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Supporting Information

A new ternary ZnO/ZnS/MoS_2 SERS substrate derived from polyoxomolybdate/ZIF-8 host-guest framework

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The calculation method of the enhancement factor (EF)

The EF of ZnMoNCs substrate is calculated according to the following equation:

$$EF = (I_{SERS}/I_{NR}) \times (N_{NR}/N_{SERS})$$

$$= (I_{SERS}/I_{NR}) \times [(S_{laser} \times h \times C_{NR} \times N_A)/(S_{laser}/S_{MPY})]$$

Where I_{SERS} and I_{NR} are the intensities of 4-MPY in surface enhanced Raman and Raman spectra respectively; N_{SERS} and N_{NR} represent the corresponding number of molecules in the surface enhanced Raman spectra and Raman spectra respectively. C_{NR} is the corresponding concentration of 4-MPY used in the Raman spectra, and here C_{NR} is 0.5 mol/L. h is the effective layer depth within which each 4-MPY molecule yields the same contribution to the Raman signal as those localized in the ideally focused plane and here h is calculated to be 17.88 μm. S_{laser} is the area of laser focused on the sample (here, laser diameter is 1 μm); S_{MPY} is the area of per 4-MPY molecule. N_A is the Avogadro constant. The intensity of the band at 1023 cm^{-1} is used to calculate the value of the EF. The ratio of intensity (I_{SERS}/I_{NR}) is about 70 on the basis of the spectra shown in Fig 4. The value of EF is estimated to be around 1.4×10^8.

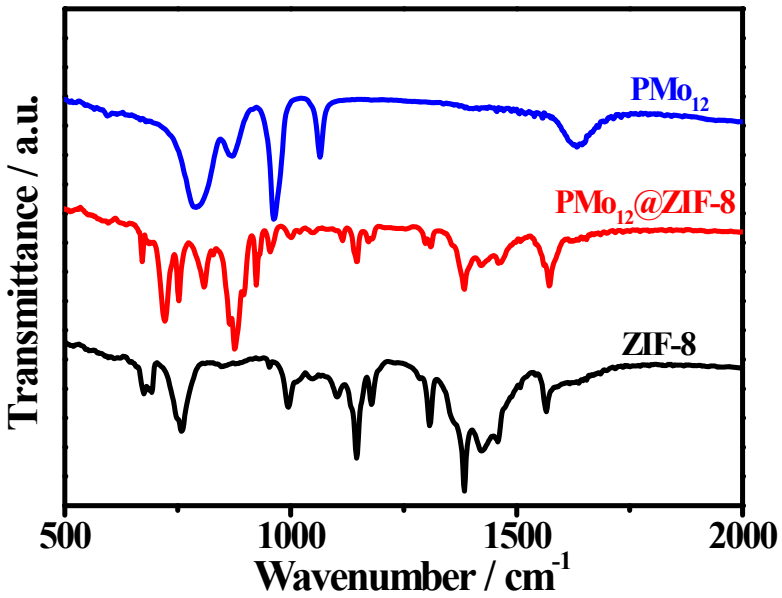

Fig. S1 FTIR spectra of ZIF-8 and PMo_{12}@ZIF-8.

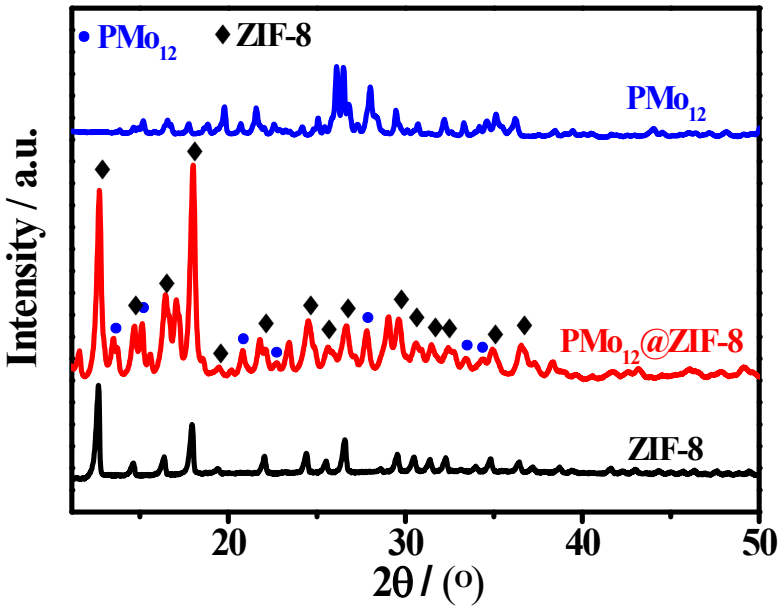

Fig. S2 XRD patterns of PMo_{12}, ZIF-8 and PMo_{12}@ZIF-8.

