Hydrogen Sulfide Sensing Mechanism of Tin Oxide by Density Functional Theory

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Detection or monitoring of hydrogen sulfide (H_2S) is of great necessity because of the high flammability and poisonousness of the molecule [1]. Tin oxide (SnO_2), with perfect gas sensing performance and stability, has been successfully utilized in commercial semi-conductive metal oxide gas sensor and extensively studied for different gas detection. Although SnO_2 nanomaterials have shown good sensing performance to H_2S [2], the underlying mechanism is still in some ambiguity that H_2S is oxidized into water and sulfur dioxide by adsorbed or lattice oxygen. Our group has also investigated H_2S sensing properties of SnO_2. Meanwhile, to reveal the surface reaction, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been performed, showing interesting result that it is sulfite and sulfate species that are produced after the reaction.

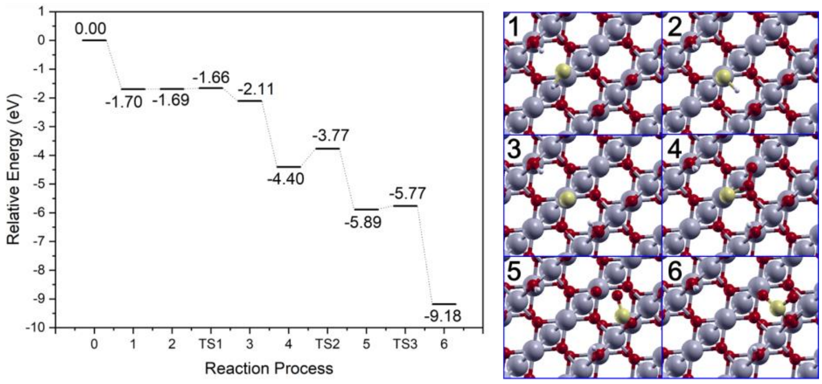

Fig. 1. Reaction processes of H_2S at SnO_2 (110) during response period. The left shows relative energy at each process, and the right shows the atomic structures. The H atom is in white, O in red, S in yellow, and Sn in grey.

Herein, density functional theory (DFT) simulation is performed to verify the discovery of DRIFTS and to have a deeper insight of the surface reaction by calculating the reaction energy, the energy barrier, the surface charge effect as well as the vibrational frequency. Two first-principle softwares, i.e. Dmol3 and Quantum ESSPRESO, have been separately utilized to perform the simulation, and similar results have been obtained. Fig. 1 shows the reaction process of H_2S at SnO_2 (110) during response period. As can be seen, H_2S is dissociatively adsorbed and then oxidized into sulfite specie with continuously releasing enormous energy but without high energy barrier. Charge analysis suggests electron donation of the surface products, explaining why H_2S can reduce the resistance of n-type SnO_2. The produced sulfite can be further oxidized into sulfate by oxygen molecule in air, which then extracts electron from the surface and thus believed to be recovery process. Both sulfite and sulfate species can tightly adhere to the surface. Their vibrational frequency can always be detected by DRIFTS during either response or recovery period. The calculated vibrational frequency shows high consistency with the experimental results.

Reference

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[2] H. Liu, S.P. Gong, Y.X. Hu, J.Q. Liu, D.X. Zhou, Sensors and Actuators B: Chemical, 140 (2009) 190-195.