Electronic Supporting Information

Improved SERS enhancement from cubic SiC-based semiconductor nanowhiskers by adjusting energy level

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1 The electronic structures of SiCNWs and B-SiCNWs are calculated by plane-wave-density functional theory (DFT) using the CASTEP program package. In the calculated models, the B atoms (B/Si= 0.067, mole ratio) are incorporated into the SiC lattice and partly substitute the Si sites



Figure S1. Calculated band structure of (a) SiC and (b) B-SiCNWs

2 UV-Vis profile of these two kinds of nanowhiskers.



Figure S2. UV-Vis profile of two kinds of nanowhiskers, SiC and B-SiC, respectively.

3. XRD and Raman spectrums of the SiCNWs



Figure S3. XRD (a) and Raman (b) spectrums of SiCNWs.

4 XRD and EELS spectrum of B-SiCNWs.



Figure S4. (a) XRD and (b) EELS spectrum of B-SiCNWs.

5 The calculation of the enhancement factor (EF)

To quantify the SERS activity of the nanowhiskers, EF was calculated by comparing the intensity of a single molecule from the SERS signal with that from the bulk Raman signal by the formula as follows:

$$EF = (I_{SERS}/N_4) / (I_{bulk}/N_{4m})$$
⁽²⁾

Where I_{SERS} and I_{4m} are the intensities of the same mode in the SERS and non-SERS spectra, and N_{SERS} and N_{4m} are the average number of 4-MBA molecules in scattering area for SERS and non-SERS measurement respectively. I_{SERS} and I_{4m} were obtained experimentally under identical conditions. Assuming that the probed molecules are distributed on the substrate uniformly, the number of probe molecules contributing to the signal *N* can be estimated by

$$N = N_A \times C \times V_{droplet} / A_{spot} \times A_{laser}$$
(3)

Where N_A is the Avogadro's number, *C* is the concentration of the used 4-MBA, $V_{droplet}$ is the volume of the 4-MBA droplet, A_{spot} is the area of the spot formed by the 4-MBA droplet, and A_{laser} is the area of the laser spot. Since the specimens for SERS and bulk Raman tests are prepared in the same way and measured with the same parameters, equation (2) can be written as

$$EF = (I_{SERS}/I_{4m}) (N_{4m}/N_{SERS})$$
$$= (I_{SERS}/I_{4m}) (C_{4m}/C_{SERS})$$
(4)

Where C_{4m} and C_{SERS} are the concentrations of the 4-MBA (1×10⁻¹M) and 4-MBA on the SiCNWs respectively.

6 The peak of the S-H stretching mode at 2570 cm⁻¹ of 4-MBA before and after adsorbed onto SiCNWs.



Figure S6. Raman spectra of 4-MBA (1×10⁻¹M) with SH stretching mode at 2570 cm⁻¹ (denoted by the black arrows), and 4-MBA adsorbed onto SiCNWs, the above mode disappeared.

7. The calculation of the contribution of photo-induced charge transfer (CT) to the molecular polarizability tensor in the semiconductor-molecule system:

Based on the Herzberg-Teller theory, the contribution of photo-induced charge transfer (CT) to the molecular polarizability tensor in the semiconductor-molecule system was calculated. The calculation in this communication is derived from the treatment in a semiconductor-molecule system reported by Lombardi and Wang[1-4], except that the vibronic coupling of the conductor band states S and the valance band states S' of the semiconductor with the molecular exited state K and the molecular ground state I in the semiconductor-molecule system were included.

The intensity of a Raman transition may be obtained from the molecular polarizability tensor by the expression:

$$I_{Raman} = \left[8\pi \left(\omega_0 \pm \omega_{IF} \right)^4 I_0 / 9c^4 \right] \sum \left| \alpha_{\rho\sigma} \right|^2$$
(1)

Where, I_0 is the incident laser intensity at ω_0 , and ω_{IF} is a molecular transition frequency between states *I* and *F* (presumably two different vibronic levels of the ground electronic state *Ie*). Using second-order perturbation theory, the polarizability tensor may be shown as:

$$\boldsymbol{\alpha}_{\sigma\rho} = \sum_{K \neq I,F} \left(\frac{\langle I | \boldsymbol{\mu}_{\sigma} | K \rangle \langle K | \boldsymbol{\mu}_{\rho} | F \rangle}{E_{K} - E_{I} - h\boldsymbol{\omega}_{0}} + \frac{\langle I | \boldsymbol{\mu}_{\rho} | K \rangle \langle K | \boldsymbol{\mu}_{\sigma} | F \rangle}{E_{K} - E_{F} + h\boldsymbol{\omega}_{0}} \right)$$
(2)

Where, *K* represents all the other states of the molecule, μ is the dipole moment operator, the subscripts σ and ρ represent the three directions in space (*X*, *Y*, *Z*). Following Albrecht and Lombardi, using the zero-order Born-Oppenheimer approximation, all the states (*I*, *K*, *F*) as products of the electronic and vibrational wave functions can be written as following:

$$|I\rangle = |I_e\rangle|i\rangle , |F\rangle = |I_e\rangle|f\rangle , |K\rangle = |K_e\rangle|k\rangle$$
(3)