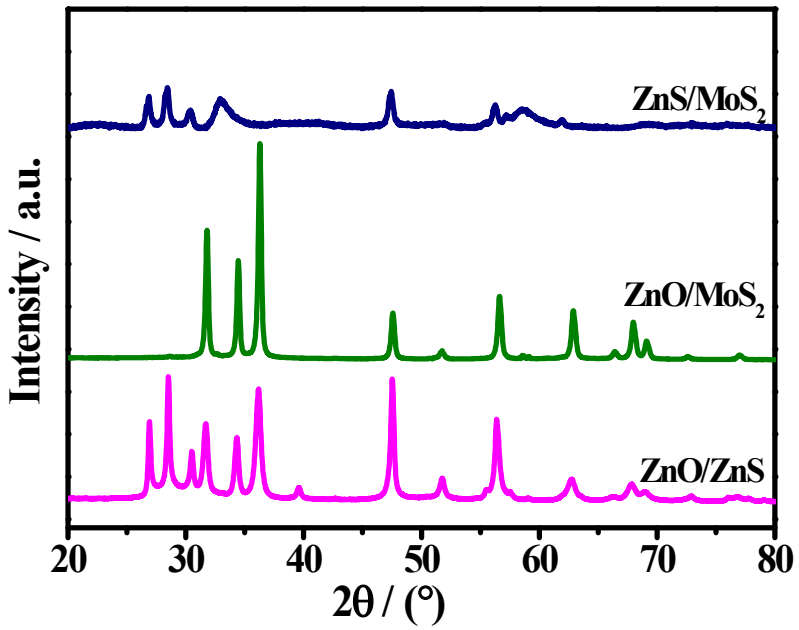

Fig. S3 XRD patterns of ZnO/ZnS, ZnO/MoS_2 and ZnS/MoS_2.

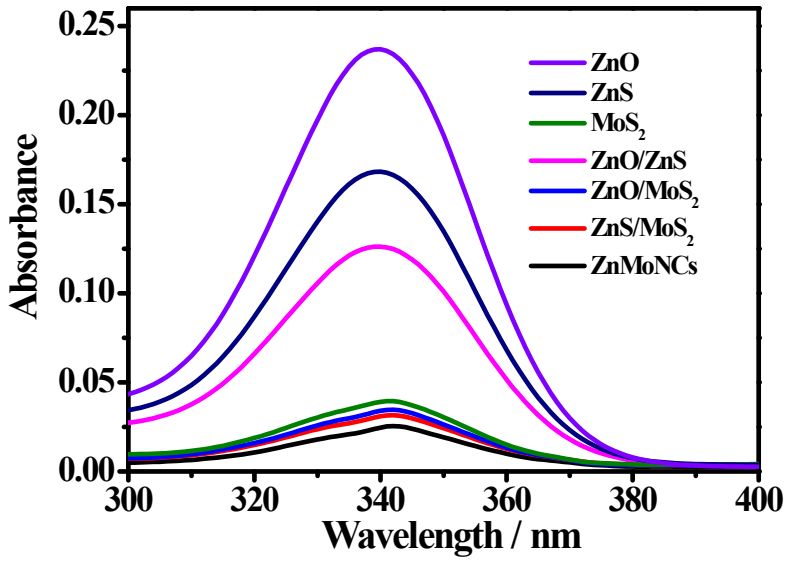

Fig. S4 UV-vis absorption spectra of residual solution after adsorption of 4-MPY (1×10^{-3} M) on different samples.

