SUPPORTING INFORMATION FOR:

Ultrahigh Stable SnOX (X= S, Se) Nanotubes with a Built-in Electric Field as a Highly Promising Platform for Sensing NH_3, NO and NO_2: A Theoretical Investigation

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1. Hückel Molecular Orbital (HMO) theory to calculate the charge density of NO_x (x = 1, 2)

For the isolated NO_x (x = 1, 2), it always gets the wrong information, e.g., the dipole direction and the charge, from the Gaussian software if one does not choose the appropriate basis sets. In this work, by using HMO theory as referred to the textbook, we give a correct picture that how the information of NO_x are.

For NO_2, the HMO of Π orbital can be expressed as $\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3$, here $\varphi_1, \varphi_2, \varphi_3$ are the $2p_z$ atomic orbitals (AO). The eigenvalue equation of HMO is:

$\begin{pmatrix} \alpha_O - E & \beta_{NO} & 0 \\ \beta_{NO} & \alpha_N - E & \beta_{NO} \\ 0 & \beta_{NO} & \alpha_O - E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$, it can be deduced to:

$\begin{pmatrix} \frac{\alpha_O - E}{\beta_{NO}} & 1 & 0 \\ 1 & \frac{\alpha_N - E}{\beta_{NO}} & 1 \\ 0 & 1 & \frac{\alpha_O - E}{\beta_{NO}} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$. Assuming $\frac{\alpha_O - E}{\beta_{NO}} = \chi$, $\frac{\alpha_O - \alpha_N}{\beta_{NO}} = k$ ($k > 0$), so $\frac{\alpha_N - E}{\beta_{NO}} = \frac{\alpha_O - E}{\beta_{NO}} + \frac{\alpha_N - \alpha_O}{\beta_{NO}} = \chi - k$. Then, the eigenvalue equation of HMO can be simplified to $\begin{pmatrix} \chi & 1 & 0 \\ 1 & \chi - k & 1 \\ 0 & 1 & \chi \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$. And the secular determinant is $\begin{vmatrix} \chi & 1 & 0 \\ 1 & \chi - k & 1 \\ 0 & 1 & \chi \end{vmatrix} = 0$, thus $\chi(\chi^2 - k\chi - 2) = 0$. Solving the equation, we can get $\chi_1 = \frac{k - \sqrt{k^2 + 8}}{2} = k' < 0,\ \chi_2 = 0,\ \chi_3 = \frac{k + \sqrt{k^2 + 8}}{2} = k'' > 0$. And the HMO energy levels are:

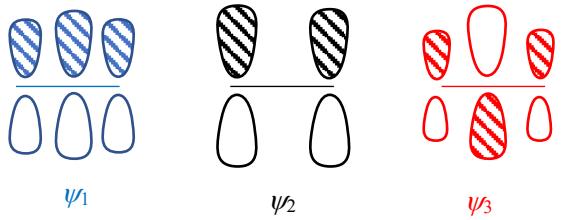
$$\begin{cases} E_1 = \alpha_O - k'\beta_{NO} \\ E_2 = \alpha_O \\ E_3 = \alpha_O - k''\beta_{NO} \end{cases}$$

If we substitute χ_1, χ_2, χ_3 to the HMO determinant equation, and taking the normalization condition into consideration, the HMO orbitals are:

$$\begin{cases} \psi_1 = \frac{1}{\sqrt{2 + k'^2}} \cdot (\varphi_1 - k'\varphi_2 + \varphi_3) \\ E_2 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_3) \\ \psi_3 = \frac{1}{\sqrt{2 + k''^2}} \cdot (\varphi_1 - k''\varphi_2 + \varphi_3) \end{cases}$$

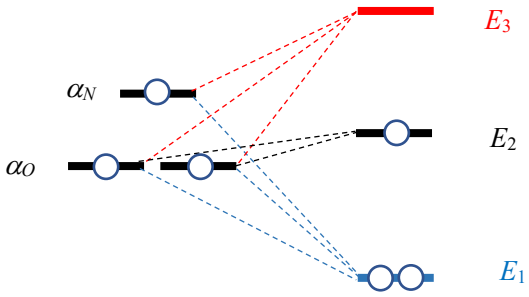
If we assume $k = 0.276$, so $k' = -1.283,\ k'' = 1.559$, and then:

