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Review

A review of recent developments in tin dioxide composites for gas sensing application

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ABSTRACT

SnO_2 has been extensively investigated and used to detect a variety of gases for practical application. SnO_2 nanomaterials with different morphologies and spatial assemblies have been fabricated in the last few years in order to improve the gas sensing performances. Meanwhile, many reports on the fabrication and gas sensing research using SnO_2-based composites have been also published recently. In this work, we reviewed the recent developments of conductivity type of gas sensors for various SnO_2-based composites, including SnO_2/inorganic metal oxide, SnO_2/carbon nanomaterials, SnO_2/noble metals, SnO_2/polymer, and SnO_2/other materials in the last five years. Most of reports demonstrated that using a composite the properties of the gas sensing material could be greatly improved, such as high sensitivity, low working temperature, quick response, excellent stability or low detection limit. Each component had its unique effect to influence the sensing properties of the composite. The possible development directions were also discussed.

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Introduction

Gas sensing technology is receiving much attention in the practical applications including industrial and academic fields. It chiefly involves discriminating and monitoring the concentration of gases in the industrial processes as well as in everyday life [1]. Its potential application areas can be industrial production, automotive industry, medical application, indoor air quality supervision and environmental monitoring, *etc.* [2,3]. Thus, various materials such as inorganic semiconductors, conjugated polymers and carbon nanomaterials have been explored to fabricate gas sensors that can be used to detect combustible, flammable and toxic gases, and/or oxygen depletion [4,5]. Among them, inorganic semiconducting metal oxides are currently being intensively investigated because of their low cost, flexibility in production, easy usage and various gases validation. Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases by the conductive measurements [6]. A lot of papers about metal oxide gas sensors have been published in recent years.

Due to the high demand for reliable and robust gas sensing devices, academic research continues to play an important role in this field. Meanwhile, with the rapid development of nanoscience, the superior control over the shape and the size of the nanocrystals enable sensors with an enhancement in sensitivity and selectivity [7]. Small size, lightweight and high surface-to-volume ratios of these nanostructures are the best choice for improving the capability to detect gas species. Tin dioxide (SnO_2) is one of the most commonly used gas sensing materials and it is n-type semiconductive material whose electrical conductivity is dependent on the density of pre-adsorbed oxygen ions on the surface. Its excellent electrical and optical properties and well chemical stability make SnO_2 as a suitable material for gas sensors. The basic detection principle of its sensor is still the change of the resistance of the sensing layer with gas adsorption, where target gases have red-ox reactions with the surface of SnO_2. The resistance of SnO_2 changes with the variation of target gas concentration [2]. Thus, nanostructured SnO_2 materials can offer great potential for environmental applications including gas sensing [8–10].

By now, many kinds of SnO_2-based materials with good sensing characteristics have been obtained, including nanofibers [11–14], nanowires [15–19], nanotubes [20,21], hollow spheres [22,23], hierarchical structures [9,24–27], nanoslab [28,29], *etc.* However, in addition to precisely controlling the size and morphologies of SnO_2 materials [30], there are also other efficient strategies to improve their sensing properties such as elemental doping, composites assembly, noble metal function. There have been many published review papers related on SnO_2 and its gas sensors [9,10,31–40], but few of them paid special attention to its composite. This is the main motivation of this review paper.

As a simple review of SnO_2-based gas sensor materials, the main attention in this work will be focused on various composites containing SnO_2 which have been published in the recent five years. The discussion and contents involve the composites of inorganic oxides/SnO_2, carbon materials/SnO_2, polymer/SnO_2, noble metals/SnO_2 and their potential uses as gas sensing materials. By focusing on SnO_2 composites (excluding doped SnO_2), we hope to provide readers better understanding on the recent development in gas sensing, uncovering their possible research in future.

Gas sensing mechanism of SnO_2

Materials that can change their properties depending on the ambient gas can be used as gas sensing materials. The most common used sensing materials are semiconductive metal oxides, which can provide sensors with several advantages such as low cost and high sensitivity. The sensing material is very important for sensors and is usually deposited as a polycrystalline film or layer on a substrate with integrated electrodes and heating to make a gas sensor. Some typical important properties for a gas sensor are its sensitivity, operating temperature, selectivity and long-term stability.

Though many metal oxides are suitable for detecting gases, the most widely used semiconductor gas sensing material is SnO_2 with n-type conductivity, high adsorption capacity, highly chemical and thermal stability in air. Its band gap is 3.6 eV (300 K). The mechanisms responsible for SnO_2 gas sensing are not completely understood and subject to ongoing discussion. An empirical model to explain the fundamental gas sensing mechanism is as follows. According to this model, chemisorption of oxygen from the gas phase creates extrinsic surface acceptor states that immobilize conduction band electrons from the near surface region of the n-type semiconductor. Thus a depletion layer is created at the interfaces of the sensor material (*e.g.*, SnO_2) as a result of adsorbed oxygen from air under ambient conditions. The presence of other gases with either reducing or oxidizing properties will consequently affect the density of charge carriers in the near-surface region of each SnO_2 grain [40]. Reducing gases will abstract surface-bound oxygen atoms, a process that release immobilized some of the charge carriers (conduction electron). In contrast, oxidizing gases will immobilize further conduction-band electrons from the near-surface region by creating additional surface-acceptor states. As a result, the foreign gases cause a decrease (reducing gases) or increase (oxidizing gases) of the depletion layer thickness by tuning the surface-state density of SnO_2. Then, the charge transfer between the surface adsorbed gaseous species and SnO_2 surface atoms leads to change in carrier concentration of SnO_2 and widening or narrowing of the depletion layer [41]. Reducing gases in general increase the conductivity of SnO_2 material, while the opposite is observed for oxidizing gases. A simple schematic image for this process is depicted in Fig. 1. Some more comprehensive discussion of the underlying principles can be found elsewhere [2,40,41].

To greatly improve the sensitivity of SnO_2 materials, it is important to develop active materials with large surface areas and huge porosity, ensuring the easy reaction between SnO_2 and analyte gases. Thus, it is generally accepted that a hierarchical SnO_2 nanostructure with open porous features has a better performance than the dense nanoparticles aggregates. So, three-dimensional (3D) SnO_2 nanomaterials have received much attention recently. In addition to this, SnO_2 composites also can have a large surface area and provide effective diffusion of target gases, as well as additional possibilities for further modification such as guest metal loadings.

SnO_2 composite gas sensing materials

SnO_2/inorganic metal oxides

Heterostructured SnO_2 with other semiconducting metal oxides will provide another promising strategy to develop novel high-performance gas sensors. As mentioned above, gas sensors of individual SnO_2 materials are attractive due to their high sensitivity, quick response, and good stability but still have the main drawbacks of large band gap (3.6 eV, which can only respond to UV illumination) and high electron–hole recombination rate [10]. However, these can be effectively modulated or overcome by compositing SnO_2 with other metal oxides such as n-type TiO_2, ZnO, WO_3, In_2O_3, CaO, MgO, V_2O_5, Nb_2O_5, *etc.*, and p-type NiO, Co_3O_4, Sb_2O_3, La_2O_3, Cu_2O, Ag_2O, CeO_2, *etc.* (see Table 1 for more details).

The heterojunctions formed between SnO_2 and these metal oxides exhibit interesting electronic properties by coupling the

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