Ni/Ag bimetallic nanoparticles-engineered $Ti_3C_2T_x$ MXene composite as SERS substrate for trace detection of thiram pesticide

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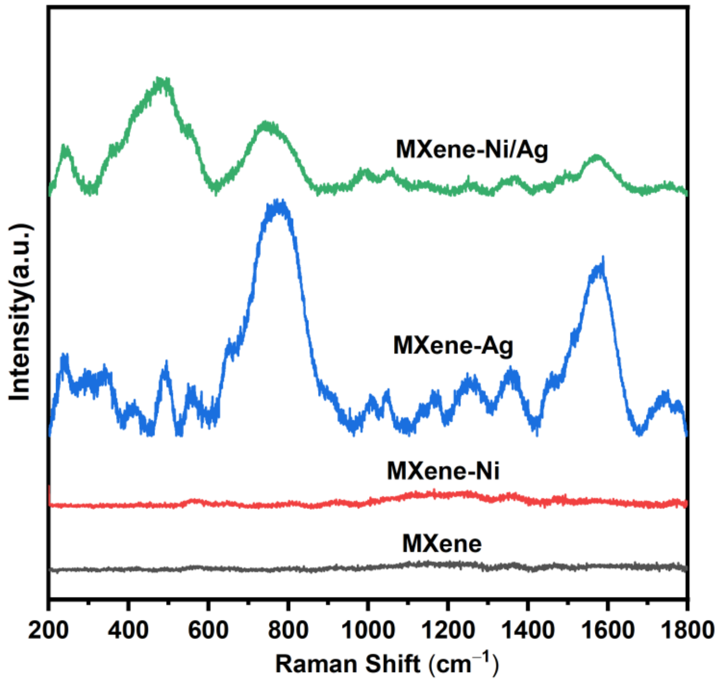

Figure S1. Intrinsic Raman spectra of different SERS substrates.

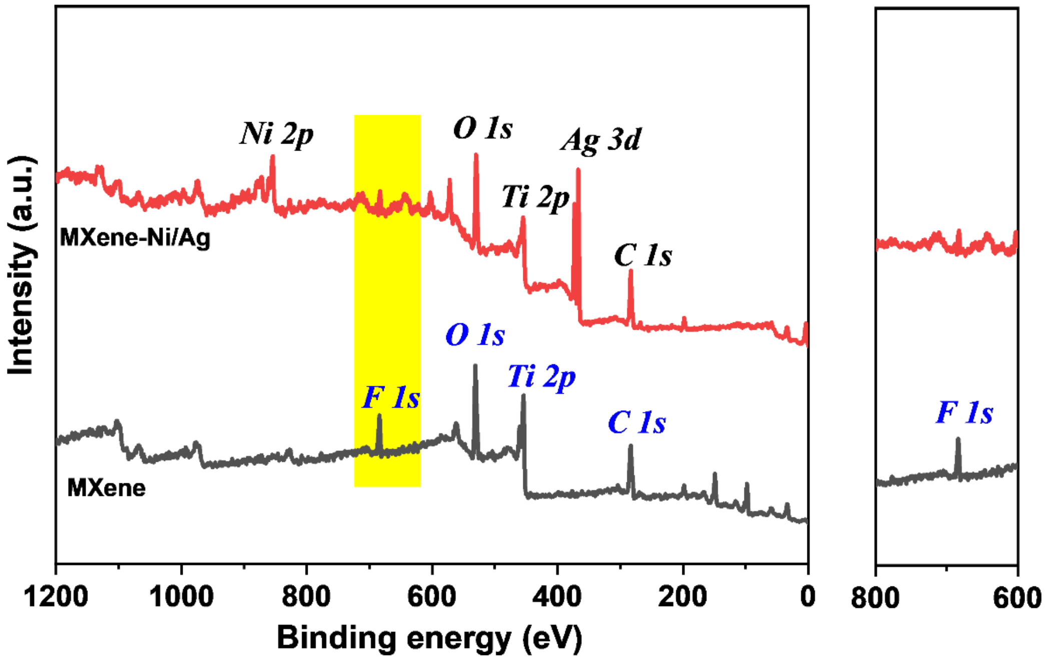

Figure S2. The XRD of the F 1s comparison spectra between the original MXene sample and MXene Ni/Ag.

