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PAPER

One-pot synthesis of uniform mesoporous rhodium oxide/alumina hybrid as high sensitivity and low power consumption methane catalytic combustion micro-sensor†

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Uniform mesoporous rhodium oxide/alumina hybrid have been prepared following a facile one-pot self-assembly approach using P123 as template. Such hybrid nanomaterials display a high dispersion of both the noble metal oxide and the alumina within mesoporous structure in a broad Rh/Al mole ratio up to 8 : 1, which makes them attractive materials for catalytic applications. After coating on MEMS micro-heater, a catalytic combustion type methane gas micro-sensor was fabricated and investigated for its sensing performance. The mesostructure-based sensor demonstrated a short T_{90} response time, relatively high signal output, high enough signal/noise ratio and extraordinarily low power consumption.

Introduction

Over the last decade, the development of sensitive and reliable sensors for combustible gases and organic vapours below the lower explosion limit (LEL) has gained considerable attention for social safety, energy saving and environmental applications.[1–11] There are many gas detection methods (such as thermal conductivity, optical interferometry, IR absorption, ultrasonic measurement, catalytic combustion and so on.), however, the most common and widely used in industry is the catalytic combustion technique due to its portability, high accuracy and reliability, which is based on the exothermic reaction between the detected gases and oxygen. In catalytic combustion gas sensors, there are two elements strung onto the opposite arms of a balanced Wheatstone-bridge circuit. One is called "active" element coated with catalyst that allows combustion to occur on the surface. The other, "reference" element, lacks the catalyst outer coating but in other respects exactly resembles the active element. If combustible vapours are present, they will be catalytically combusted on the surface of the active element, heating it to a higher temperature. The difference between the temperatures of the two elements produces a change in the electrical resistance in the circuit that is proportional to the amount of combustible gas present. Thus, for the same catalytic system, the performances of catalytic combustion gas sensors are directly dependent on catalytic performance of the catalysts, which is closely related to its specific surface area and morphology.[12]

With the rapid development of micro-electro-mechanical systems (MEMS), many micro-machining ways were well developed and used, which made the micromation, low power consumption and intelligence of sensors possible.[13,14] During the development of MEMS methane catalytic combustion sensor, it was found that the signal was very low accompanied by high noise when a traditional matrix and catalyst were used. This can be attributed to the very limited heating area of the catalytic element (the heating area of a micro-heater is only about 0.01 mm^2), which is only about one percent of that of traditional catalytic combustion sensor. The straightforward and effective way to improve the sensitivity of the MEMS sensor is to enlarge the valid contact area between catalyst and target gases.

Mesoporous material has high surface area and well defined pore structure which has been proven to be excellent in fabricating highly active catalysts or catalyst supports, and also shows very high gas responsivity and rapid gas responding kinetics in various gas sensor devices.[1,2,13–17] If such mesostructure can be intruduced into MEMS catalytic combustion sensor, the loaded catalyst amount and contacted area between methane and the catalyst will be greatly enhanced compared with that using traditional catalyst structure, and much higher sensitivity can be obtained. However, as a main kind of catalyst for methane catalytic combustion sensor, noble metals or noble metal oxides are difficult to form mesoporous structure directly. When loaded on other mesoporous matrix, the inculsions of either preformed metal nanoparticles, or *in situ* grown ones from metal precusors

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in the presence of reducing agents, are usually accomplished in multi-steps, which is not only time-consuming, but sometimes also not applicable for the preparation of the composite mesoporous films on the small area of a MEMS micro-heater. Moreover, the loaded metal or metal oxide nanoparticles will inevitably block the mesopore channels, especially at high loading content, leading to greatly reduced specific area of the film. Therefore, the fabrication of such a mesoporous film with high content of catalyst and controlled porosity by a simple and flexible method, is still a challenge.

