Electronic Supplementary Material (ESI) for CrystEngComm

Facile synthesis of SnO_2 nanocrystalline tubes by electrospinning and their fast response and high sensitivity to NO_x at room temperature

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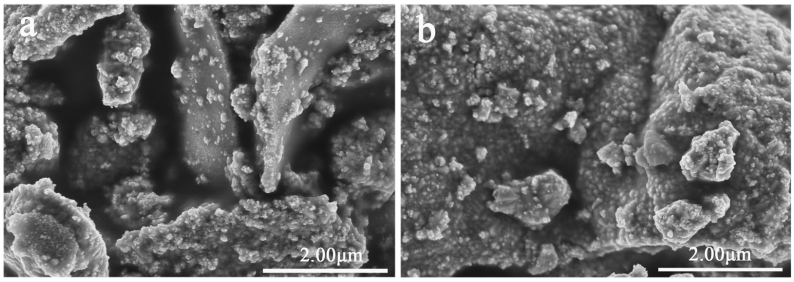

Fig. S1 SEM of (a) sample S2 of SnO_2 powder using PVP without electrospinning and (b) sample S3 of SnO_2 powder without electrospinning and PVP.

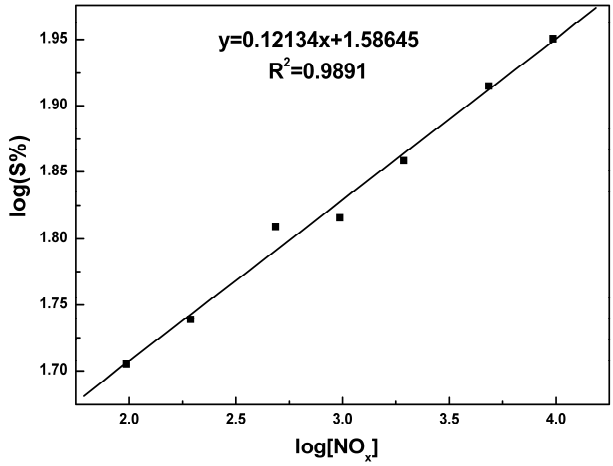

Fig. S2 NO_x calibration curve of the TONTs sensor from 97 ppb to 9.7 ppm.

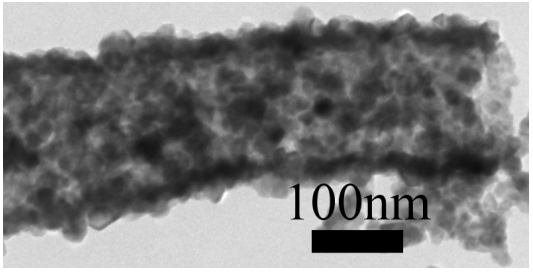

Fig. S3 HRTEM image of TONTs

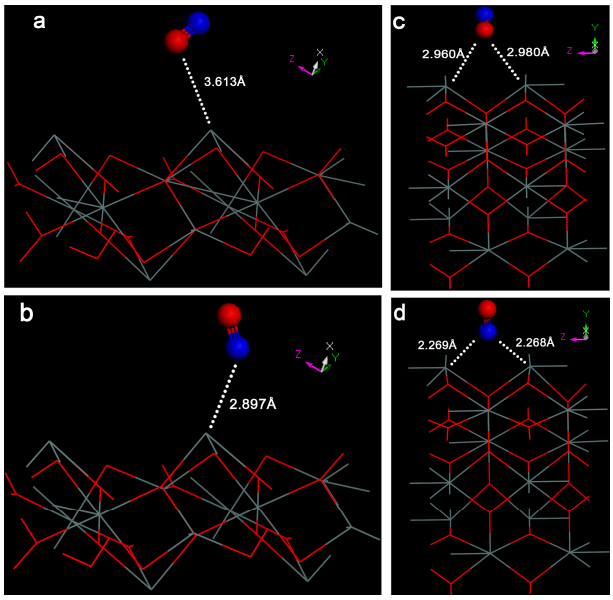

Fig. S4 Optimized structure of NO molecule adsorption on two differents crystal surfaces of the Sn site of stoichiometric SnO_2. (a) the oxygen-orientation of NO molecule adsorption on the (211) crystal surface (b) the nitrogen-orientation of NO molecule adsorption on the (211) crystal surface (c) the oxygen-orientation of NO molecule adsorption on the (110) crystal surface (d) the nitrogen-orientation of NO molecule adsorption on the (110) crystal surface. Red, grey and blue atoms correspond to O, Sn and N,respectively.