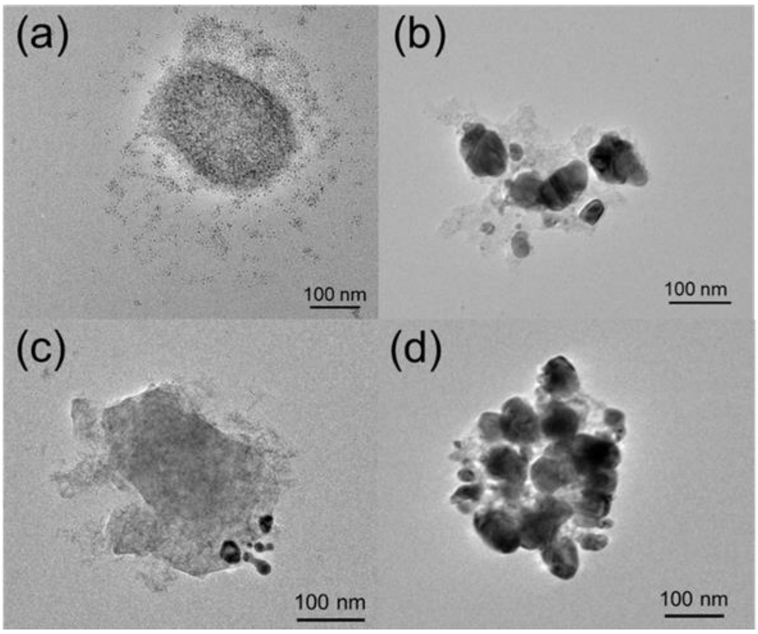

Figure S3. TEM image of MXene-Ni (a), MXene-Ag (b), MXene-Ni/Ag=1:1 (c) and MXene-Ni/Ag=1:4 composite (d).

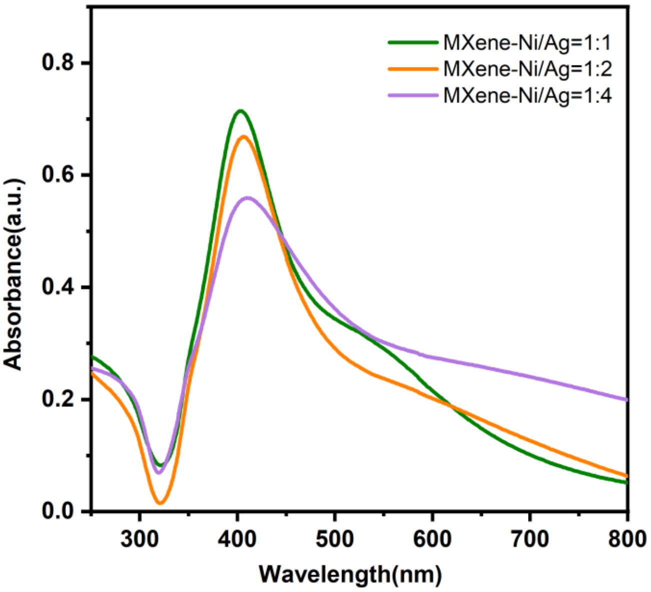

Figure S4. UV-vis absorbance spectra of MXene-Ni/Ag composite substrates with different Ni-Ag ratios.