$\begin{cases}\psi_1 = 0.524\varphi_1 + 0.672\varphi_2 + 0.524\varphi_3 \\ \psi_2 = 0.707\varphi_1 + 0.707\varphi_3 \\ \psi_3 = 0.475\varphi_1 - 0.741\varphi_2 + 0.475\varphi_3\end{cases}$. The pictures of these MO look like:



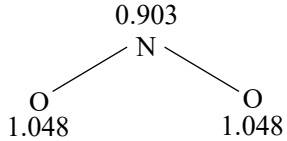
ψ_1 ψ_2 ψ_3

And the electron distribution of Π_3^3 looks like:



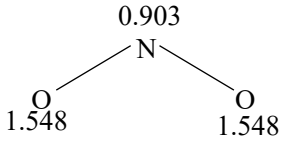
So, we can calculate the charge density of Π_3^3:

$\begin{cases}\rho_1 = 2c_{11}^2 + c_{21}^2 = 2\times 0.524^2 + 0.707^2 = 1.048 \\ \rho_2 = 2c_{12}^2 + c_{22}^2 = 2\times 0.672^2 + 0 = 0.903 \\ \rho_3 = \rho_1 = 1.048\end{cases}$



If NO_2 is dimerized, the Π is always believed as Π_3^4. In this case, the charge density is

$\begin{cases}\rho_1 = 2c_{11}^2 + 2c_{21}^2 = 2\times 0.524^2 + 2\times 0.707^2 = 1.548 \\ \rho_2 = 2c_{12}^2 + 2c_{22}^2 = 2\times 0.672^2 + 0 = 0.903 \\ \rho_3 = \rho_1 = 1.548\end{cases}$



Similarly, for the NO, the πMO is written as $\psi = c_1\varphi_1 + c_2\varphi_2$. Here φ_1, φ_2 are the $2p_x$ AO or $2p_y$ AO. The eigenvalue equation of HMO is $\begin{pmatrix}\alpha_N - E & \beta_{NO} \\ \beta_{NO} & \alpha_O - E\end{pmatrix}\begin{pmatrix}c_1 \\ c_2\end{pmatrix} = \begin{pmatrix}0 \\ 0\end{pmatrix}$, it can be deduced to $\begin{pmatrix}\frac{\alpha_N - E}{\beta_{NO}} & 1 \\ 1 & \frac{\alpha_O - E}{\beta_{NO}}\end{pmatrix}\begin{pmatrix}c_1 \\ c_2\end{pmatrix} = \begin{pmatrix}0 \\ 0\end{pmatrix}$. Assuming $\frac{\alpha_O - E}{\beta_{NO}} = \chi$, $\frac{\alpha_O - \alpha_N}{\beta_{NO}} = k$ $(k > 0)$. So the eigenvalue equation is simplified to $\begin{pmatrix}\chi - k & 1 \\ 1 & \chi\end{pmatrix}\begin{pmatrix}c_1 \\ c_2\end{pmatrix} = \begin{pmatrix}0 \\ 0\end{pmatrix}$. And the HMO determinant equation is $\begin{vmatrix}\chi - k & 1 \\ 1 & \chi\end{vmatrix} = 0$, so we get $\chi^2 - k\chi - 1 = 0$. Solving this equation, we can get

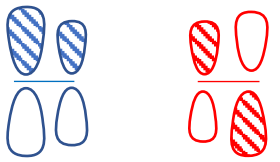
$\chi_1 = \dfrac{k - \sqrt{k^2+4}}{2} = k' < 0,\ \chi_2 = \dfrac{k + \sqrt{k^2+4}}{2} = k'' > 0$. And the HMO energy levels are $\begin{cases} E_1 = \alpha_O - k'\beta_{NO} \\ E_2 = \alpha_O - k''\beta_{NO} \end{cases}$.

Substituting χ_1, χ_2 to the HMO determinant equation, and using the normalization condition, the HMO orbitals are:

$$\begin{cases} \psi_1 = \dfrac{1}{\sqrt{1+k'^2}} \cdot (\varphi_1 - k'\varphi_2) \\ \psi_2 = \dfrac{1}{\sqrt{1+k''^2}} \cdot (\varphi_1 - k''\varphi_2) \end{cases}$$