Rhodium catalyst is one of the main noble metal catalytic systems for methane catalytic combustion reaction, in addition to the palladium/platinum system.[12] In this report, we present that rhodium can directly fabricated into uniform mesoporous structure with poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) template only after adding some aluminium as additives. Such a novel co-assembly route endows the composite Rh_2O_3/Al_2O_3 catalyst with high noble metal content, high specific surface area and thermal stability, which is necessary for its application in methane gas sensors of extra-high sensitivity and fast sensor response.

Experimenal

Synthesis of mesoporous alumina

In a typical synthesis, 1.0 g of poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (P123) and 0.01 M $AlCl_3$ were successively added to 10 ml anhydrous ethanol. The resultant mixture was vigorously stirred at room temperature for 60 min. The final mesoporous alumina colloidal was transferred to an oven and underwent heat treatment at 60 °C for 48 h in static air for complete solvent evaporation. The resulting xerogel was calcined at 550 °C for 1 h to remove the template.

Synthesis of mesoporous rhodium oxide/alumina hybrid

A series of mesoporous rhodium oxide/alumina hybrid were synthesized in a co-self-assembly route of rhodium and alumina precursors. $RhCl_3 \cdot xH_2O$ was first dissolved in water, and then solution was added into above mesoporous alumina colloidal. The mixture was sonicated by ultrasonic for 30 min. The final mesoporous rhodium oxide/alumina hybrid colloidal was transferred to an oven and heated at 60 °C for 48 h to evaporate the solvent, and finally the product was calcined at 550 °C for 1 h to remove the template.

Characterization of the materials

X-ray diffraction (XRD) data were collected using a Bruk D8 Focus powder diffractometer with graphite mono chromatized Cu-Kα radiation ($\lambda = 0.15405$ nm). N_2 adsorption and desorption isotherms were measured at 77 K on a micromeritics ASAP 2020 system. The specific surface area and the pore size distribution were calculated using the BET and Barrett-Joyner-Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) observations were performed on a field emission JEM-3000F (JEOL) electron microscope operated at 300 kV equipped with a Gatan-666 electron energy loss spectrometer and energy dispersive X-ray spectrometer.

MEMS sensor preparation and measurement

A MEMS combustion-type sensor, employing mesoporous rhodium oxide/alumina hybrid as a sensor materials and mesoporous alumina as a compensating materials was fabricated by spin-coating method. For active element (catalytic element), mesoporous rhodium oxide/alumina hybrid colloidal were dropped onto the MEMS micro-heater with integrated platinum electrodes. After spin-coating, the micro-heater was slowly and electrically heated up to 550 °C and then maintained at this temperature for 1 min to remove the template. This procedure was repeated twice to ensure a fully coverage of the film. As to reference element, the produce was similar to that of the above active element using mesoporous alumina colloidal as film precursor.

A computer-controlled gas test bench was used to characterize the sensor materials. It consisted of a gas delivery system, Teflon sensor chambers, and a Wheatstone-bridge measurement for voltage determinations. Operating mode and data acquisition and processing were controlled through Labview software (National Instrument).

Results and discussion

Fig. 1 depicts the TEM images of the hybrids Rh_2O_3/Al_2O_3 with different Rh/Al mole ratios. The uniform sponge-like structure is somewhat similar to that of mesoporous alumina.† Different from other noble metal (oxide)/alumina hybrid, there is not any large noble metal (oxide) nano-particle visible either within or out of the mesoprous structure. The mesostructues are uniform and the pore network distribute homogeneously throughout the particles, as can be found in the TEM images, in the Rh/Al ratio form 1 : 1 to 8 : 1. The corresponding selected-area electron diffraction (SAED) patterns of the samples show a faint ring pattern, lattice constant measured agree with (110) plane in the standard data (JCPDS, 36-1451), revealing the existence of