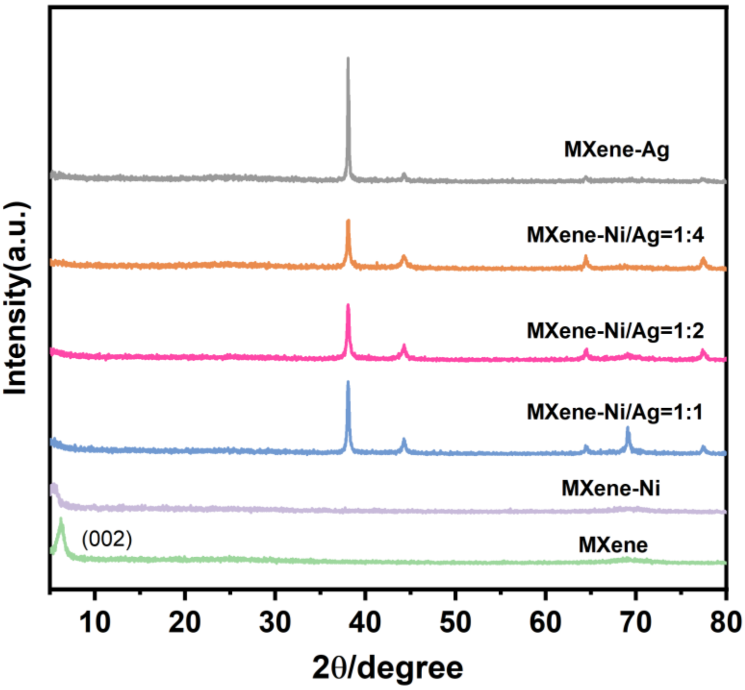

Figure S5. XRD spectra of MXene, MXene-Ni, MXene-Ag, and MXene-Ni/Ag composite substrates with different Ni-Ag ratios.

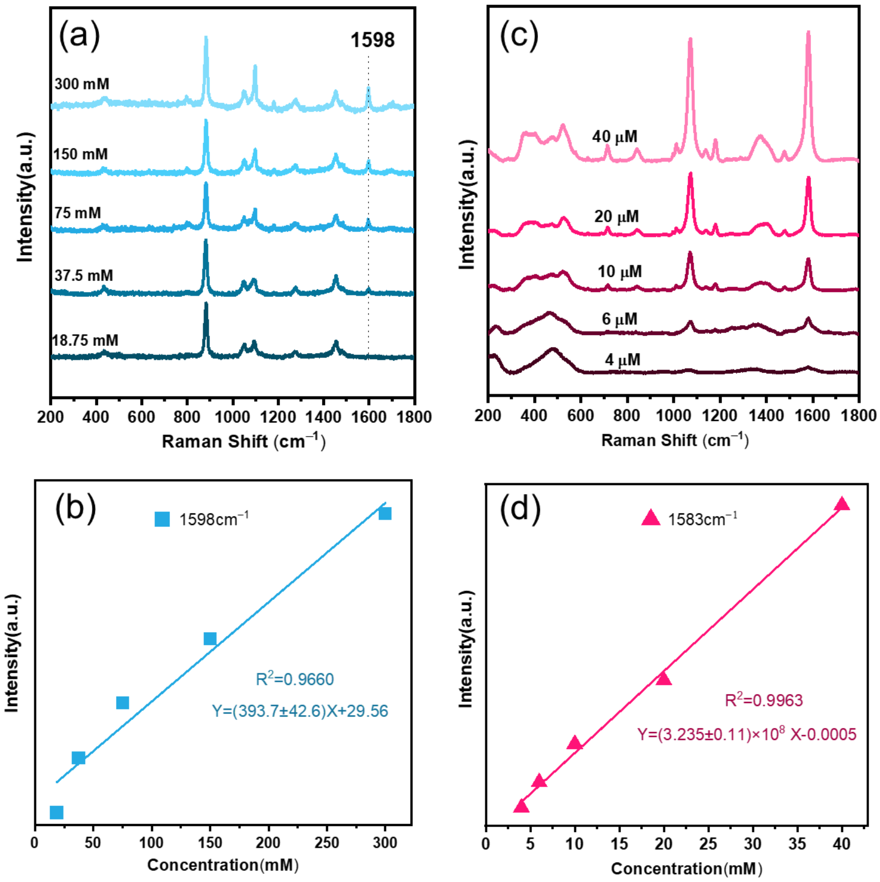

Figure S6. MBA concentration-dependent normal Raman spectra (a) and Raman intensities at 1598 cm^{-1} (b), MBA concentration-dependent SERS spectra (c) and Raman intensities at 1583 cm^{-1} (d).

