Supporting Information

Plasmonic metal carbide SERS chips

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Contents List

Section S1: The UV-vis absorption spectra of different tungsten carbide chips (Page S2; Fig. S1)

Section S2: The Raman spectrum of tungsten carbide chips (Page S3; Fig. S2)

Section S3: Preparation and characterizations of the Ag chips (Page S4; Fig. S3)

Section S4: Calculation of the enhancement factor (Page S5)

- Section S5: Simulation of the electromagnetic field distribution (Page S6-S7; Fig. S4 and Table S1)
- Section S6: Raman spectra of other organic compounds adsorbed on tungsten carbide chips (Page S8; Fig. S5)

Section S7: The height profile of metal carbide chips (Page S9; Fig. S6-S8)

Section S8: The XRD patterns of metal carbide chips (Page S10; Fig. S9)

Section S9: The XPS spectra of metal carbide chips (Page S11-S12; Fig. S10-S12 and Table S2)

Section S10: Price comparison of different targets (Page S13; Table S3)

- Section S11: Raman spectra of R6G adsorbed on original and high temperature treated metal carbide chips (Page S14; Fig. S13-S15)
- Section S12: Raman spectra of R6G adsorbed on original and SiO₂ coated metal carbide chips (Page S15; Fig. S16-S18)

References (Page S16)

Section S1: The UV-vis absorption spectra of different tungsten carbide chips



Fig. S1 The UV–vis absorption spectra of different tungsten carbide chips (inset: SEM images). Tungsten carbide chips (the absorption peak concerted in 463 nm) were prepared on Si(100) wafer in argon (15 sccm) using a direction current magnetron co-sputtering system. The powers of tungsten and graphite target were 30 W and 70 W, respectively. The sputtered time was 500 s with a pressure of 1.69 Pa. The sputtered temperature was room temperature.

Section S2: The Raman spectrum of tungsten carbide chips



Fig. S2 The Raman spectrum of tungsten carbide chips.

Section S3: Preparation and characterizations of the Ag chips

Silver chips were prepared on Si(100) wafer in a argon (40 sccm) atmosphere using a direction current magnetron system at room temperature. A high purity silver plate (99.99%, 50mm-diameter) was used as a target. The power of silver was 60 W and the sputtered time is 1200 s with a pressure of 2.21 Pa.



Fig. S3 (a) Low- and (b) high-magnification SEM image of Ag chip.

Section S4: Calculation of the enhancement factor (EF)

The EF of the sample could be estimated using the equation below:

$EF = (I_{SERS}/N_{SERS}) / (I_{bulk}/N_{bulk})$	(1)
$N_{SERS} = CVN_A A_{Raman} / A_{Sub}$	(2)
$N_{bulk} = \rho h A_{Raman} N_A / M$	(3)

 I_{SERS} and I_{bulk} are the intensities of the selected Raman peak in the SERS and non-SERS spectra, respectively. N_{SERS} and N_{bulk} are the average number of molecules in scattering area for SERS and non-SERS measurement. The data of bulk R6G is used as non-SERS-active reference. *C* is the molar concentration of R6G solution and *V* is the volume of the droplet (20 µL). N_A is Avogadro constant. A_{Raman} is the laser spot area. A_{Sub} is the effective area of the substrate, which is approximately 9 π mm². The confocal depth *h* of the laser beam is 21 µm. The molecular weight M of R6G is 479 g mol⁻¹ and density ρ of bulk R6G is 1.15 g cm⁻³.

Section S5: Simulation of the electromagnetic field distribution

The finite element method (FEM) simulations are carried out on COMSOL. Plasmonic modes are excited by a plane wave source with incident direction perpendicular to the plane of structure. The incident light wavelength is 532 nm, and its electric field intensity is 1 V/m. The scattering boundary conditions are applied to the model. The dielectric constants of tungsten carbide are set as $\varepsilon' = -5.55$ and $\varepsilon'' = 15.60$. From the SEM image (see Fig. 1(a)), it can be seen that the particles with the size between 20 and 40 nm are randomly distributed on the sample surface, which gives rise to the uncertain grain spacing. Therefore, we simulated the electromagnetic field distribution with the gap value of particles from 1 to 10 nm, respectively. When the gap value of particles is reduced from 10 to 1 nm, the maximum local electromagnetic field enhancement factor (EEF) increases from 16 to 62. The theoretical Raman enhancement factor (EF) has been described by the following expression:

 $EF = (|E_{loc}(\omega_0)|^2 / |E(\omega_0)|^2) \times (|E_{loc}(\omega_R)|^2 / |E(\omega_R)|^2)$ (4)

where $E_{loc}(\omega_0)$ is the enhanced local electric field at the incident frequency (ω_0) , $E(\omega_0)$ is the incident electric field at the incident frequency (ω_0) , $E_{loc}(\omega_R)$ is the enhanced local electric field at the Raman scattered frequency (ω_R) , and $E(\omega_R)$ is the incident electric field at Raman scattered frequency (ω_R) . For the low-frequency vibrational modes of adsorbed molecules, the incident frequency can be considered roughly equal to the Raman scattered frequency. Therefore, The Raman enhancement factor is approximately proportional to the fourth power of the EEF. When the gap size of particles is 1, 2, 3, 5, 7 and 10 nm, the maximum Raman EF is 1.48×10^7 , 2.09×10^6 , 1.05×10^6 , 4.57×10^5 , 1.05×10^5 and 6.55×10^4 , respectively. Because of the randomly distributed gap values, the Raman EF obtained from experiments is an averaged value (~ 2.31×10^5). It is between the highest and lowest simulated results from Table S1, indicating the coincidence between experiments and simulations.



Fig. S4 The electromagnetic field distribution of tungsten carbide chips, the gap value of particles is (a) 1, (b) 2, (c) 3, (d) 5, (e) 7, and (f) 10 nm.

Table S1 Maximum local electromagnetic field enhancement factor and Raman enhancement factor calculated from the simulation of electromagnetic field distribution.

Gap value of the particles	Maximum EEF	Maximum Raman EF
1 nm	62	1.48×10 ⁷
2 nm	38	2.09×10 ⁶
3 nm	32	1.05×10^{6}
5 nm	26	4.57×10 ⁵
7 nm	18	1.05×10 ⁵
10 nm	16	6.55×10 ⁴





Fig. S5 Raman spectra of (a) 4-nitrothiophenol (4-NTP), (b) 4-mercaptobenzoic acid (4-MBA), (c) fuchsin acid (FA), and (d) Sudan III adsorbed on tungsten carbide chips.

Section S7: The height profile of metal carbide chips



Fig. S8 The height profile of NbC_x films.

Section S8: The XRD patterns of metal carbide chips



Fig. S9 The XRD patterns of MoC_x , NbC_x , and TiC_x chips.

Section S9: The XPS spectra of metal carbide chips



Fig. S10 The Mo 3d XPS spectrum of MoC_x chips.



Fig. S12 The Nb 3d XPS spectrum of NbC_x chips.

Metal carbides	Valence state	Atomic percentage (%)
WC _x	W^{2+}	41.1
	W^{4+}	47.5
	W^{6+}	11.4
MoC _x	Mo ³⁺	19.2
	Mo ⁴⁺	80.8
TiC _x	Ti ²⁺	29.2
	Ti ³⁺	48.5
	Ti ⁴⁺	22.3
NbC _x	Nb ²⁺	41.1
	Nb ³⁺	47.5
	Nb ⁵⁺	11.4

Table S2 The atomic	percentage of metal	carbide chips	by the XPS spectra.
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Section S10: Price comparison of different targets

Targets (50 mm-diameter and 3 mm- thickness)	Price (yuan/per plate)
Au	40950
Ag	600
W	400
Мо	300
Ti	200
Nb	400
С	400

 Table S3 Price comparison of different targets.

Section S11: Raman spectra of R6G adsorbed on original and high





Fig. S13 Raman spectra of R6G adsorbed on original and high temperature treated MoC_x chips.



Fig. S14 Raman spectra of R6G adsorbed on original and high temperature treated TiC_x chips.



Fig. S15 Raman spectra of R6G adsorbed on original and high temperature treated NbC_x chips.

Section S12: Raman spectra of R6G adsorbed on original and SiO₂ coated

metal carbide chips



Fig. S16 Raman spectra of R6G adsorbed on original and SiO₂ coated MoC_x chips.



Fig. S17 Raman spectra of R6G adsorbed on original and SiO_2 coated TiC_x chips.



Fig. S18 Raman spectra of R6G adsorbed on original and SiO₂ coated NbC_x chips.

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