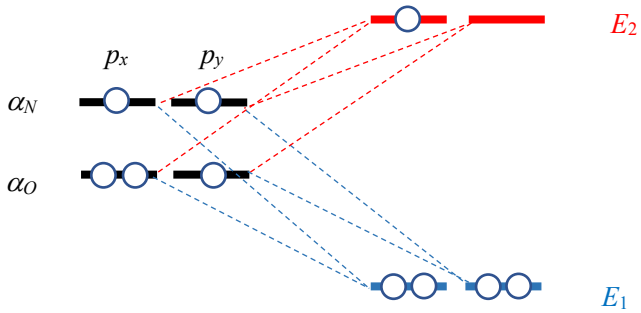
If we assume $k = 0.276$, then $k' = -0.871,\ k'' = 1.147$, so $\begin{cases} \psi_1 = 0.754\varphi_1 + 0.657\varphi_2 \\ \psi_2 = 0.657\varphi_1 - 0.754\varphi_2 \end{cases}$.

The pictures of MOs look like:



ψ_1 ψ_2

And the electron distribution of $2\Pi_2^2$ looks like:



So, we can calculate the charge density of $2\Pi_2^2$:

$$\begin{cases} \rho_1 = 4c_{11}^2 + c_{21}^2 = 2 \times 0.754^2 + 0.651^2 = 2.705 \\ \rho_2 = 4c_{12}^2 + c_{22}^2 = 4 \times 0.657^2 + 0.754^2 = 2.295 \end{cases}$$

2.705 2.295

N O

From these calculations, we can clearly see that the N atom is positively charged in NO_2 whereas it is negatively charged in NO.

2. Supplemented Tables and Figures

Table S1. Comparison of adsorption energy (E_{ad}, in eV) between using full NTs and the curved NTs.

E_{ad}	(6,6)	(7,7)	(8,8)
Full-NTs	-0.63	-0.70	-0.72
Curved-NTs	-0.59	-0.61	-0.63

Table S2. The primary geometrical parameters of SnOS and SnOSe NTs. D_i: inner diameter; D_o: outer diameter; D: middle diameter (the diameter from the middle layered Sn to the center of the NTs); T: thickness; B_i: inner bond length of Sn-O; B_o: outer bond length of Sn-S/Sn-Se. All the data are in Å.

SnOS NTs	**D_i**	**D_o**	**D**	**T**	**B_i**	**B_o**
(4, 4)	5.92	10.66	7.766	2.34	2.080	2.716
(5, 5)	7.80	12.56	9.652	2.38	2.088	2.637
(6, 6)	9.38	14.27	11.29	2.44	2.097	2.602
(7, 7)	11.32	16.20	13.22	2.44	2.104	2.582
(8, 8)	13.02	17.96	14.95	2.47	2.109	2.569
(10, 10)	16.63	21.61	18.57	2.49	2.114	2.554
(12, 12)	20.45	25.42	22.38	2.49	2.128	2.548
(14, 14)	24.27	29.25	26.20	2.49	2.132	2.546
(16, 16)	28.10	33.07	30.07	2.48	2.145	2.542
(18, 18)	33.89	36.83	31.93	2.48	2.150	2.540
(20, 20)	35.75	40.72	37.66	2.48	2.155	2.538
(24, 24)	43.40	48.36	45.30	2.48	2.166	2.537
(6, 0)	5.426	9.96	7.124	2.27	2.106	2.776
(8, 0)	7.254	11.97	9.074	2.36	2.116	2.666
(12, 0)	11.26	16.14	13.16	2.44	2.126	2.593
(16, 0)	15.48	20.41	17.39	2.46	2.137	2.568
(18, 0)	17.62	22.56	19.51	2.47	2.143/	2.558
(20, 0)	19.74	24.70	21.62	2.48	2.145	2.554
(22, 0)	21.79	26.77	23.72	2.49	2.164	2.549
(28, 0)	28.42	33.39	33.39	2.48	2.157	2.545
(32, 0)	32.84	37.80	34.74	2.48	2.163	2.539
SnOSe NTs	**D_i**	**D_o**	**D**	**T**	**B_i**	**B_o**
(4, 4)	5.92	10.93	7.75	2.51	2.087	2.784
(5, 5)	7.87	12.90	9.70	2.52	2.095	2.738
(6, 6)	9.48	14.64	11.37	2.58	2.104	2.710