The Calculation of SERS Performance Factor (*SPF*)[1].

$$SPF = \frac{\Delta I_{SERS}}{\Delta C_{SERS}} / \frac{\Delta I_{Raman}}{\Delta C_{Raman}}$$

$\frac{\Delta I_{Raman}}{\Delta C_{Raman}}$: **Normal Raman Measurement.** Figure S6a showed the MBA concentration-dependent normal Raman spectra in ethanol solution, characteristic Raman peak at 1598 cm^{-1} attributed to $\boldsymbol{\nu}_8$ (ring-breathing vibration) of MBA. By plotting the Raman intensity of the peak against the MBA concentration, a linear relationship (R^2=0.9660) was obtained as shown in Figure S6b. According to the slope, $\frac{\Delta I_{Raman}}{\Delta C_{Raman}}$ was 393.7±42.6.

$\frac{\Delta I_{SERS}}{\Delta C_{SERS}}$: **SERS Measurement.** Figure S6c showed the MBA concentration-dependent SERS spectra with the MXene-Ni/Ag as the SERS substrate. Due to the strong adsorption of MBA on the Ag NPs surface via the formation of the Ag−S bond, the characteristic Raman peak shifted 1598cm^{-1} to 1583cm^{-1}. It can be observed that the Raman intensity of the peak increased with the increased MBA concentration from 4.0 to 40 μM (Figure S6d). Thereby, $\frac{\Delta I_{SERS}}{\Delta C_{SERS}}$ was obtained as the slope, which was (3.235±0.11) × 10^8 for the peaks.

Recalling the aforementioned, $SPF = \frac{\Delta I_{SERS}}{\Delta C_{SERS}} / \frac{\Delta I_{Raman}}{\Delta C_{Raman}}$ =8.2×10^6.

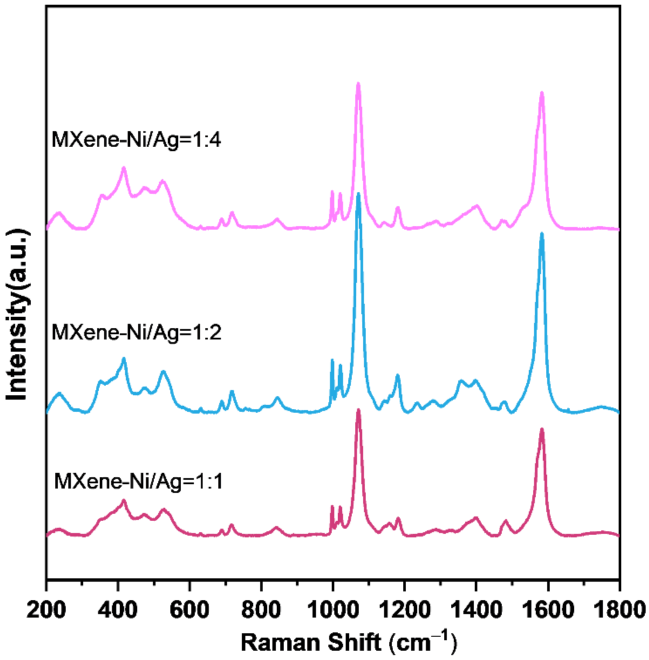

Figure S7. SERS spectra of MBA (10^{-5} M) on MXene-Ni/Ag composite substrates with different Ni:Ag ratios

