Band gap engineering of bulk and nanosheet SnO: Insight into the interlayer Sn-Sn lone pair interactions

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1. The bond diagram for SnO

Fig. S1 shows the calculated projected density of states and crystal orbital overlap populations for single-layer SnO which is absent of inter-layer interaction. Similar with the revised lone pair model proposed by Aron Walsh et al., Sn $5p$ state hybridizes with the anti-bonding states between Sn $5s$ and O $2p$. This stabilizing effect is achieved by distorting the lattice. Taking into account the projected density of states, the top of valence band and the bottom of conduction band mainly come from Sn $5p_z$ - O $2p$ - Sn $5s$ interactions and Sn $(5p_x+5p_y)$ - O $2p$ interactions. Whereas, when inter-layer Sn-Sn interactions are allowed and bonding-antibonding splitting occurs for the each of $5s$, $5p_z$ and $(5p_x + 5p_y)$ states through weak hybridization with the corresponding atomic orbitals of the counterpart Sn atoms on a different layer. Our COOP calculations show that anti-bonding interactions of Sn $5s$ and Sn $5p_z$ are consist of top of the valence band, while bonding interactions of Sn $(5p_x + 5p_y)$ contribute to the bottom of conduction band (Fig. S2(a)). These states associated with Sn-Sn interactions are responsible for the band edges of bulk SnO as schematically illustrated in Fig. S2(b)
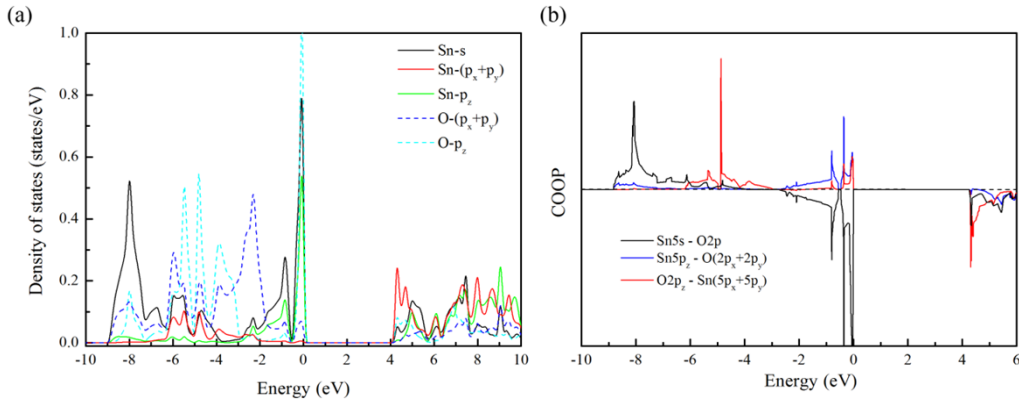

Figure S1. (a) Projected density of states and (b) crystal orbital overlap populations for Sn-O interaction in single-layer SnO.
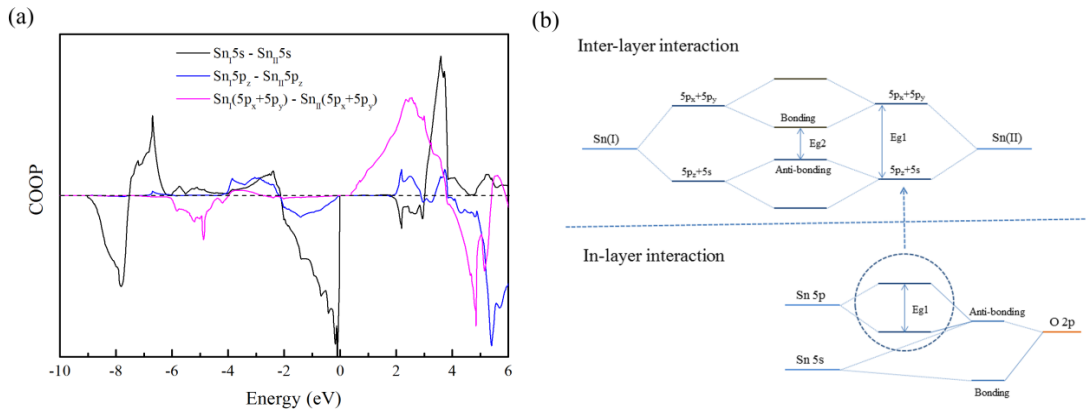

Figure S2. Crystal orbital overlap populations for inter-layer interaction in bulk SnO (Sn$_{(I)}$ and Sn$_{(II)}$ indicate Sn atoms in different layers, respectively).

