Supporting Information

Metallic and Plasmonic MoO₂ Monocrystalline Ultrathin Mesoporous Nanosheets for Highly Sensitive and Stable Surface-Enhanced Raman Spectroscopy

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Experimental Sections

Materials: The materials used in the experiments were all of analytical grade and used directly without further purification. All the materials were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of Hierarchical $Mo(OH)_4$ Nanosheet Microspheres: In a typical synthesis, 3 mmol of molybdenyl acetylacetonate ($C_{10}H_{14}MoO_6$) and 1 mmol urea (H_2NCONH_2) were dissolved in a mixed solution of 30 mL of distilled water, 15 mL of ethanol, 5 mL of isooctanol, and 2 mL of oleic acid. The obtained mixed solution was then transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. A black flocculent precipitate was collected, purified with absolute ethanol and distilled water for 3 times, and dried in vacuum at 40 °C for 2 h.

Synthesis of MoO₂ Monocrystalline Ultrathin Porous Nanosheets (MUPNs): In a typical procedure, 0.1 g of the pre-synthesized Mo(OH)₄ nanosheet microspheres were dispersed in an alumina crucible. The alumina crucible was then transferred to a vacuum atmosphere furnace, which was heated to 450 °C at 0.001 bar for 5 min. Finally, a black loose powder was collected, purified with absolute and distilled water, and dried in vacuum at 50 °C for 3 h.

Synthesis of ZnO Monocrystalline Ultrathin Porous Nanosheets (MUPNs): In a typical synthesis, 25 mL of 0.4 mol L⁻¹ Zn(CH₃CO₂)₂ and 1mL of oleic acid (99.5% mass ratio) was added into 30 mL of 0.5 mol L⁻¹ H₂NCONH₂. The mixtures were moved to Teflon-lined stainless-steel autoclaves and heated at 120 °C for 8 h, and a white flocculent precipitate ($Zn_5(CO_3)_2(OH)_6$) was obtained. The white product was dispersed in an alumina crucible, and was heated to 500 °C at 0.001 bar for 10 min in a vacuum atmosphere furnace. Finally, the white loose powder was collected, purified with absolute and distilled water, and dried in vacuum at 50 °C for 3 h.

Synthesis of NiO Monocrystalline Ultrathin Porous Nanosheets (MUPNs): In a typical synthesis, 25 mL of 0.4 mol L⁻¹ Ni(CH₃CO₂)₂ • 4H₂O and 1 mL of oleic acid (99.5% mass ratio) was added into 30 mL of 0.8 mol L⁻¹ H₂NCONH₂. The mixtures were moved to Teflon-lined stainless-steel autoclaves and heated at 160 °C for 8 h,

and a green flocculent precipitate (Ni(OH)₂) was obtained. The green product was dispersed in an alumina crucible, and was heated to 500 °C at 0.001 bar for 10 min in a vacuum atmosphere furnace. Finally, the black loose powder was collected, purified with absolute and distilled water, and dried in vacuum at 50 °C for 3 h.

Raman Tests. In order to evaluate the SERS performance of the as-synthesized MoO₂ MUPNSs, a confocal-micro Raman spectrometer (Renishaw-inViaQontor) was used as the measuring instrument. In all SERS tests, if no special statement, the adopted excitation wavelength is always 532 nm, the laser power is 0.5 mW, and the magnification of the objective is \times 50 L. A series of standard solutions, such as Rh6G with concentrations of 10⁻⁶-10⁻¹⁰ M were adopted as the standard probe molecules. To improve the signal reproducibility and uniformity, the MoO₂ MUPNSs were added into the probe molecule aqueous solution maintained for 20 min for maximum adsorption. Then, the obtained suspension was uniformly coated on a glass slide by spin coating, and dried in air for 10 min under the irradiation of an infrared light. In all SERS detections, the laser beam is perpendicular to the top of the sample to be tested with a resultant beam spot diameter of 5 µm.

