Tailoring the synthesis of $V_{0.25}(Zr_{1.75})C$ MXene for sensitive SERS quantification of ciprofloxacin antibiotics: Spectroscopic and DFT investigation

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Supplementary Information

a. Silver nanospheres (AgNSs) synthesis

In accordance with our previously published work, AgNSs were prepared by a chemical reduction method. With a standard procedure in a 200 mL round-bottom flask, 0.1 ml of the 0.10 M $AgNO_3$ solution, 3.4 mL of the 0.17M sodium citrate, and 0.6 mL of the 0.17 M tartaric acid were added simultaneously. After allowing the mixture to stabilize at room temperature for three minutes, 0.2 mL (0.5 mM) of newly produced $NaBH_4$ was added dropwise. The mixture was then let stand for five minutes to maintain the uniform size distribution of AgNSs, followed by adding 95 mL of deionized water. The final mixture was boiled for 20 minutes at 100 ^oC and then cooled down in an ice bath.

The use of 25% laser power (~0.5–2 mW/μm²) was carefully optimized to balance signal enhancement and MXene stability. At this laser power, the local temperature rise remains below 50°C, preventing thermal degradation (e.g., oxidation or defect formation), as confirmed by TEM and the absence of ZrO_2-like Raman peaks in the Raman spectra. Higher power (>30%) risks desorbing ciprofloxacin (CP) or damaging oxygen terminations, which are critical for chemical enhancement (CM), while lower power reduces electromagnetic (EM) enhancement. Our control experiments showed that 25% power maintains: (i) signal linearity ($R^2 > 0.98$ for concentration studies), (ii) reproducibility (RSD < 5%), and (iii) molecular integrity (stable peak positions ±1 cm^{-1}), aligning with recent MXene-SERS protocols. This power range also avoids detector saturation, ensuring accurate quantification of the observed SERS intensity (~22,450 counts vs. ~2980 cm^{-1} in normal Raman).

b. Enhancement factor (EF) calculation

For our SERS substrate AgNSs@$V_{0.25}(Zr_{1.75})$CTx, the 16 mm diameter disc provided an ample active area for analyte deposition and detection. Using a 50× objective (NA = 0.55) with 25% laser power (~1.2 mW at sample), the illumination spot area was approximately 5 μm in diameter (~20 μm² area), containing numerous plasmonic hot spots within the laser focal volume. The large substrate area (201 mm^2 total) relative to the spot size created an effective diffusion zone about 10^4 times larger than the measurement area, enabling significant molecular pre-concentration. This configuration, combined with the MXenes hydrophilic nature (contact angle ~40°) and negative surface charge (ζ-potential = -38 mV at pH 7), promoted efficient ciprofloxacin diffusion ($D \approx 2.1 \times 10^{-8}$ cm^2/s) to the detection zone, with SERS signal stabilization occurring within 90-120 seconds as molecules reached equilibrium distribution between the bulk substrate and measurement area. The moderate 25% laser power prevented localized heating while maintaining sufficient signal intensity, as verified by stable spectral features during prolonged measurements (RSD < 6% over 10 acquisitions). This optimized geometry allowed a reproducible detection while minimizing photothermal effects on both the MXene substrate and analyte molecules.

Experimental Parameters:

- Substrate diameter: 16 mm (201 mm^2 area)

- Objective: 50× (NA 0.55)

- Laser spot: ~5 μm diameter (20 μm^2 area)

- Laser power: 25% (~1.2 mW at sample)

- Diffusion area/spot area ratio: ~10^4:1

- Signal stabilization time: 90-120.

c. Sample preparation for synthetic urine study

The solutions of CP drug were prepared in D.I water in the wide range of concentrations ranging from 10^{-4} to 10^{-16} M using subsequent dilution method at ambient conditions. Furthermore, the solution was incubated for 7 days in a refrigerator and the Raman spectra were recorded at different time intervals, no change in the spectral pattern was observed neglecting the hydrolysis. To

simulate the human urine, synthetic urine was prepared by dissolving key organic and inorganic salts (Urea 22%, creatinine 2%, NaCl 7%, Phosphates sulfates and calcium chloride as 0.2% in 100 ml distilled water) to mimic the key components of the human urine. The mixture included urea, as primary metabolite along with sodium chloride, magnesium sulfate and phosphates were added as major electrolytes to reflect the natural urine composition. The pH was adjusted to a range of 6.0-6.5 to ensure the accurate replica of the real sample for our study.