(8, 8)	15.05	18.36	13.15	2.61	2.115	2.684
(10, 10)	17.01	22.23	18.90	2.61	2.130	2.676
(12, 12)	20.85	26.07	22.74	2.61	2.140	2.669
(14, 14)	24.73	29.96	26.63	2.61	2.150	2.667
(16, 16)	28.58	33.80	30.47	2.61	2.155	2.664
(18, 18)	32.49	37.70	34.36	2.61	2.161	2.662
(20, 20)	36.39	41.62	38.28	2.61	2.166	2.659
(24, 24)	44.82	49.98	46.66	2.58	2.198	2.670
(6, 0)	5.48	10.25	7.15	2.38	2.126	2.871
(8, 0)	7.35	12.32	9.14	2.49	2.128	2.778
(10, 0)	9.36	14.43	11.20	2.54	2.133	2.732
(12, 0)	11.48	16.69	13.34	2.56	2.141	2.721
(14, 0)	13.56	18.73	15.43	2.58	2.144	2.694
(16, 0)	15.74	20.92	17.61	2.59	2.151	2.685
(20, 0)	20.09	25.30	21.98	2.61	2.159	2.689
(22, 0)	22.39	27.59	24.26	2.60	2.166	2.673
(24, 0)	24.58	29.79	26.46	2.60	2.167	2.669
(28, 0)	28.98	34.19	30.85	2.61	2.173	2.665

Table S3. Energy levels of LUMO and HOMO of NO_x.

Gas	LUMO (eV)	HOMO (eV)
NO	-4.6	-11.2
NO_2	-5.2	-6.7

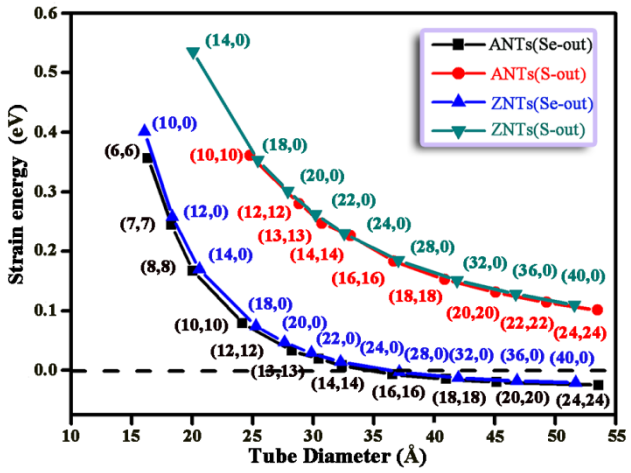


Fig. S1 Strain energy of SnSSe NTs versus tube diameter.

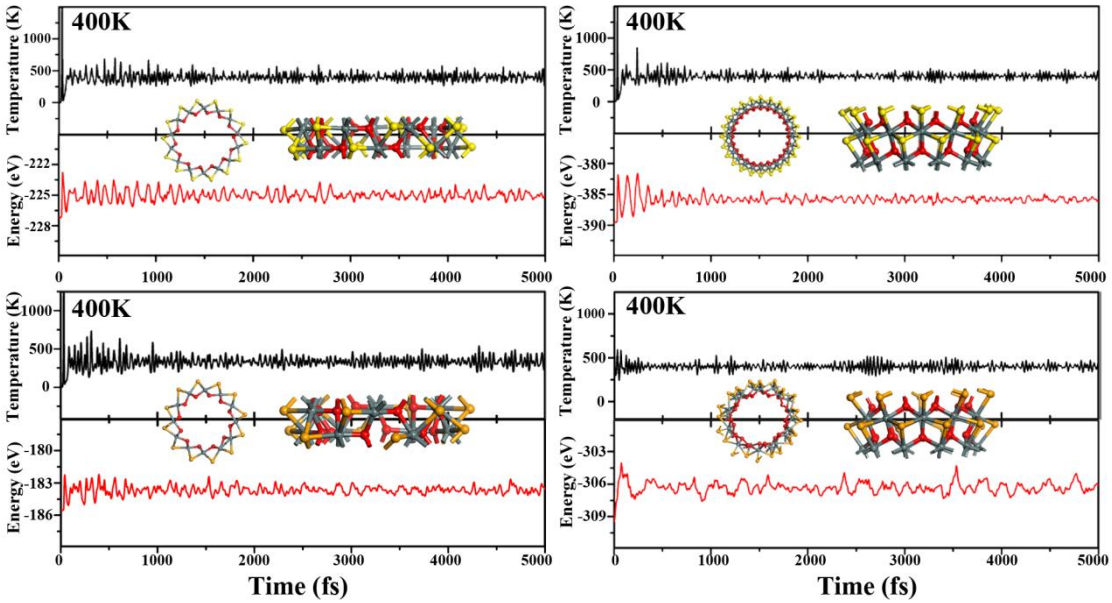


Fig. S2 Temperature and total energy vs time for AIMD simulations of SnOS ANT, SnOS ZNT, SnOSe ANT and SnOSe ZNT. Insets show the top and side views of a snapshot of the final atomic configuration. The simulation is run at 400 K for 5 ps with a time step of 1 fs.