Raman Enhanced Factor (EF) Calculation

To calculate the EF of the MoO₂ MUPNSs, the ratio of SERS to normal Raman spectra (NRS) of R6G was determined by using the following calculating formula 1

 $EF = (I_{SERS}/I_{NRS}) \times (T_{NRS}/T_{SERS}) \times (C_{NRS}/C_{SERS})$ (1)

where I_{SERS} and I_{NRS} refer to the peak intensities of the SERS and NRS, respectively. T_{NRS} and T_{SERS} refer to the integration of the NRS and SERS, respectively. C_{NRS} and C_{SERS} refer to the concentrations of the probe molecules of the NRS and SERS, respectively. In the SERS measurements, Raman scattering characteristic peak, R_1 at 612 cm⁻³ was selected for the calculations of the EF. For comparison, the peak intensities of the R6G (1 × 10⁻² M, aqueous solution) directly placed on bare glass slide were detected as NRS data. For the NRS data, the integration time is 4000 s, while for the SERS data, the integration time is 10 s.

Characterization: XRD patterns of the products were recorded on a Bruker D8 Focus X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) images were recorded with a field emission scanning electron microscopy (HITACHI–S4800). Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of nanocrystal dispersion in absolute ethanol on amorphous carbon–coated copper grids. High–resolution TEM (HRTEM) characterization was performed with a FEI Tecnai G2 F30 operated at 300 kV. The HAADF-STEM imagewere recorded from an aberration-corrected high resolution electron microscopy Titan G2 80-200 ChemiSTEM, FEI.UV–vis absorption spectra were recorded with a Shimadzu UV-3600 with integrating sphere. X-ray Photoelectron Spectroscopy (XPS) experiments were performed in a ESCALab250Xi using monochromated Al K α X-rays at hv = 1486.6 eV. Peak positions were internally referenced to the C1s peak at 284.6 eV. Figures



Figure S1. SEM images of the as-synthesized Mo(OH)₄ precursors.



Figure S2. XRD pattern of the as-synthesized monoclinic MoO_2 MUPNSs. Insets: the photograph of the obtained MoO_2 sample and the crystal structure of monoclinic MoO_2 .



Figure S3. EDS spectrum of the as-synthesized MoO₂ MUPNSs.



Figure S4. XPS spectrum of the as-synthesized MoO_2 MUPNSs. Note: These Mo^{6+} signals originate from a small amount of oxide layer on the surface of the sample.



Figure S5. (a-c) High-magnification SEM images of the as-synthesized MoO_2 MUPNSs.



Figure S6. TEM images with different magnifications of the MoO₂ MUPNSs.



Figure S7. HRTEM images of the MoO₂ MUPNSs, which confirms its single-crystalline nature.



Figure S8. (a) The low-magnification TEM image of the MoO_2 polycrystalline nanosheets are formed at one bar pressure. (b) The high-magnification TEM image and the corresponding SAED pattern of the MoO_2 polycrystalline nanosheets.



Figure S8. (a-b) SEM and TEM images of the ZnO MUPNSs prepared by this decompressing decomposition route, which suggests the universality of this method. (c) The high-magnification TEM image and the corresponding FFD pattern of the ZnO MUPNSs.



Figure S9. (a) TEM image of the NiO MUPNSs prepared by this decompressing decomposition route. (b) The high-magnification TEM image and the corresponding SAED pattern of the NiO MUPNSs.



Figure S11. This new type of SERS substrate has long-term stability, even if it is placed in air for three months, these MoO₂ MUPNSs still show almost invariable XRD pattern (a) and EFs (b).



Figure S12. SERS spectra of a series of common high concern chemicals obtained on the MoO₂ MUPNSs. (a) MB. (b) RhB. (c) 2,5-DCP. (d) BHA.



Figure S13. (a-b) The Raman mapping of R_1 and R_2 peaks obtained from one sinlge MoO₂ nanosheet microsphere adsorbed with 10⁻⁹ M R6G, respectively. (c-d) Statistical RSD obtained from 40 randomly selected measuring points in the MoO₂ MUPNS substrate by using the intensities of R_1 and R_2 at 10⁻⁹ M, respectively.