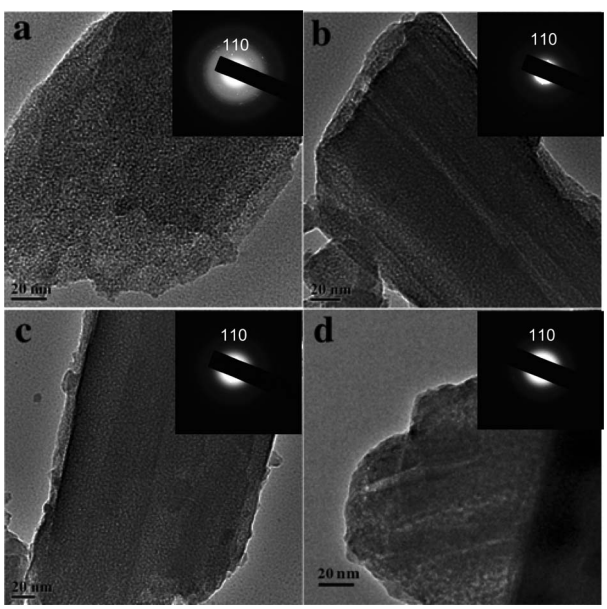

Fig. 1 TEM images of the hybrids with different Rh/Al mole ratios: (a) Rh/Al = 1/1, (b) Rh:Al = 2/1, (c) Rh/Al = 4 : 1, (d) Rh/Al = 8 : 1.

multi-crystalline Rh_2O_3. The size, distribution and morphologies of the rhodium oxide crystalline were further analyzed by HRTEM analysis.† A homogeneous distribution of small Rh_2O_3 crystalline, with different density but similar size (about 2 nm), can be determined. It seems the content of crystalline varies directly with the mole ratio of Rh/Al. The effect of the alumina content on N_2 adsorption isotherms and the corresponding pore size distributions of the hybrid materials are shown in Fig. 2. In all cases, the isotherms are type IV suggesting mesoporous structure and the appearance of H4 hysteresis loops indicate the formation of very narrow slit-like mesopores. The specific areas of the hybrids are to be expected to be substantially lower than that of the pure mesoporous alumina at increased rhodium content.† Meanwhile, the average pore sizes are all at about 4 nm. It seems that the Rh/Al mole ratio hardly affects the pore size of the final materials.

The XRD patterns of the hybrid materials are shown in Fig. 3. There is not any diffraction peaks in the small angle range indicating the disordered pore arrangement. A very broadened peaks at 2θ value of 35° can be found in the wide angle area, which can be attributed to the characteristic diffractions of the (110) plane of Rh_2O_3 crystal, suggesting the nano-crystallized state of rhodium oxide. From the full width at half-maximum of the (110) diffraction peak, the calculated crystallite size of rhodium oxide are only about 2 nm. All these corresponding well with that of SAED and HRTEM analysis. Fig. 4 shows the typical X-ray photo-electron spectrum of Rh_2O_3/Al_2O_3 hybrid in the Rh $3d_{5/2}$, Rh $3d_{3/2}$ binding energy region with a spin separation of 5 eV. The Rh $3d_{3/2}$ peak is centred at 314 eV and the Rh $3d_{5/2}$ peak at 309 eV, these match well with Rh^{3+} $3d_{3/2}$ and Rh^{3+} $3d_{5/2}$ and no obvious peak of Rh^0 was observed. This confirms that all the rhodium elements in the hybrid exist in the form of sesquioxide. This result consists well with the above XRD analysis.

The catalytic efficiency and gas sensor properties of the hybrid Rh_2O_3/Al_2O_3 materials were evaluated after coated as catalyst on