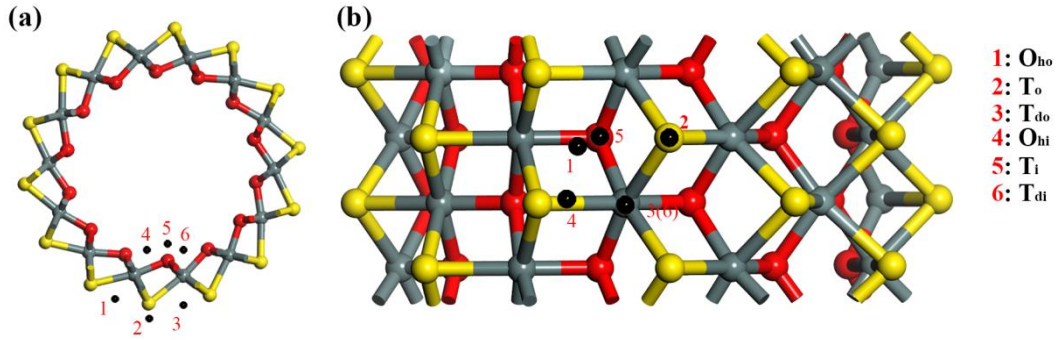


Fig. S3 Structure of SnOS ANT from (a) top and (b) side views with possible adsorption positions for NH_3, NO and NO_2 molecules, respectively.

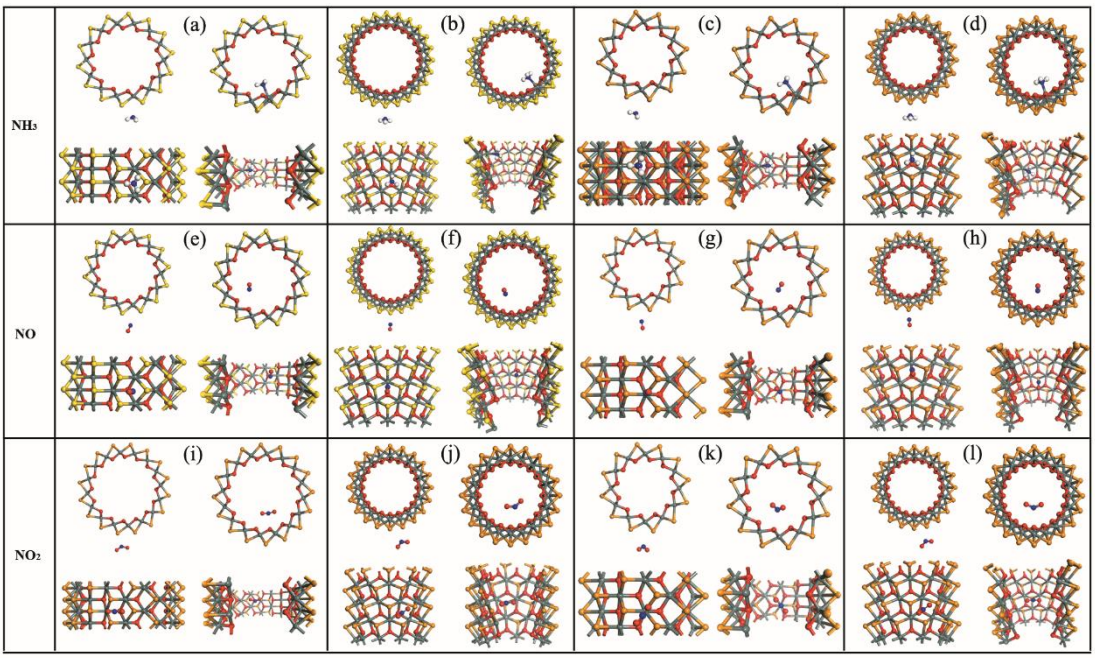


Fig. S4 Adsorption configurations of NH_3, NO and NO_2 on the NTs. NH_3 (a) - (d), NO (e) – (h), NO_2 (i) – (l) adsorbed on the SnOS ANT, SnOS ZNT, SnOSe ANT, and SnOSe ZNT, respectively.

