs on 2D heterostructure           | R6G     | 532 nm     | 5×10⁻¹⁰ M          | CM + EM   | 11   |
| hBN-AuNPs            | Transferring hBN on deposited AuNPs                  | R6G     | 532 nm     | 10⁻⁹ M             | CM + EM   | 12   |
| AuNPs-hBN-AgNPs      | Self-assemble of AgNPs + transfer of hBN + spray deposition of AuNPs | R6G | 514 nm | 10⁻¹² M | CM + EM | 13   |
| hBN-AuNPs            | Transfer & annealing                                 | R6G     | 514 nm     | ~10⁻⁸ M            | CM + EM   | 14   |

Supplemental references

1. Tao, L., Chen, K., Chen, Z., Cong, C., Qiu, C., Chen, J., Wang, X., Chen, H., Yu, T., Xie, W., et al. (2018). 1T’ Transition Metal Telluride Atomic Layers for Plasmon-Free SERS at Femtomolar Levels. J. Am. Chem. Soc. 140, 8696–8704.

2. Feng, S., dos Santos, M.C., Carvalho, B.R., Ly, R., Li, Q., Fujisawa, K., Elias, A.L., Lei, Y., Pereia-Lopez, N., Endo, M., et al. (2016). Ultrasensitive molecular sensor using N-doped graphene through enhanced Raman scattering. Sci. Adv. 2, e1600322.
3. Lombardi, J.R., Birke, R.L., Lu, T., and Xu, J. (1986). Charge-transfer theory of surface enhanced Raman spectroscopy: Herzberg–Teller contributions. J. Chem. Phys. 84, 4174–4180.

4. Lombardi, J.R. (2017). The theory of surface-enhanced Raman scattering on semiconductor nanoparticles; toward the optimization of SERS sensors. Faraday Discuss. 205, 105–120.

5. Zuo, P., Jiang, L., Li, X.X., Li, B., Ran, P., Li, X.X., Qu, L., and Lu, Y. (2018). Metal (Ag, Pt)–MoS2 Hybrids Greenly Prepared Through Photochemical Reduction of Femtosecond Laser Pulses for SERS and HER. ACS Sustain. Chem. Eng. 6, 7704–7714.

6. Li, Z., Jiang, S., Xu, S., Zhang, C., Qiu, H., Li, C., Sheng, Y., Huo, Y., Yang, C., and Man, B. (2016). Few-layer MoS2-encapsulated Cu nanoparticle hybrids fabricated by two-step annealing process for surface enhanced Raman scattering. Sensors Actuators B Chem. 230, 645–652.

7. Li, J., Zhang, W., Lei, H., and Li, B. (2018). Ag nanowire/nanoparticle-decorated MoS2 monolayers for surface-enhanced Raman scattering applications. Nano Res. 11, 2181–2189.

8. Zheng, X., Guo, Z., Zhang, G., Li, H., Zhang, J., and Xu, Q. (2019). Building a lateral/vertical 1T-2H MoS2/Au heterostructure for enhanced photoelectrocatalysis and surface enhanced Raman scattering. J. Mater. Chem. A 7, 19922–19928.

9. Wang, P., Liang, O., Zhang, W., Schroeder, T., and Xie, Y.-H.H. (2013). Ultra-Sensitive Graphene-Plasmonic Hybrid Platform for Label-Free Detection. Adv. Mater. 25, 4918–4924.

10. Zhang, X., Si, S., Zhang, X., Wu, W., Xiao, X., and Jiang, C. (2017). Improved Thermal Stability of Graphene-Veiled Noble Metal Nanoarrays as Recyclable SERS Substrates. ACS Appl. Mater. Interfaces 9, 40726–40733.

11. Alamri, M., Sakidja, R., Goul, R., Ghopry, S., and Wu, J.Z. (2019). Plasmonic Au Nanoparticles on 2D MoS2/Graphene van der Waals Heterostructures for High-Sensitivity Surface-Enhanced Raman Spectroscopy. ACS Appl. Nano Mater. 2, 1412–1420.

12. Kim, G., Kim, M., Hyun, C., Hong, S., Ma, K.Y., Shin, H.S., and Lim, H. (2016). Hexagonal Boron Nitride/Au Substrate for Manipulating Surface Plasmon and Enhancing Capability of Surface-Enhanced Raman Spectroscopy. ACS Nano 10, 11156–11162.

13. Kim, N.-Y., Leem, Y.-C., Hong, S.-H., Park, J.-H., and Yim, S.-Y. (2019). Ultrasensitive and Stable Plasmonic Surface-Enhanced Raman Scattering Substrates Covered with Atomically Thin Monolayers: Effect of the Insulating Property. ACS Appl. Mater. Interfaces 11, 6363–6373.

14. Cai, Q., Mateti, S., Yang, W., Jones, R., Watanabe, K., Taniguchi, T., Huang, S., Chen, Y., and Li, L.H. (2016). Boron Nitride Nanosheets Improve Sensitivity and Reusability of Surface-Enhanced Raman Spectroscopy. Angew. Chemie Int. Ed. 55, 8405–8409.