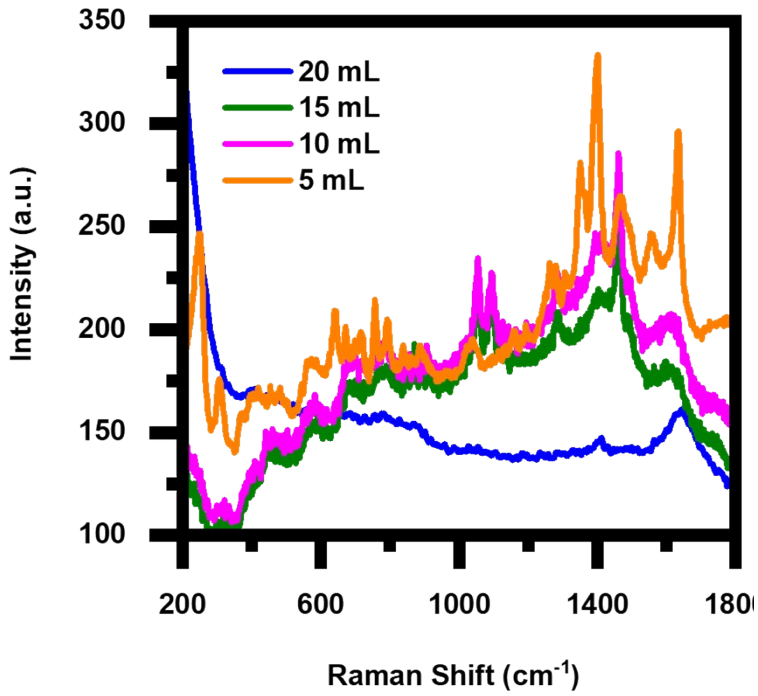

Figure S1. Raman spectra (CP) recorded at different volume ratios of AgNSs to bimetallic MXenes. Enhanced peak intensities in the orange and magenta curves confirm the SERS effect, with the highest intensity observed at the optimal AgNSs-to-MXenes ratio (5 mL). The changes in spectral profile and intensity reflect the influence of AgNSs concentration on SERS performance.

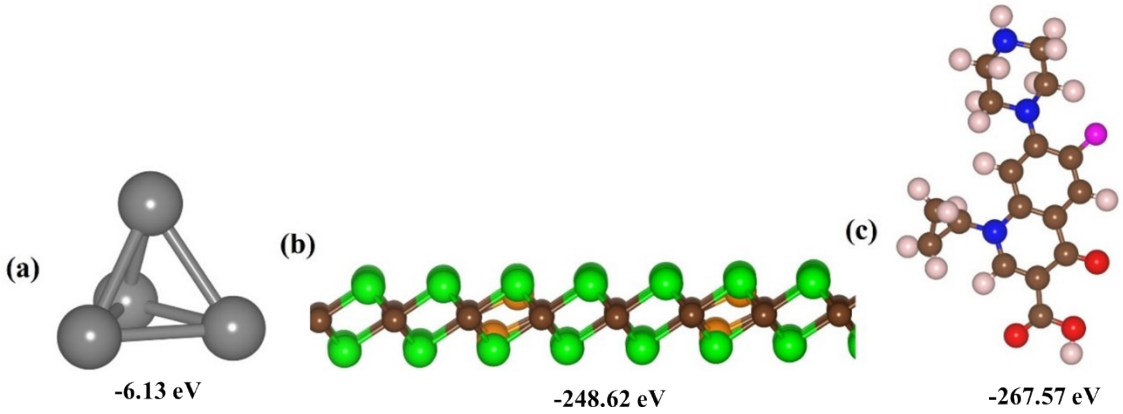

Figure S2: The optimized structures of (a) the silver nanocluster, (b) a clean $V_{0.25}(Zr_{1.75})C$ surface, and (c) the ciprofloxacin (CP) molecule, along with their total energies. The red, white, brown, green, orange, blue, gray, and pink spheres represent oxygen, hydrogen, carbon, zirconium, vanadium, nitrogen, silver, and fluorine atoms, respectively.

