Gas Sensing Mechanism in Au@SnO_2 Nanoparticle-Based Chemiresistor Studied by *in-situ* Surface-Enhanced Raman Spectroscopy

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Efficient sensing of harmful gases (such as H_2S, H_2, and volatile organic compounds) are significant to public safety, industrial production, and so on.[1] Understanding the gas sensing mechanisms can provide a fundamental guideline for designing higher-performance gas sensors. However, the mechanisms are still under controversy between Langmuir-Hinshelwood and Mars-van Krevelen (MvK) models.

This work constructs an in-situ surface-enhanced Raman spectroscopy (SERS) platform and prepared Au@SnO_2 NPs for tracing the classical ethanol gas sensing. In Au@SnO_2 NPs, the SnO_2 shell is electrically sensitive to ethanol, and the Au core has a strong SERS effect for the in-situ SERS tracing.[2-3] The gas exposure was realized by injecting ethanol gas with given concentrations and volumes into a chamber in which the sensor coated with the Au@SnO_2 NPs was fixed. The electrical sensing signals were collected by the recorder that connects to the sensor. The operating temperature was controlled by the voltage applied to the heater. The in-situ SERS signals excited by 632.8-nm He-Ne laser radiation, are collected through the window at the bottom of the chamber.

The observed Raman bands in in-situ SERS spectra were well assigned to SnO_2 A_{1g} mode associated with bridging oxygen vacancies (OVs), SnO_2 A_{2g} mode related to the in-plane OVs, and some IR-active modes. When the Au@ SnO_2 NPs are exposed to the gaseous ethanol, the A_{1g} band weakens, the A_{2g} band is stable, and some of these bands of IR-active modes strengthen. This indicates that the sensing follows a Mars-Van-Krevelen (MvK) mechanism, in which the bridging lattice oxygen is selectively reacted to from bridging oxygen vacancies (OVs). Investigations also show that this mechanism is universal at different sensing conditions (including operating temperatures from 35 to 150 ^oC, ethanol gas concentrations from 50 to 1000 ppm) and for sensing other gases (such as toluene, acetone, hydrogen sulfide, and trichloromethane). This work presents a universal, efficient and in-situ tracking strategy for gas sensing and discovers that Au@SnO_2 NP-based sensing follows the bridging-lattice-oxygen selective MvK mechanism.

Reference

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