Ag Decoration on Na₂Ti₃O₇ Nanowires for Improved SERS and PHE

Performance

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Raman shift (cm ⁻¹)		Dond aggionmental
633 nm	514 nm	Band assignments
999	998	Non-totally symmetric $v(CC)$, b_2
1013	1012	Non-totally symmetric $v(CC)$, b_2
1076	1077	In-plane ring breathing $+v(C-S)$, a_1
1138		υ(CH), b ₂
1182	1181	υ(CH), a ₁
1365	1362	Asymmetric v(COO ⁻)
1586	1586	Totally symmetric $v(CC)$, a_1

Table S1. Assignments of SERS bands of MBA

 υ , stretching; β , bending. For ring vibrations, the corresponding vibrational modes of benzene and the symmetry species under C_{2 υ} symmetry are indicated, where a₁ and b₂ represent totally and non-totally symmetric vibrational modes of the molecules, respectively.



Fig. S1. (a), (c) High-magnification TEM images and (b), (d) the lattice spacings of Ag-NTO nanowires.



Fig. S2. (a) SERS spectrum of 10⁻³ M MBA adsorbed on Ag-NTO-3 obtained with 514 nm excitation light. (b) RSD of the band intensity at 1591 cm⁻¹.



Fig. S3. SEM images of sea urchin-shaped nanostructure after four PHE cycles.



Fig. S4. UPS spectra of (a) NTO and (b) Ag-NTO.

CB and VB Energy Determination. The band gap positions of the Ag/ITO systems were calculated according to the following equations:

$$W_{\rm F} = hv - \Delta E \qquad (1)$$
$$VB = W_{\rm F} + b \qquad (2)$$
$$CB = VB - E_{\rm g} \qquad (3)$$

where, hv is 21.22 eV, ΔE is the tangent value a in the graph, and the values a and b are both obtained by taking the tangent. The VB levels of NTO and Ag-NTO can be calculated as 7.42 and 7.02 eV (vs. vacuum), respectively. Furthermore, the calculated VB levels are 2.92 and 2.52 eV (vs. NHE), respectively.

References

1 B. Han, L. Chen, S. Jin, S. Guo, J. Park, H. S. Yoo, J. H. Park, B. Zhao and Y. M. Jung, Modulating Mechanism of the LSPR and SERS in Ag/ITO Film: Carrier Density Effect, *J. Phys. Chem. Lett.*, 2021, **12**, 7612–7618.