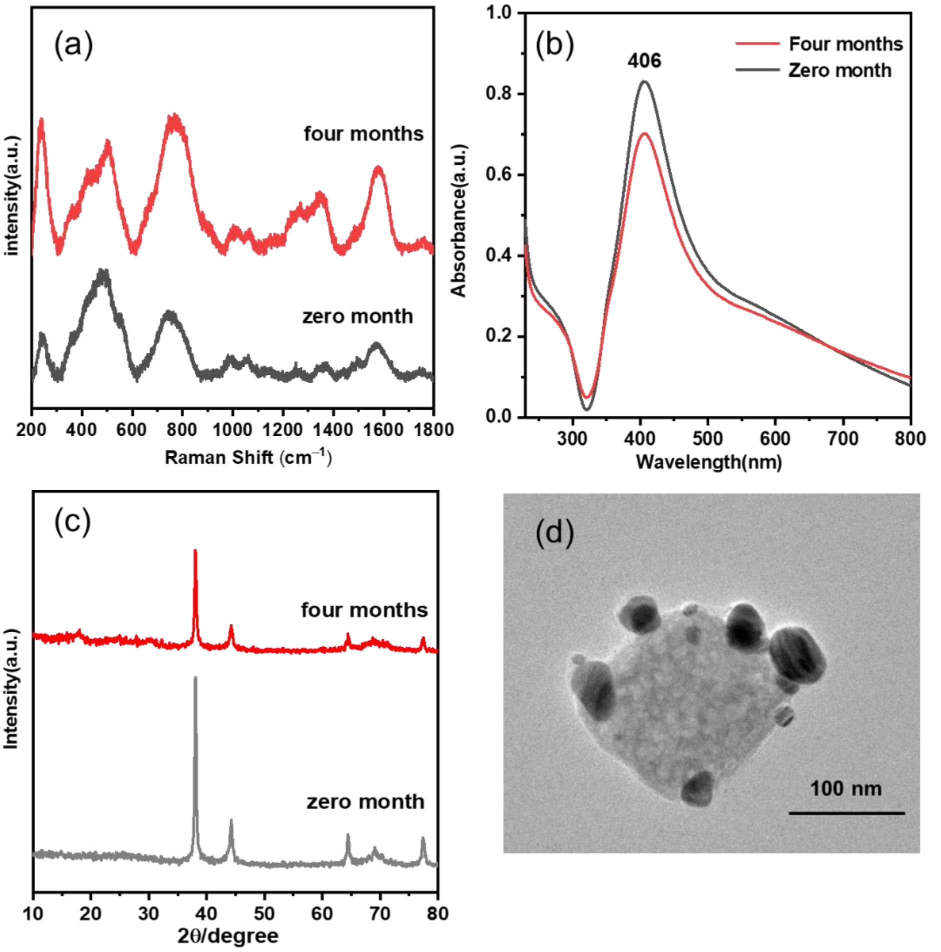

Figure S8. Raman (a), UV-vis (b), XRD (c), and TEM image (d) of the MXene-Ni/Ag SERS substrates after four months of storage.