Where the subscript *e* indicates a purely electronic state, and lowercase letters represent vibrational functions. Based on the Herzberg-Teller theory that even small vibrations may cause mixing of zero-order Born-Oppenheimer states, vibronic functions in the semiconductor-molecule system can be written as

$$\left|K_{e}\right\rangle = \left|K_{e},0\right\rangle + \sum_{S}\lambda_{KS}Q\left|S_{e},0\right\rangle$$
(4)

$$\left|I_{e}\right\rangle = \left|I_{e},0\right\rangle + \sum_{S'}\lambda_{IS'}Q\left|S'_{e},0\right\rangle$$
(5)

$$\lambda_{ks} = h_{KS} / \left(E_K^0 - E_S^0 \right) = h_{KS} / \omega_{KS}$$
(6)

$$\lambda_{IS'} = h_{IS'} / \left(E_I^0 - E_{S'}^0 \right) = h_{IS'} / \omega_{IS'}$$
(7)

$$h_{ks} = \left\langle k_{e}, 0 \left| \partial H_{eN} \right| \left\langle \partial Q \right| S_{e}, 0 \right\rangle$$
(8)

$$h_{Is'} = \left\langle I_e, 0 \left| \partial H_{eN} / \partial Q \right| S'_e, 0 \right\rangle \tag{9}$$

Where, zero refer to zero-order Born-Oppenheimer states, $|s_e\rangle$ indicate the electronic states lying in conductor band of the semiconductor, $|S_e\rangle$ indicate the electronic states lying in valence band of the semiconductor, H_{e_N} is the electron nuclear attraction term in the Hamiltonian, evaluated at the equilibrium nuclear positions (0). $h_{\kappa s}$ is the coupling matrix element representing the degree to which a particular vibration Q can mix states S_e with state K_e . Similarly, h_{κ} is the coupling matrix element representing the degree to which a particular vibration Q can mix states S' with state I_e . For the purely electronic transition moment between states, it can be written as:

$$M_{IK} = \langle I_e | \mu | K_e \rangle \quad M_{S'K} = \langle S'_e | \mu | K_e \rangle \quad M_{IS} = \langle I_e | \mu | S_e \rangle$$
(10)

Now we consider the situation that the frequency of the exiting light is far from any molecular resonance frequency ($\omega_0 < \omega_{IK}$). In our condition, because the location of the state *I* is much lower than that of S', we don't take photo-induced charge transfer of molecule-to-semiconductor into account. The polarizability tensor $\alpha_{\sigma\rho}$ can be written as following:

$$\alpha_{\sigma\rho} = A_s + C' \tag{11}$$

$$A_{S} = (2 / h) \sum_{S'e} M^{\sigma}_{S'K} M^{\rho}_{S'K} \langle i | k \rangle \langle k | f \rangle \frac{\omega_{S'k}}{\omega_{S'K}^{2} - \omega_{0}^{2}}$$
(12)

$$C' = \left(2 / h^{2}\right) \sum_{Ke \neq le} \sum_{S'e \mid e} \left[M_{KI}^{\sigma} M_{S'K}^{\rho} + M_{KI}^{\rho} M_{S'K}^{\sigma} \right] \times \frac{\left(\omega_{lk} \omega_{S'k} + \omega_{lK}^{2}\right) h_{lS'} \left\langle i | \mathcal{Q} | f \right\rangle}{\left(\omega_{lK}^{2} - \omega_{0}^{2}\right) \left(\omega_{lK}^{2} - \omega_{S'K}^{2}\right)}$$
(13)

Where As represents similar molecular resonance contribution due to the photo-induced charge transfer of semiconductor-to-molecule, which is from one of semiconductor valence band states S' to the molecular excited state $K \cdot C'$ represents the contributions of the photo-induced charge transfer of semiconductor-to-molecule, which is from one of the

semiconductor valence band states S' to the molecular exited state K. This transition obtains its intensity via $M_{S'K}$ through intensity borrowing from the (assumed) allowed transition $I \rightarrow K$. The borrowing mechanism is vibronic coupling through $h_{IS'}$ which represents coupling of the semiconductor valence band states S' to the molecular ground state I through some vibrational mode Q. This is illustrated in Figure. S7.



Figure S7. The scheme for the photo-induced charge transfer of semiconductor-to-molecule in semiconductor-molecular system under the situation of $\omega_0 < \omega_{lK}$.

8 The whiskers without treating by HF which has a layer of SiO_2 out of the SiC was used as

the substrate to verify the importance of the CT process in SERS



Figure S8. (a) SEM and (b) TEM images of SiO₂@SiCNW; (c) Raman spectra of 4-MBA on SiO₂@SiCNW substrate

9 In order to further confirm the SERS performance of these two kinds of nanowhiskers,

similar experiments were performed using 5×10⁻⁶ M Rhodamine 6G (R6G) as the probe molecule under 514.5 nm laser



Figure S9. Raman spectrum of the 5×10^{-6} M Rhodamine 6G solution on SiCNWs and B-SiCNWs substrates. The inset is the SERS of 5×10^{-7} M Rhodamine 6G on the B-SiCNWs

substrate.

Reference

- [1] Lombardi J R, Birke R L, Lu T, et al. J. Chem. Phys. 1986, 84, 4174-4180.
- [2] Lombardi J R, Birke R L. J. Chem. Phys. 2007, 126, 244709.
- [3] Lombardi J R, Birke R L. J. Phys. Chem. 2014, 118, 11120-11130.
- [4] Wang X. T.; Shi W. S.; She G. W.; Mu, L. X. J. Am. Chem. Soc. 2011, 133, 16518-16523.