

Harnessing Multi-phase Interactions in Sn/SnO/SnO₂ Tri-phase Material for Gas Sensing

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Summary:

Tin oxide is a redox-active material, yet controlled tuning of its surface oxidation states remains elusive due to non-selective reduction pathways. Here, we report a urea-assisted thermal treatment that enables surface-selective transformation of SnO₂, leading to Sn/SnO/SnO₂ multiphase nanocomposites with controlled phase coexistence. This platform allows direct interrogation of multiphase interfaces, revealing distinct roles of metallic Sn and SnO in signal transduction and surface reaction kinetics in gas sensing.

Keywords: Multiphase interface, tin oxide, surface states, signal transduction, gas sensing

Background and objective

Tin oxide is one of the most widely used materials in chemiresistive gas sensing due to its chemical stability, low cost, and compatibility with scalable synthesis methods^[1]. Despite its extensive use, however, the role of different oxidation states in governing sensing performance remains insufficiently understood.

Conventional reduction strategies, including hydrogen- and carbon-assisted treatments, inherently lack selectivity and often induce bulk reduction rather than surface-confined transformation^[2-3]. This leads to particle coarsening, loss of surface-defined structures, and simultaneous changes in morphology and electronic properties, making it difficult to isolate the intrinsic contribution of surface oxidation states.

Controlled reduction to induce coexistence of metallic, suboxidic, and oxidic phases is therefore highly desirable, as metallic Sn can enhance electronic conduction pathways, while sub-oxide SnO phases affect surface adsorption and reaction kinetics^[4-5]. However, achieving such multiphase configurations in a stable and controllable manner remains challenging.

Here, we address this limitation using a urea-assisted thermal treatment that enables surface-selective transformation of SnO₂. Driven by the decomposition chemistry of urea, this single-step and scalable approach allows gradual tuning of phase composition without triggering extensive bulk reduction or sintering. As a result,

Sn/SnO/SnO₂ multiphase nanocomposites with preserved morphology and well-defined interfacial structures are obtained.

This platform provides direct access to the coexistence of multiple oxidation states within a single material system, enabling systematic investigation of how multiphase interfaces influence gas sensing behavior.

Results

The urea-assisted thermal treatment enabled controlled transformation of SnO₂ into Sn-containing multiphase nanocomposites. X-ray diffraction (XRD) analysis revealed the gradual emergence of metallic Sn with increasing urea content, while the peak width remained largely unchanged, indicating that the primary effect was the increase in Sn fraction rather than particle growth (Fig. 1a). This suggested that the reduction process proceeded without significant degradation of the oxide framework.

Transmission electron microscopy further confirmed that small, well-dispersed particles were formed on the SnO₂ surface, with comparable particle sizes across samples prepared with different urea ratios. Especially, Sn⁰ particles were partially reduced on the surface of SnO₂ (Fig. 1b). These observations indicated that the urea-assisted process enabled compositional tuning while preserving the overall nanostructure.

In addition, controlled post-oxidation led to the formation of SnO, allowing access to Sn/SnO/SnO₂ tri-phase systems.

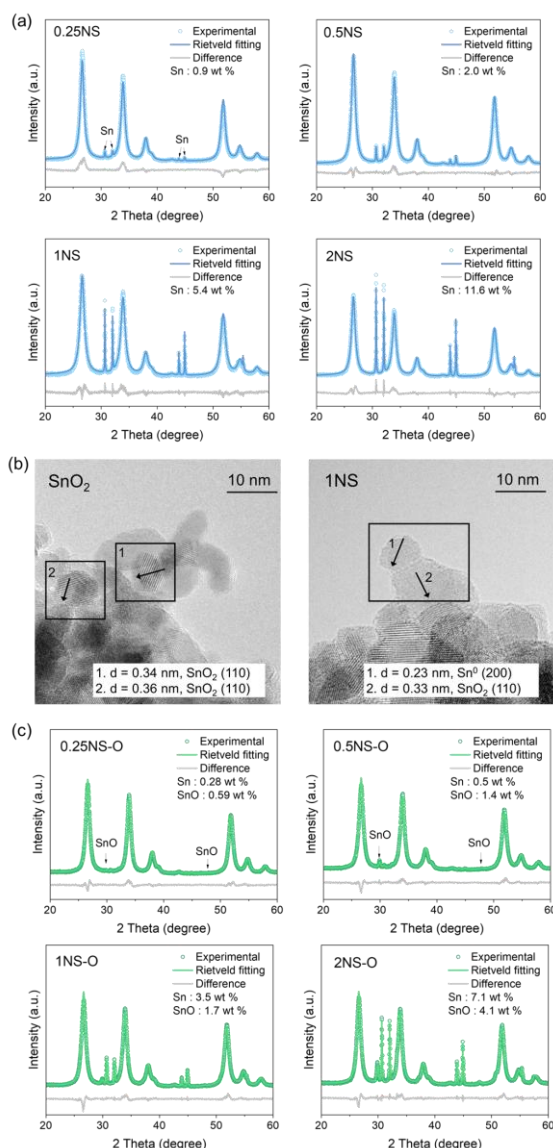


Fig. 1. (a) XRD results of Sn/SnO₂ bi-phase materials, (b) TEM images of SnO₂ and 1NS. (c) XRD results of Sn/SnO/SnO₂ tri-phase materials.

To identify the chemical origin of the reduction process, various species derived from urea decomposition, including H₂, CO, and nitrogen-containing intermediates, were systematically examined. Among them, NH₃ was found to be the key factor enabling partial reduction of SnO₂ while preserving the overall oxide structure, in contrast to other species that led to either insufficient or excessive reduction.

In the resulting multiphase system, metallic Sn acted as an efficient electronic pathway that facilitated charge transport through the sensing layer, thereby lowering the baseline resistance and promoting a stronger transduction response. By contrast, SnO likely played a different role at the surface. Rather than primarily enhancing electronic conduction, it appeared to moderate excessive analyte adsorption and facilitate the

oxygen-mediated surface reaction kinetics, which could help suppress irreversible surface accumulation of adsorbates and improve signal recovery. The coexistence of Sn, SnO, and SnO₂ therefore suggested a complementary division of functions within a single material platform, where metallic Sn favored electronic transport, while SnO helped maintain a more balanced and reversible surface state.

References

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