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Efficient hierarchical mixed Pd/SnO_2 porous architecture deposited microheater for low power ethanol gas sensor

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ABSTRACT

A novel gas microsensor combining SnO_2 submicron/nanostructured porous sensitive film with Micro-Electro-Mechanical systems (MEMS) microheater was successfully fabricated. The film was made of hierarchically mixed Pd/SnO_2 (HM-PTO) composites composed of Pd/SnO_2 hollow submicrospheres (Pd/SnO_2-HSs) and Pd/SnO_2 nanoparticles (Pd/SnO_2-NPs) deposited on the microheater platform using the microdispensing method. The as-prepared HM-PTO sensors exhibited high sensitivities, fast response/recovery rates, good selectivity, reliable reversibility, and relevant stability towards ethanol at low power consumption. The resulting superior sensing performances were attributed to the unique hierarchical structure. The internal void architecture of Pd/SnO_2-HSs provided large specific surface areas, proper mesopore size distribution, large number of active adsorption/interaction sites, as well as promoted the chemisorption and dissociation of gas molecules due Pd-doping to yield superior gas response. In particular, the nano-sized SnO_2 particles ensured the uniform deposition of the materials to yield enhanced local conductivities, and possibly faster phase transfer reactions responsible for the extremely good response/recovery performance. This simple fabrication procedure combined with high sensing performances look promising for the development of hierarchical morphologies of novel materials for gas sensing applications.

1. Introduction

Micro-Electro-Mechanical Systems (MEMS) have gained great interests in the field of gas sensors and actuators used in microheaters suspended in a cavity of silicon for thermal insulation, where sensing materials are deposited [1–3]. Unlike traditional ceramic platforms consuming more power, MEMS-based microheaters convert electric energy into stable heat energy at small scale with low-powered consumption [4]. This greatly facilitates their integration and deployment with other devices for low-cost mass production and small size mobile applications [5,6]. However, the technology still requires advanced coating techniques to efficiently deposit sensing layers on the microheater due to the significant reduction in sensor size. Traditional deposition methods like screen printing coating techniques require the direct contact between the printing surfaces, which may damage the fragile device structure during application in MEMS [7,8]. Microdispensing technologies are essentially the same as inkjet printings but the fluid is not heated, preventing damage of certain samples [9]. Because of the flexible and accurate microscale patterning, jetting solutions or turbid suspensions with small particle size onto addressable sites of specific substrates is considered as an alternative lift-off process to achieve direct patterning without using any masks at small scale [10,11]. This is generally a more controllable process, with material saving and compatible with most MEMS integrated devices.

Sensing materials play a key role in microsensing performance. In addition to the development of MEMS-based microheater platforms for gas sensors, tremendous efforts have been devoted to the construction of diversified sensing materials with special morphologies and structures to improve gas sensing performances [12,13]. With respect to this, metal oxides like SnO_2 [14,15], ZnO [16,17], TiO_2 [18], Cu_2O [19], In_2O_3 [20–22] and WO_3 [23,24] have been extensively investigated as intriguing candidates in gas detection devices. SnO_2, with functional wide band gap (ca. 3.6 eV, T = 300 K) n-type semiconductor, attracted appreciable interests owing to its appealing features, such as low cost, environmental friendliness, tunable morphology and crystallinity, chemical stability, and excellent gas sensitivity [25,26]. Due to the unique

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architectural interior void space, hollow SnO_2-based sensing materials have extensively been prepared with various morphologies, including cubes [27], spheres [28,29], fibers [30], tubes [31], etc. In addition to morphology, the composition and structure of sensing materials greatly influence the sensing performances [32]. Thereby, single SnO_2 structures are commonly fabricated and functionalized with noble metals like Au, Pt, Pd, Rh [23–38] or decorated with other metal oxides like CuO [39], NiO [40], Co_3O_4 [41] and Fe_2O_3 [42,43]. Very recently, hierarchical structure materials were discovered as promising candidates for gas sensing because of their advanced geometrical structures and atom arrangement. These features result in relatively lower density, high surface area, and well-aligned porosity structures, which can offer novel properties [26,32,44,45]. Nevertheless, to the best of our knowledge, the synthesis of exquisite SnO_2-based hierarchical mixed architecture materials with particular morphologies and dimensions for gas sensing remains scarcely explored.

Herein, we present a new micromachined gas sensor based on a microheater platform deposited with Pd-doping SnO_2-based hierarchical mixed (HM-PTO) composites composed of Pd/SnO_2 hollow submicrospheres (Pd/SnO_2-HSs) and Pd/SnO_2 nanoparticles (Pd/SnO_2-NPs) using the microdispensing method. The resulting HM-PTO composites demonstrated special hierarchical architecture with highly diversified composition. The interior void and the uniform porous surface of Pd/SnO_2-HSs provided high surface areas and promoted the catalytic active chemical sites. Furthermore, the embedded SnO_2 NPs conducting networks across the surface offered high electrical conductivities. Specifically, the introduced non-spherical SnO_2 NPs resisted the capillary flow and suppressed the coffee ring effect from SnO_2 HSs to guarantee well-defined sensitive films. The developed HM-PTO-based sensor was successfully used for ethanol detection and exhibited improved sensing performance when compared to single SnO_2 with hollow spherical and particle morphologies. The combined diversity of hierarchical control composites with low-power microheater platform might put forward a proposal to construct high-performance microsensors, suggesting the favorable potential for mass production of such sensing devices in batches industry.