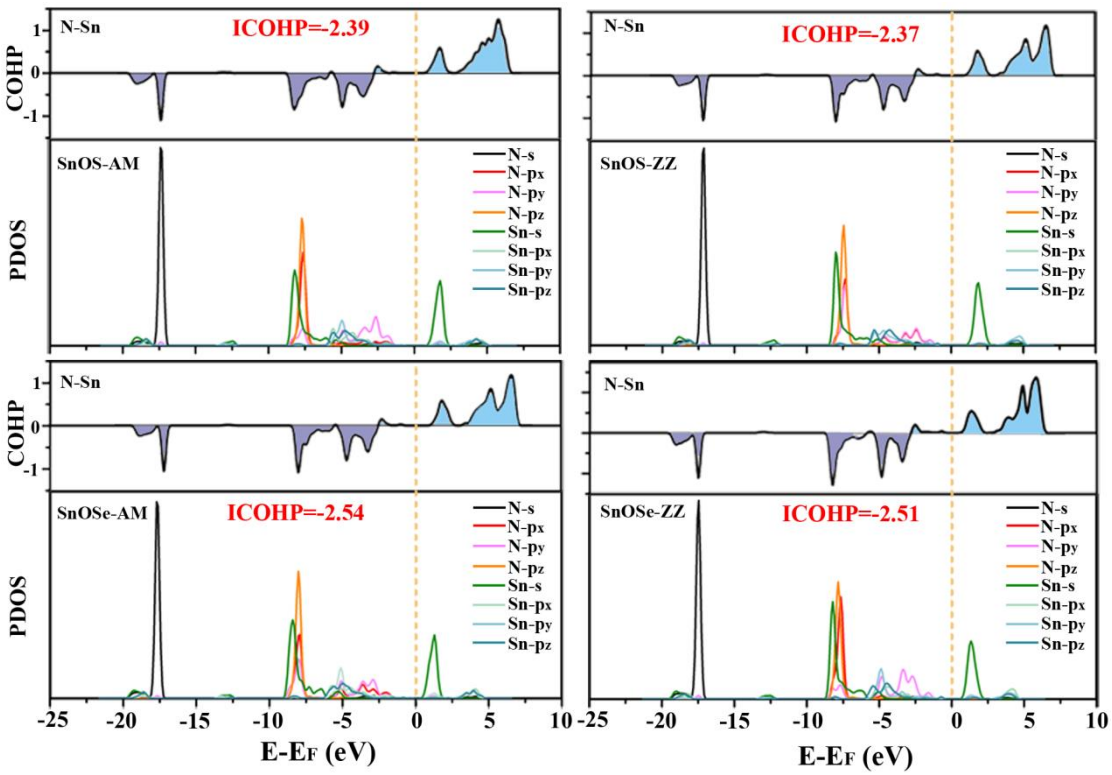


Fig. S5 Calculated PDOS and the ICOHP of NH_3 adsorbed on NTs. The bonding and antibonding states in COHP are depicted by purple and blue shaded areas, respectively. The s, p_x, p_y, p_z orbitals of N and Sn atom are black, red, pink, orange, olive, yellow green, green grey and dark green, respectively.