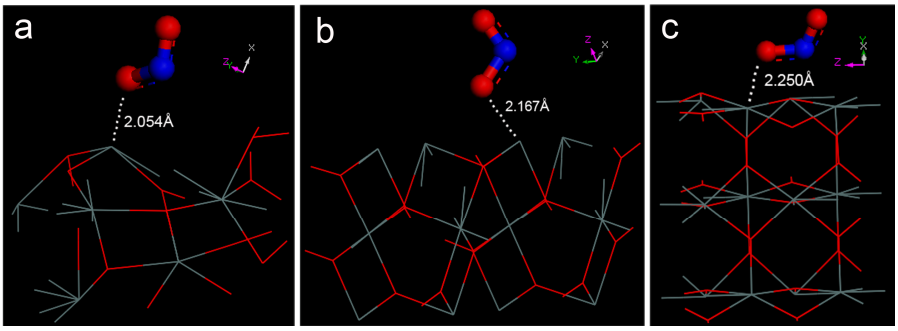

Fig. S5 Optimized structure of NO_2 perpendicular adsorption on three different crystal faces of stoichiometric SnO_2. (a) NO_2 perpendicular adsorption on the (211) crystal surface (b) NO_2 perpendicular adsorption on the (101) crystal surface (c) NO_2 perpendicular adsorption on the (110) crystal surface. Red, grey and blue atoms correspond to O, Sn and N, respectively.

We have investigated the oxygen-orientation of NO_2 adsorption modes of the chelate-type, perpendicular and bridged configuration, and the nitrogen-orientation of NO_2 adsorption mode on SnO_2 different crystal surfaces by theoretical calculation. The results of the E_{ads} and charge transfer of the differenct optimized structures are showed in Table S1. Compare the E_{ads} and charge transfer of NO_2 to these of NO on SnO_2 for the different crystallographic planes. It can be shown that the adsorption energies of NO_2 adsorption modes are all lower than that of NO adsorption and the charge transfer of NO_2 adsorption modes are all larger than that of NO adsorption. In other words, SnO_2 is more likely to adsorb NO_2 molecule than NO molecule. Compared with the different adsorpion optimized structures, NO_2 perpendicular of optimized structure has the lowest adsorption energy. Therefore, it can indicate that NO_2 perpendicular of optimized structure is the stable adsorption structure.

Table S1. Adsorption energies E_{ads} and electron transfer for NO_2 of different optimized structures on several adsorption sites of three different crystal surfaces of SnO_2.

Crystal face	211	211	101	101	101	110	110	110
Adsorption site	O-Sn		O-Sn		N-Sn	O-Sn		N-Sn
Adsorption mode	Chelate-type	perpendicular	Chelate-type	perpendicular	-	Bridge	perpendicular	-
E_{ads} (eV)	-2.525	-2.978	-1.078	-1.531	-0.532	-3.355	-3.413	-3.325
Charge transfer of NO_2 (e)	-0.301	-0.397	-0.365	-0.476	-0.328	-0.441	-0.383	-0.381

Fig. S5 displays the optimized structures of NO_2 perpendicular adsorption on the

(211), (101) and (110) crystal faces. The E_{ads} of NO_2 perpendicular adsorption on (110) crystal surface is the lowest. The E_{ads} of NO_2 perpendicular adsorption on (211) is lower than that on (101). It indicates that the energy barrier of NO_2 molecule desorpting from SnO_2 (110) surface is the highest and (101) crystal surface is the lowest among the three crystal surface. The electron transfer from SnO_2 to NO_2 molecule of (101) plane is the biggest among the three crystal surfaces.

From the above mentioned, the NO_2 perpendicular adsorption on SnO_2 (110) crystal surface is the most stable among the three crystal faces. It can be inferred that more energy is needed for the NO_2 molecule desorption from SnO_2 (110) crystal surface and it is unfavourably for gas sensors. Instead, the biggest electron transfer on (101) crystal surface and the highest adsorption energy of NO_2 perpendicular adsorption are benefit to gas sensors, since the more electron transfer, the higher sensitivity is. If the adsorption energy is lower, it needs more energy that the NO_2 molecules desorb from SnO_2 surface. However, the lower adsorption energy and smaller electron transfer of NO_2 perpendicular adsorption on (211) crystal surface are also unfavourable factors for gas sensors. The results are similar with that of NO adsorption on SnO_2. Therefore, the (101) crystal plane is the most benefit to gas detection owing to the suitable adsorption energy and largest electron transfer among the three crystal surfaces.