2. The absorption coefficients for single-layer, double-layer and bulk SnO.

The absorption coefficients for single-layer, double-layer and bulk SnO were calculated with the density functional perturbation theory as implemented in VASP code, in which only the direct transitions are taken into account. And the exciton effect is not included. The calculated results (Fig.S3) show that the steeper rise of the absorption is observed for the SnO with reduced dimensionality that has less dispersive valence band structure. It implies the photo-excitation through direct transitions is promoted in the SnO nanosheets.
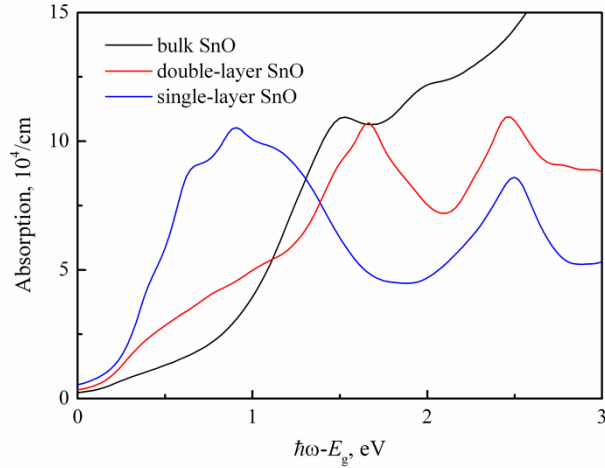

Figure S3. The calculated absorption coefficients for single-layer, double-layer and bulk SnO (the direct band gap E_g was subtracted in the energy).

3. Hole effective mass

In this work, the hole effective mass (m^*) was calculated with the equation below:

$$E(k) = E_0 + \frac{h^2 k^2}{2m^*} \tag{1}$$

where $E(k)$ is the energy of a hole at wave vector k in the VBM which is obtained by fitting the band diagram, and E_0 is a constant giving the edge of energy of band.

4. The phonon calculations

As for phonon calculations, the force constants were obtained from 4×4×1 supercells. The calculated phonon spectrum for bulk and double-layer SnO (un-strained and with 8% tensile strain) are shown in Fig. S4. The results indicate the considered structures are dynamically stable.
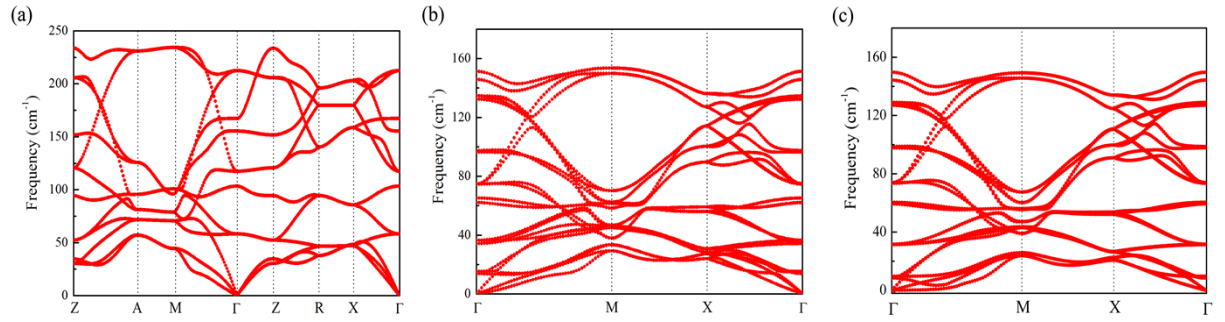
Figure S4. Phonon spectrum for (a) bulk and double-layer ((b) un-strained and (c) with 8% tensile strain) SnO structures.

5. The relationship between stress and uniaxial strain along [001] direction

We examined the stress (σ) required to divide bulk SnO into nanosheets by applying uniaxial strain (ε) along the [001] direction, using the following equation:

$$\sigma = \frac{\partial E}{V(\varepsilon) \times \partial \varepsilon}$$

(1)

where E and V are the total energy and crystal volume after the application of strain, respectively. As shown in Fig. S5, the stress reaches a maximum value of 0.5 GPaforuniaxial tensile strain of 25 % along the [001] direction. This relatively small stress indicates that mechanical exfoliation is a possible way to separateSnO layers.
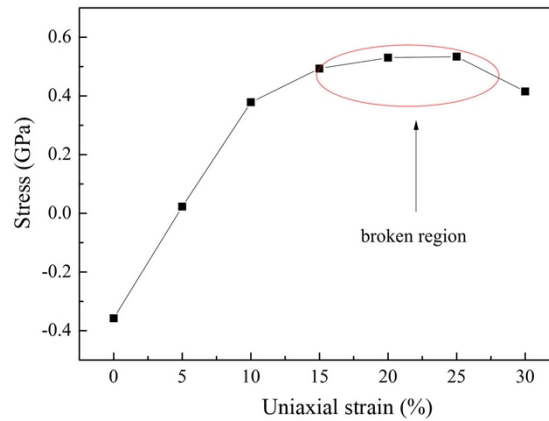

Figure S5. Relationship between stress and strain along the [001] crystal direction.