Figure S14. N₂ adsorption/desorption isotherms of the MoO₂ MUPNSs.

Material	Probe	EF	Excited	Author
	molecule		wavelength	
			(nm)	
core-shell	4-Mpy	6.5×10 ⁵	514	X. X. Zou et al. ¹
TiO ₂ –Ag				
TiO ₂ photonic	MB	2×10 ⁴	532	D. Qi et al. ²
microarray				
CdTe	4-Mpy	104	514.5	Y. F. Wang et al. ³
nanopartilces				
W ₁₈ O ₄₉ nanowires	Rh6G	3.4×10 ⁵	532.8	S. Cong et al. ⁴
CuO	4-Mpy	10 ²	514.5	Y. Wang et al. ⁵
nanoparticles				
CdS nanoparticels	4-Mpy	10 ²	514.5	Y. F. Wang et al. ⁶
Cu ₂ O	Rh6G	8×10 ⁵	674	J. Lin et al. ⁷
superstructure				
Fe ₂ O ₃	4-Mpy	2.7×10 ⁴	514.5	X. Q. Fu et al. ⁸
nanoparticles				
Au–CdSe	CV	104	633	G. Das et al. ⁹
nanowires				
Colloidal ZnO	D266	50	488	H. Wen et al. ¹⁰
DFH-4T	MB	3.4×10 ³	785	Mehmet Yilmaz et al. ¹¹
TiO ₂	Nitrothio	10 ²	488	Teguh et. al. ¹²
	Phenol			
ZnO nanorods	4-ABT	22	514.5	Kim et. al. ¹³
InAs/GaAs	Pyridine	10 ³	514.5	Quagliano et. al. ¹⁴
quantum dots				
H-Si nanowire	Rh6G	8-28	532	Wang et. al. ¹⁵
Graphene	Phthalocy	2-17	632.8	Ling et. al. ¹⁶
	anine			
GaP	CuPc	700	514.5	Hayashi et. al. ¹⁷
WO ₂ /C nanowires	Rh6G	1.3×10 ⁶	532	He et al. ¹⁸
MoO ₂	Rh6G	3.75×10 ⁶	532	Zhang et al. ¹⁹
nanodumbbells				
MoS ₂	Rh6G	106	532	Zhao et al. ²⁰
core-shell Au-Ag	thiophenol	106	632	Chandrabhas
nanostructure				Narayana, C. et al. ²¹
Ag nanospheres	Pathogens	2.47×10 ⁷	632	Joseph Irudayaraj et al. ²²
Au nanocones	1,2-bis-(4-pyri	- 406		Anja Boisen et al. ²³
	dyl)-ethylene	5×10°	514	

Table S1: Some of the Previously Reported EFs of Semiconductor SERS Substrates

Ag Shell–Au Satellite	R6G	1.4×10 ⁶	532	Dae Hong Jeong et al. ²⁴
Hetero-Nanostruc				
ture				
Ag nanoparticles	R6G	1.2×10 ⁷	532	Shangjr Gwo et al. ²⁵
MoO ₂ MUPNSs	R6G	6.5×10 ⁷	532	The Present Work