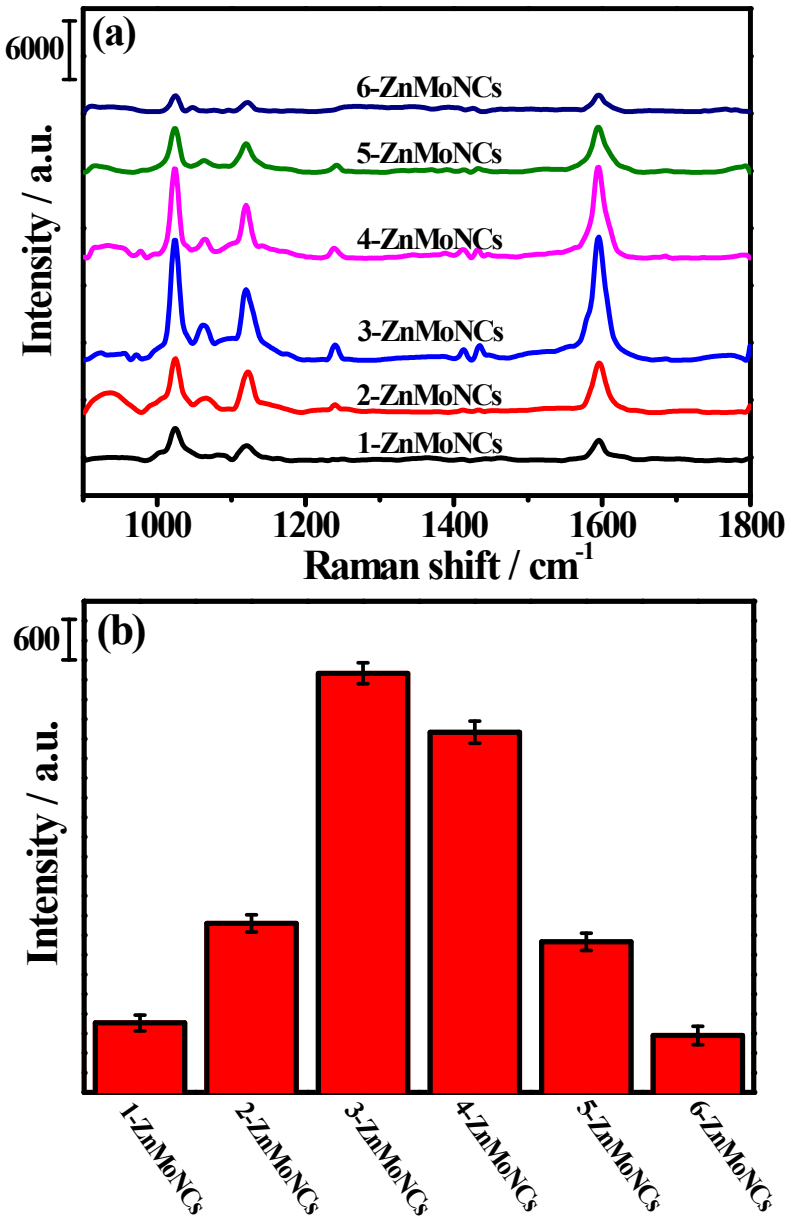

Fig. S5 (a) SERS spectra of 4-MPY adsorbed on different ZnMoNCs substrates; (b) the histogram of the Raman intensity of 4-MPY at 1023 cm^{-1} on different ZnMoNCs substrates (the error bars indicate the standard deviations from five measurements).

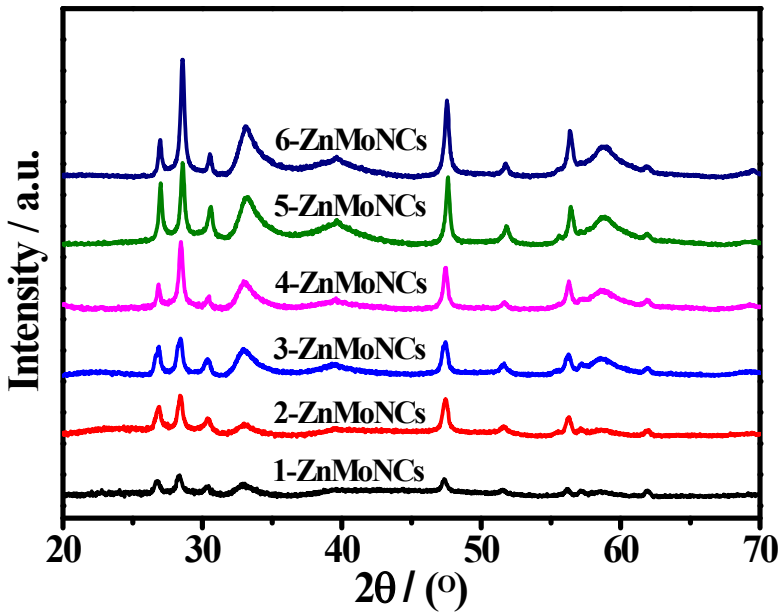

Fig. S6 XRD patterns of the different ZnMoNCs substrates.