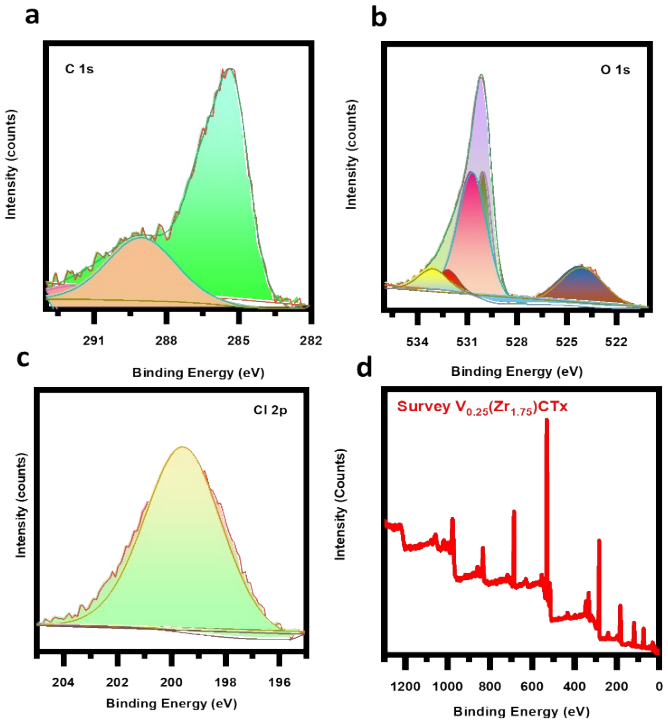

Figure S3: (a) and (b) Deconvoluted XPS spectra showing the elemental composition and binding energy states of V and Zr in $V_{0.25}(Zr_{1.75})CT_x$, confirming successful synthesis. (c) High-resolution C 1s spectrum indicating surface functional groups. (d) XPS survey spectrum validating the presence of key elements in $V_{0.25}(Zr_{1.75})CT_x$.

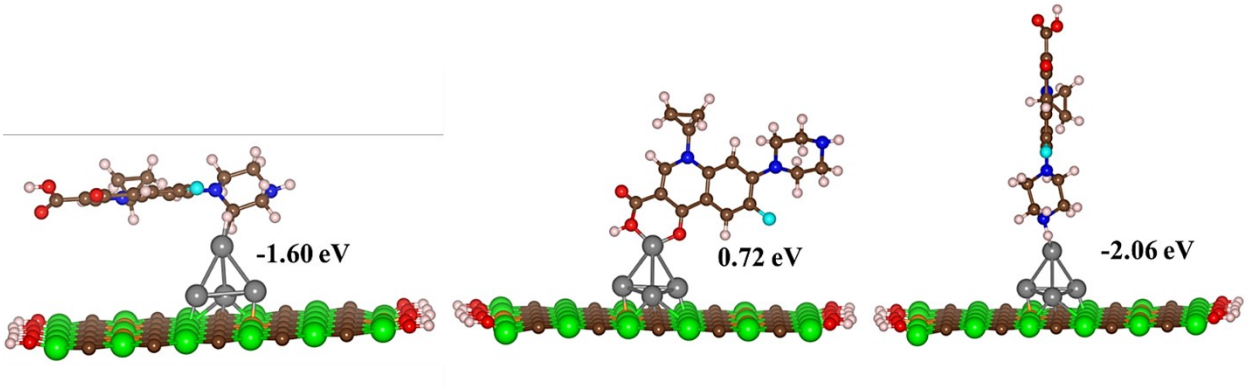

Figure S4: Various adsorption configurations of the ciprofloxacin molecule on the plane Ag@$V_{0.25}(Zr_{1.75})C$ bimetallic 2D sheet, where the red, white, brown, green, orange, blue, gray, and aqua spheres represent oxygen, hydrogen, carbon, zirconium, vanadium, nitrogen, silver, and fluorine atoms, respectively.

Table S1: Peak fitting parameters for Zr 3d XPS spectrum, including binding energy (B.E), full width at half maximum (FWHM), and relative area percentages.

Component	**BE (eV)**	**Assignment**	**FWHM (eV)**	**Area (%)**
Zr $3d_{5/2}$	182.2	Zr^{4+} (ZrO_2)	1.45	27.2
Zr $3d_{3/2}$	184.6	Zr^{4+} (ZrO_2)	1.45	18.1
Zr $3d_{5/2}$	180.3	Zr–C	1.50	22.7
Zr $3d_{3/2}$	182.7	Zr–C	1.50	15.2
Minor shoulder	183.3	Zr–OH / ZrO_x-H	1.20	16.8

Note: Total area normalized to 100%. All peaks were fitted with a Voigt profile and constrained to an area ratio of 3:2 between Zr $3d_{5/2}$ and Zr $3d_{3/2}$ for each doublet, with a spin-orbit splitting of 2.4 eV.