References

- X. X. Zou, R. Silva, X. X. Huang, J. F. Al-Sharabc, T. A. Asefa, *Chem. Commun.* 2013, 49, 382-384.
- 2. D. Qi, L. Lu, L. Wang, J. Zhang, J. Am. Chem. Soc. 2014, 136, 9886-9889.
- Y. F. Wang, J. H. Zhang, H. Y. Jia, M. J. Li, J. B. Zeng, B. Yang, B. Zhao, W. Q. Xu, J. Phys. Chem. C. 2008, 112, 996–1000.
- S. Cong, Y. Y. Yuan, Z. G. Chen, J. Y. Hou, M. Yang, Y. L. Su, Y. Y. Zhang, L. Li,
 Q. W. Li, F. X. Geng, Z. G. Zhao, *Nat. Commun.* 2015, *6*, 7800.
- Y. Wang, H. Hu, S. Jing, Y. Wang, Z. Sun, B. Zhao, C. Zhao, J. R. Lombardi, *Anal. Sci.* 2007, 23, 787–791.
- Y. F. Wang, Z. H. Sun, Y. X. Wang, H. L. Hu, B. Zhao, W. Q. Xu, J. R. Lombardi, Spectrochimica. Acta. Part. A. 2007, 66, 1199–1203.
- J. Lin, Y. Shang, X. X. Li, J. Yu, X. T. Wang, L. Guo, Adv. Mater. 2017, 29, 1604797.
- X. Q. Fu, F. L. Bei, X. Wang, X. J. Yang, L. D. Lu, *J. Raman Spectrosc.* 2009, 40, 1290–1295.
- G. Das, R. Chakraborty, A. Gopalakrishnan, D. Baranov, E. D. Fabrizio, R. Krahne, J. Nanopart. Res. 2013, 15, 1596.
- H. Wen, T. J. He, C. Y. Xu, J. Zuo, F. C. Liu, *Molecular Physics*. 1996, 88, 281–290.
- M. Yilmaz, E. Babur, M. Ozdemir, R. L. Gieseking, Y. Dede, U. Tamer, G. C. Schatz, A. Facchetti, H. Usta, G. Demire, *Nat. Mater.* 2017, *16*, 918-924.
- 12. J. S. Teguh, F. Liu, B. Xing, E. K. L. Yeow, Chem. Asian J. 2012, 7, 975-981.
- 13. K. Kim, K. L. Kim, K. S. Shin, Phys. Chem. Chem. Phys. 2013, 15, 9288-9294.
- 14. L. G. Quagliano, J. Am. Chem. Soc. 2004, 126, 7393-7398.

- 15. X. Wang, W. Shi, G. She, L. Mu, J. Am. Chem. Soc. 2011, 133, 16518-16523.
- X. Ling, L. Xie, Y. Fang, H. Xu, H. Zhang, J. Kong, M. Dresselhaus, J. Zhang, Z. F. Liu, *Nano Lett.* 2010, *10*, 553-561.
- 17. S. Hayashi, R. Koh, Y. Ichiyama, K. Yamamoto, Phys. Rev. Lett. 1988, 60, 1085.
- C. Y. He, H. Bai, W. C. Yi, J. Y. Liu, X. S. Li, X. Li, G. C. Xi, *J. Mater. Chem.* C 2018, 6, 3200-3205.
- Q. Q. Zhang, X. S. Li, Q. Ma, Q. Zhang, H. Bai, W. C. Yi, J. Y. Liu, J. Han, G. C. Xi, *Nat. Commun.* 2017, *8*, 14903.
- Z. H. Zheng, S. Cong, W. B. Gong, J. N. Xuan, G. H. Li, W. B. Lu, F. X. Geng,
 Z. G. Zhao, *Nat. Commun.* 2017, *8*, 1993.
- 21. G. Kumari, C. Narayana, J. Phys. Chem. Lett. 2012, 3, 1130–1135.
- 22. Y. L. Wang, K. Lee, J. Irudayaraj, J. Phys. Chem. C 2010, 114, 16122–16128.
- M. Viehrig, A. Thilsted, M. Matteucci, K. Wu, D. Catak, M. Schmidt, K. Zór,
 A. Boisen, ACS Appl. Mater. Interfaces 2018, 10, 37417–37425.
- H. Chang, H. Kang, J. K. Yang, A. Jo, H. Y. Lee, Y. S. Lee, D. H. Jeong, ACS Appl. Mater. Interfaces 2014, 6, 11859–11863.
- H. Y. Chen, M. H. Lin, C. Y. Wang, Y. M. Chang, S. Gwo, J. Am. Chem. Soc.
 2015, 137, 13698–13705.