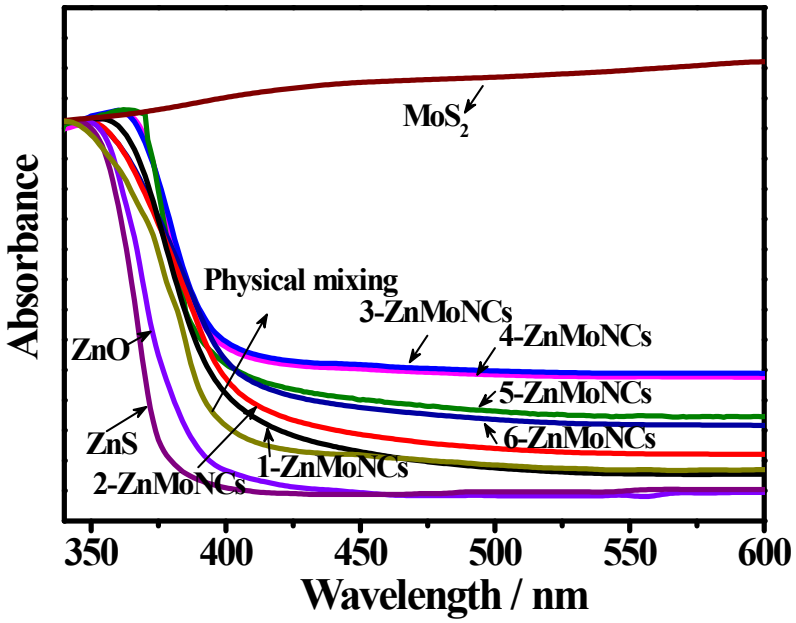

Fig. S7 UV-vis DRS spectra of the different ZnMoNCs substrates (EDS analyses for Mo elements are 7.7%, 10.1%, 21.4%, 20.6%, 15.8% and 14.7% for 1-ZnMoNCs, 2-ZnMoNCs, 3-ZnMoNCs, 4-ZnMoNCs, 5-ZnMoNCs and 6-ZnMoNCs, respectively).

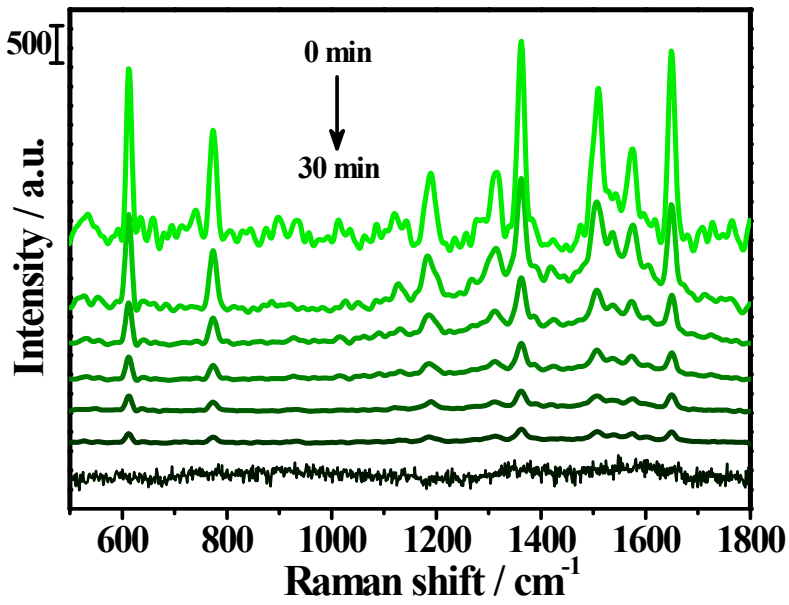

Fig. S8 SERS spectra of time-dependent catalytic degradation of rhodamine 6G on 3-ZnMoNCs substrate (the time interval is 5 min).

Table 1 The Raman/SERS shifts (cm^{-1}) and assignments of 4-MPY molecule on 3-ZnMoNCs substrate.

Raman		SERS	Assignment
Solid	**Solution**		
987 s	992 w	1024 s	a_1 ring breathing
1041 s	1046 w	1063 w	a_1 ring breathing/$\beta_{(C-H)}$
1198 m	1100 w		$9a_1$ $\beta_{(CH)}$/$\delta_{(NH)}$
		1120 m	$12a_1$ ring breathing/$\nu_{(C-S)}$
1246 vw	1277 w	1239 w	$9a_1$ $\beta_{(CH)}$
1396 m		1412 w	$\nu_{(C-N-C)}$
1457 vw	1458 w	1435 w	$19a_1$ $\nu_{(C=C/C=N)}$
1616 w		1593 s	b_2 $\nu_{(C=C)}$

ν: stretching vibration, β: rocking vibration, δ, bending vibrations; s: strong, m: medium, w: weak, vw: very weak.

Table 2 The band gap (Eg) values of different materials.

Samples	Band gap / eV
ZnO	3.24
ZnS	3.72
MoS_2	---
Physical mixing	3.09
1-ZnMoNCs	3.02
2-ZnMoNCs	2.98
3-ZnMoNCs	2.96
4-ZnMoNCs	2.95
5-ZnMoNCs	2.94
6-ZnMoNCs	2.90