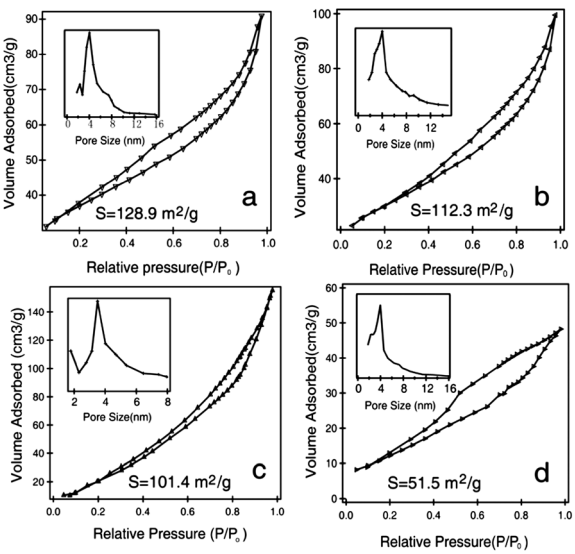

Fig. 2 N_2 adsorption-desorption isotherms and corresponding pore size distributions of mesoporous Rh_2O_3/Al_2O_3 hybrids of varied Rh/Al mole ratios: (a) Rh/Al = 1/1, (b) Rh:Al = 2/1, (c) Rh/Al = 4 : 1, (d) Rh/Al = 8 : 1.

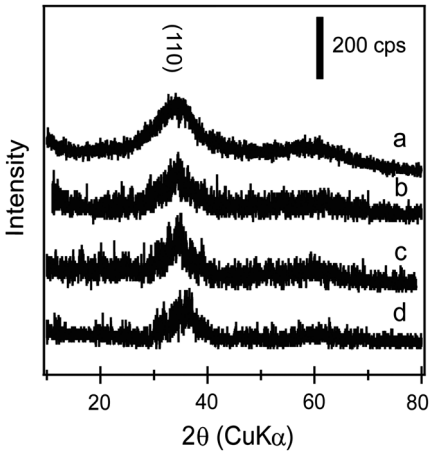

Fig. 3 Wide angle XRD pattern of mesoporous Rh_2O_3/Al_2O_3 hybrid. a: Rh/Al = 1/1, b: Rh:Al = 2/1, c: Rh/Al = 4 : 1, d: Rh/Al = 8 : 1.

micro-heater and then assembled as MEMS methane catalytic combustion sensors (Fig. 5), employing mesoporous alumina as compensating material. Fig. 6 shows the response signals of MEMS sensors with different Rh/Al mole ratio for 2 vol% (50% LEL) methane concentration at working temperature of 400 °C. It clearly shows that the output single increases with the increase of Rh content up to Rh/Al mole ratio of 4/1 due to the higher content of catalyst. However, when Rh/Al mole ratio reach to 8/1, slight decreased in response signal was observed. this can be ascribed to the highly decreased of the hybrid pore volume. In general, for methane catalytic combustion sensor, the larger content of catalyst, the stronger output signals. But for mesoporous Rh_2O_3/Al_2O_3 hybrid, when mole ratio of Rh/Al increased from 4/1 to 8/1, although the Rh content doubled, the pore volume decreased from 0.16 $cm^3\ g^{-1}$ to 0.06$cm^3\ g^{-1}$ at the same time, it's only about one third of that of Rh/Al = 4/1. In a word, the effective contact area between catalyst and methane decreased at that time resulting the decreased output signal. Thanks to the porous catalyst structure and high content of rhodium oxide, the MEMS sensor with hybrid Rh/Al = 4/1 has the highest response signal of 6.0 mV. Only about 1% heating

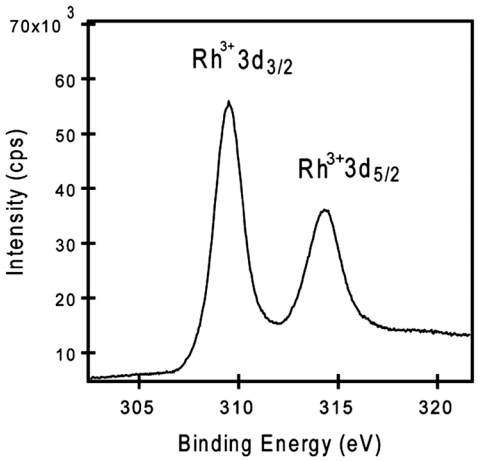

Fig. 4 Typical XPS spectrum of Rh_2O_3/Al_2O_3 hybrid.

