

Supplemental Files

Experimental and theoretical evaluation of crystal facets exposure on the charge transfer and SERS activity of ZnO films

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1. The relationship between SERS intensity of 4-NBT and deposition time of ZnO substrate

A series of ZnO with different deposition time (from 5 to 50 min) were prepared, and the SERS spectra of 4-NBT were collected from the as-prepared ZnO films. As shown in **Fig. S1**, the SERS intensity of 4-NBT molecules on ZnO substrates reaches the maximum when the deposition times are about 20–30 min. Therefore, the optimal deposition time of both three samples were selected as 30 min.

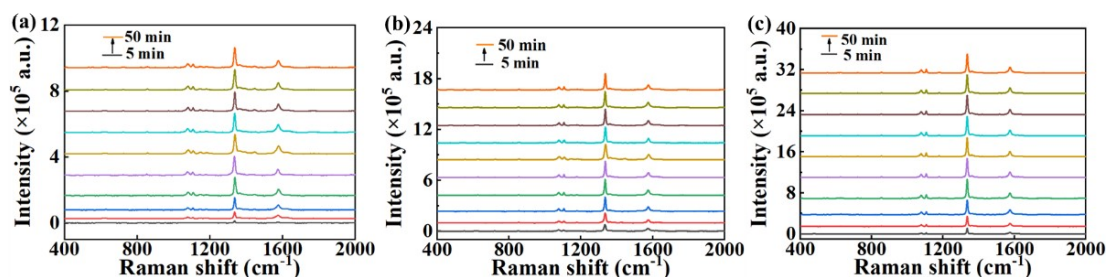


Fig. S1 SERS spectra of 4-NBT collected from (a) ZnO{10 $\bar{1}$ 0}, (b) ZnO{0001} and (c) ZnO{10 $\bar{1}$ 1} films with different electrodeposition time (from 5 to 50 min).

2. Ultraviolet–visible absorption spectra of ZnO/4-NBT system and SERS spectra of ZnO/R6G system

As shown in **Fig. S2a**, a visible CT-induced absorption band around 550 nm was detected from 4-NBT on ZnO{10 $\bar{1}$ 1} by comparing with the pristine ZnO{10 $\bar{1}$ 1} and pure 4-NBT molecules, which suggest that a CT process might happen between ZnO and 4-NBT molecule. **Fig. S2b** displays the Raman spectra of R6G solution and the SERS spectra of R6G molecule adsorbed on ZnO{10 $\bar{1}$ 0}, ZnO{0001} and ZnO{10 $\bar{1}$ 1}, respectively. As shown in **Fig. S2b**, the a'' vibration mode at 611 cm $^{-1}$ of R6G molecule was selectively enhanced than other vibration mode. According to Herzberg–Teller selection rule, if the enhanced Raman scattering was caused by CT process, the vibration modes of probe molecule would be selectively enhanced (the vibration

modes with not totally symmetric (a'') would be more heightened than totally symmetric modes (a') for probe molecule adsorbed on semiconductors). Therefore, these results both confirm the existence of CT process between the ZnO SERS substrate and probe molecule.

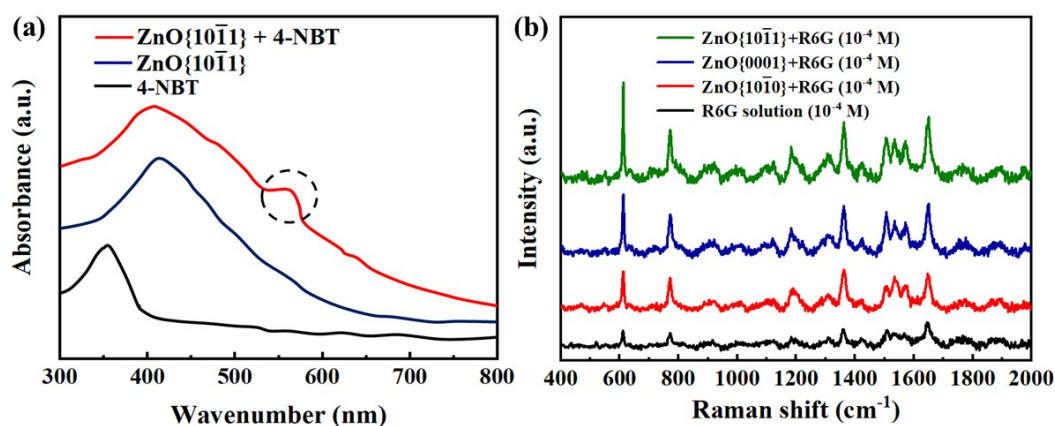


Fig. S2 (a) Ultraviolet–visible absorption spectra of 4–NBT adsorbed on ZnO{10 $\bar{1}$ 1} in comparing with that of pure 4–NBT and ZnO{10 $\bar{1}$ 1}, (b) Comparing different vibration modes between Raman spectra of pure R6G solution and SERS spectra of R6G molecule adsorbed on ZnO{10 $\bar{1}$ 0}, ZnO{0001} and ZnO{10 $\bar{1}$ 1}, respectively.

3. The EF value of as–prepared ZnO substrates compared with other reference

The relevant reports about ZnO based SERS substrates are listed in **Table S1**. The EF for 4–NBT is calculated to be about 9×10^3 , 1.6×10^4 and 2.8×10^4 for ZnO{10 $\bar{1}$ 0}, ZnO{0001} and ZnO{10 $\bar{1}$ 1}, which shown a relatively higher EF value compared with those reported ZnO substrates (**Table S1**), and certified that {10 $\bar{1}$ 1} facets dominated ZnO exhibit the highest SERS enhancement.

Table S1 The EF value of as–prepared ZnO substrates compared with other reference.

Substrates	Molecules	EF	LOD (M)	References
ZnO	D266 ^a	More than 50	–	[1]
ZnO	4–MPY ^b	10^3	–	[2]

ZnO	4-MBA ^c	–	–	[3]
ZnO	4-MPY	10 ³	–	[4]
ZnO	4-MBA	10 ³	10 ⁻⁶	[5]
ZnO	4-MPY	68	–	[6]
Amorphous ZnO	4-MPY	6.62 × 10 ⁵	–	[7]
Porous d-ZnO ^d	4-MPY	7.7 × 10 ⁵	10 ⁻⁷	[8]
Ga-doped ZnO	4-MBA	8.13 × 10 ³	–	[9]
Co-doped ZnO	4-MBA	10 ³	–	[10]
ZnO films	4-NBT	2.8 × 10 ⁴	5 × 10 ⁻⁷	Current work

^a D266: 1-methyl-1'-propylsulpho-2,2'-cyanine sulphonate.

^b 4-MPY: 4-mercaptopyridine.

^c 4-MBA: 4-mercaptobenzoic acid.

^d Porous d-ZnO: defect states in porous ZnO.

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