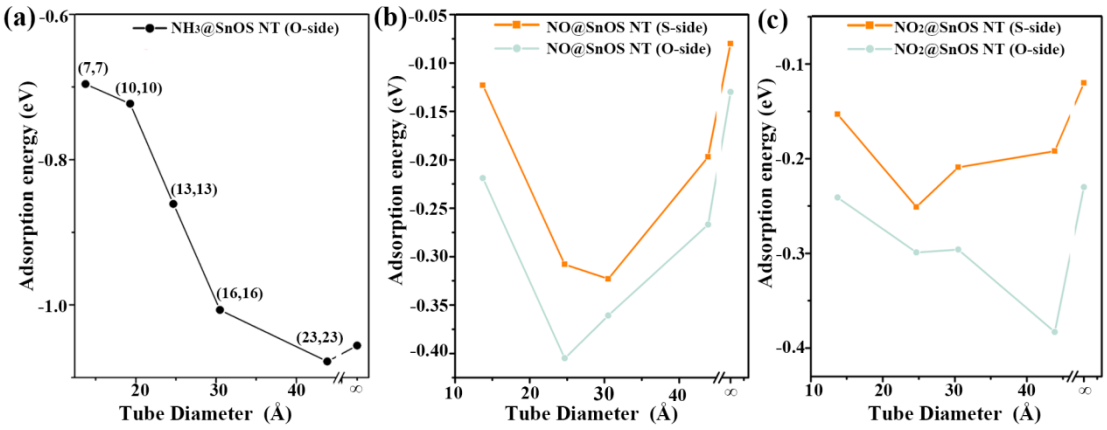


Fig. S6 Diagram of the adsorption energy versus tube diameter.

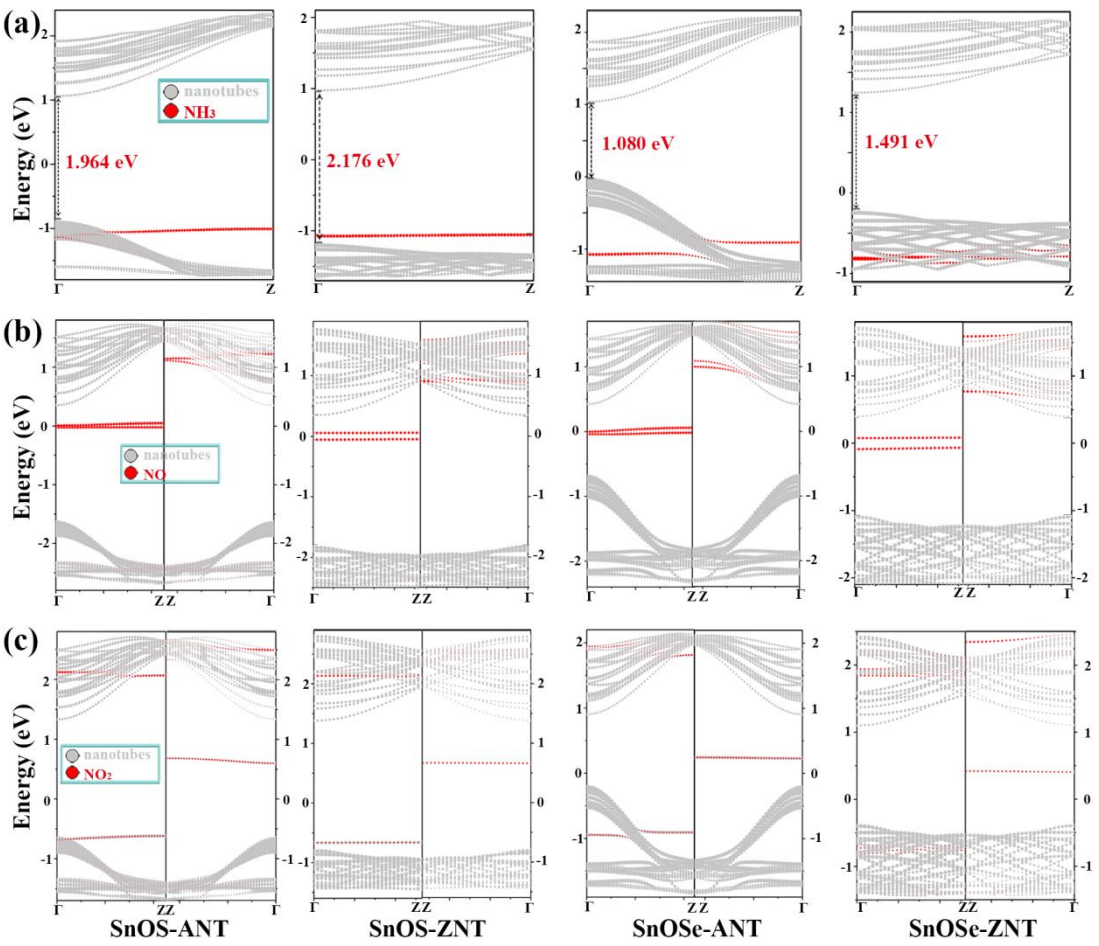


Fig. S7 Atom-projected band structures of the NH_3- (a), NO- (b), and NO_2 (c)-adsorbed on NTs. Gray and red lines represent the energy states contributed by the original nanotube and the gas molecule, respectively.