2. Experimental

2.1. Materials synthesis

All chemical reagents used in this work were analytical grade without further purification. The porous Pd/SnO_2-HSs was synthesized using a simple hydrothermal method following doping process. In a typical synthesis, $K_2SnO_3{\cdot}3H_2O$ (0.18 g) was dissolved in 30 mL ethanol-H_2O mixed solvent (40% ethanol by volume). After gentle stirring for 5 min, urea (0.18 g) was added to the solution under vigorous stirring. The resulting solution was then transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated in an electric oven holding for 24 h at 150 °C. After termination of the hydrothermal treatment, the autoclave was naturally cooled down to room temperature. The resulting white precipitate was separated by centrifugation, washed three times with deionized water and ethanol, and dried overnight at 60 °C. It was then dispersed in 50 mL deionized water for future use. An appropriate volume of a $Pd(NO_3)_2$ solution was added into the above dispersion followed by addition of ammonia dropwise to adjust the pH level to approximately 9–10 under vigorously stirring at room temperature for 5 h. The new precipitate was collected by centrifugation, washed three times with deionized water and ethanol then dried at 60 °C for 12 h. A series of 0.25, 0.35, 0.5 and 2 wt% Pd/SnO_2-HSs architectures were prepared using the as-mentioned hydrothermal and our previously published Pd-doping process [37]. The weight percentage was defined as the theoretical weight ratio of PdO to that of SnO_2 hollow spheres subjected to complete transformation. SnO_2 NPs purchased from Aladdin were used to evaluate the properties of the nano-sized particles. The synthesis of Pd/SnO_2-NPs followed the same procedure used for the Pd/SnO_2-HSs above. The hierarchical mixed Pd/SnO_2 (HM-PTO) composites were obtained by mixing 75:25 wt% submicron scale Pd/SnO_2-HSs with nanoscale Pd/SnO_2-NPs in a Thinky mixer for approximately 20 min.

2.2. Materials characterizations

The morphology of the sensing films was observed by an optical 3D microscope (Leica DCM 3D). The morphology of the products was investigated by scanning electron microscope (SEM, JEOL, JSM-5510LV), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM, JEOL, JEM-2010). The energy-dispersive X-ray spectroscopy (EDX) analysis was performed by the SEM attachment. Nitrogen adsorption/desorption isotherms at 77 K were carried out by the Micromeritics ASAP 2020 M volumetric adsorption analyzer. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 X-ray diffraction meter with Cu-Kα irradiation (λ = 0.15406 nm) at 40 kV and 20 mA over the 2θ range from 20 to 80°. Atomic force microscopy (AFM) images were acquired using a NanoScope III Multimode scanning probe microscope (Veeco, Santa Barbara, CA, USA).

2.3. Sensor fabrication

The sensing materials were deposited on the microheater platform using a non-contact microdispensing system SHOTMASTER 300 DS-s (Musashi Engineering Inc., Japan). To enable uniform deposition films, the as-synthesized samples were sonicated in mixed suspensions containing (10:30:55 wt%) of (deionized water: ethanol: isopropanol solution) prior to addition of the powder material. After sonication for 20 min, 5 wt% powder was added under constant sonication for another 20 min. The obtained suspension was then jetted onto the microheater chip (Wuhan Juzheng-EST Co., Ltd., China) with defined dot shape and loading, and the resulting chip was dried at 100 °C for 4 h followed by annealing at 400 °C for 2 h under air to ensure all solvents were evaporated.

Fig. 1 depicts the morphology of the microheater chip and the as-fabricated sensing film. The chip was diced into packages of 5 × 5 mm ceramic substrates (Fig. 1a). Each microheater chip (1.8 × 1.8 mm) consisted of resistive platinum heater and platinum interdigital electrodes, using for both samples temperature control and resistance measurements. Fig. 1b illustrates a magnified optical image of the chip, exhibiting that the working area marked by a white square was made of 16 platinum fingers electrodes and curved meander shape microheater electrodes with 10 μm and 30 μm gap spacing, respectively. Fig. 1c shows HM-PTO droplets deposited at the center of the microheater chip though dispenser to form a sensing film with highly homogenous morphology after solvent evaporation. The film diameter was estimated to about 500 μm. Detailed analyses revealed that the film contained submicron spheres of SnO_2-based HSs with a drop of coffee ring effect (Figs. S1–S2). By adding nano-sized SnO_2 NPs (Figs. S3–S4), suspensions of hierarchically mixed SnO_2 like HM-PTO could interestingly produce uniform deposits (Fig. 1c) [44,47]. The 3D image in Fig. 1d of HM-PTO sensing film between adjoining fingers estimated the thickness of the film to about 2–6 μm (height analyses in Fig. 1e).

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