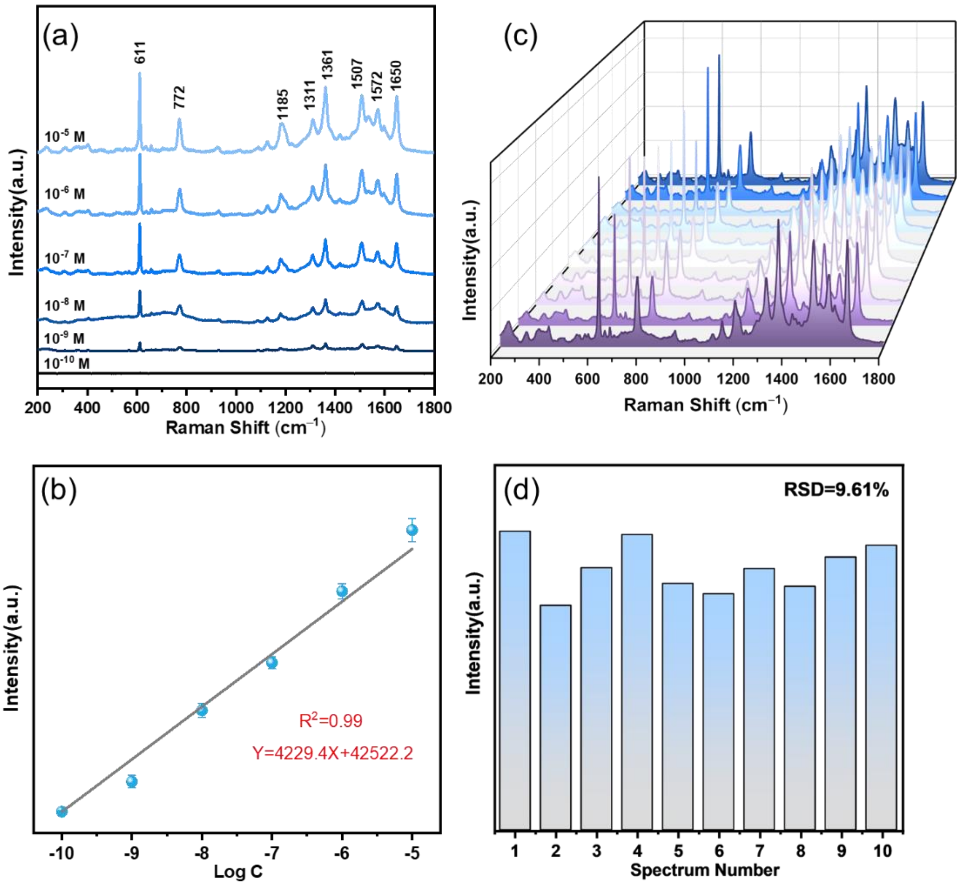

Figure S9. (a) SERS spectra of different concentrations of R6G (10^{-5}~10^{-10} M), (b) quantitative analysis of R6G, (c) histogram of R6G concentration and SERS intensity, (d) histogram of SERS intensity distribution at 1361 cm^{-1}.

The typical Raman "fingerprint" of R6G can be observed as peak at 611cm^{-1}, 772 cm^{-1},1361 cm^{-1} and 1650 cm^{-1}, corresponding respectively to the following R6G vibration modes: C–C–C stretching vibration, the aromatic stretching vibration, and the out-of-plane vibration of the deformed C–H bond[2]. As the concentration of R6G decreased from 10^{-5} M to 10^{-10} M， the Raman intensity gradually decreases, indicating a decreasing number of adsorbed R6G molecules. Notably, even at extremely low concentration of 10^{-10} M, the R6G signal remained detectable and exhibited a good linear relationship (Figure S9a and S9b). Furthermore, the reproducibility of R6G detection on MXene-Ni/Ag composite substrates was also evaluated., and the results were shown in Figure S9c, and the calculated RSD value was 9.61%.

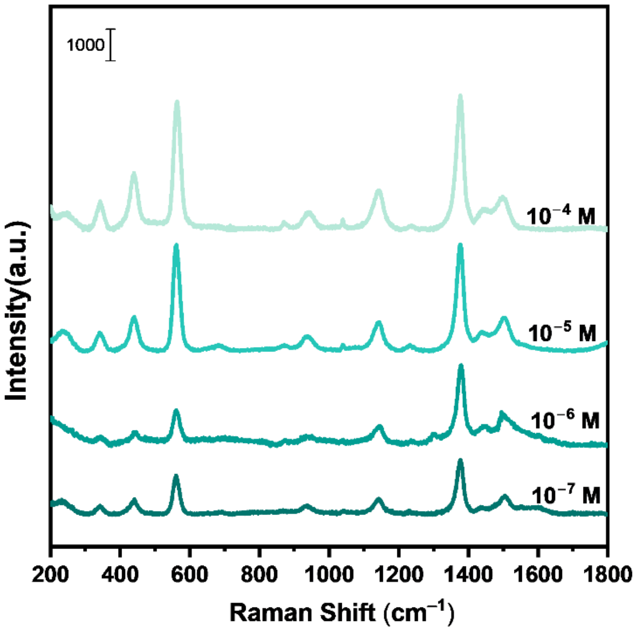

Figure S10. SERS spectra of thiram with different concentrations (10^{-4}, 10^{-5}, 10^{-6} and 10^{-7} M) on apple surface.

[1] Yue X, Yan S, Gao T, Pu S, Tang H, Pei X, Tian Z, Wang X, Ren B, Liu G. SERS Performance Factor: A Convenient Parameter for the Enhancement Evaluation of SERS Substrates[J]. *Analytical Chemistry*, 2024, **96**, 17517–17525.

[2] Michaels A M, Jiang, Brus L. Ag Nanocrystal Junctions as the Site for Surface-Enhanced Raman Scattering of Single Rhodamine 6G Molecules[J]. The Journal of Physical Chemistry B, 2000, **104**, 11965–11971.