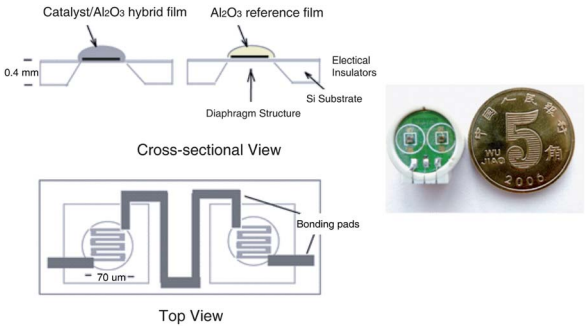

Fig. 5 Schematic diagrams and the photograph of the MEMS methane catalytic combustion sensor.

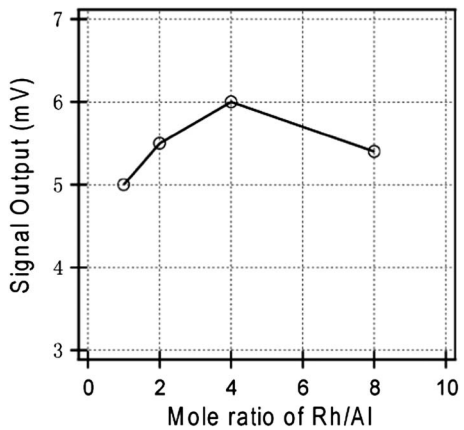

Fig. 6 Responses of the MEMS sensor based on Rh_2O_3/Al_2O_3 hybrids with different mole ratio. (50%LEL methane, 25 °C, 25% RH).

area was needed to reach 25% signal output as compared with the traditional methane catalytic combustion sensor. In the mean time, the power consumption is 25 mW, which is only one fifth of that of traditional.[18]

The response magnitudes of MEMS sensor with hybrid Rh/Al = 4/1 at different concentrations of methane were further recorded at the working temperature of 400 °C (Fig. 7). The sensor shows a fast response and decay toward the methane

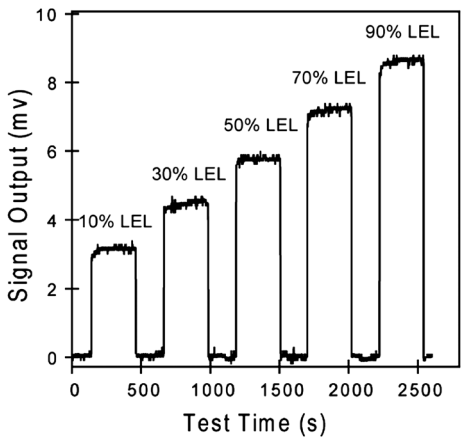

Fig. 7 Sensor responses to the methane inputs of different concentrations.

exposure and insulation at all methane concentrations. The signal output increased linearly with increasing the methane concentration. Generally, for methane gas, the lower explosion limit threshold is about 4%. According to the industry standard for catalytic combustion sensor, a gas warning system is demanded to trigger a pre-alarm at 0.4% (corresponding to 10% of the lower explosion limit, 10% LEL) and the T_{90} response time must be less than 15 s.[19] For the mesoporous Rh_2O_3/Al_2O_3 hybrid Rh/Al = 4/1 film-based MEMS sensor, the T_{90} response time lies between 3–9 s at all methane concentrations. The signal output is about 3.1 mV for 10% LEL methane concentration, the signal noise ratio is high enough for detecting when assembled in an instrument.

The influences of ambient temperature and humidity on the sensing performance were also investigated to check the applicability for practical use. The operating temperature range is the span of ambient temperatures given by their upper and lower extremes. Fig. 8a shows the influence of ambient temperature on the peak responses to 50% LEL methane in the range of −20–40 °C at the humidity of 25% RH. The measurement error is about ±1.7% mV and it equals to 0.05% methane concentration. It is obvious that the variation in sensor response is negligible under the temperature range. The voltage output errors by varied temperature has been well compensated by compensating element (mesoporous alumina film coated MEMS micro-heater), which had been pre-incorporated directly into the MEMS sensor. Fig. 8b shows the influence of humidity on the sensor peak

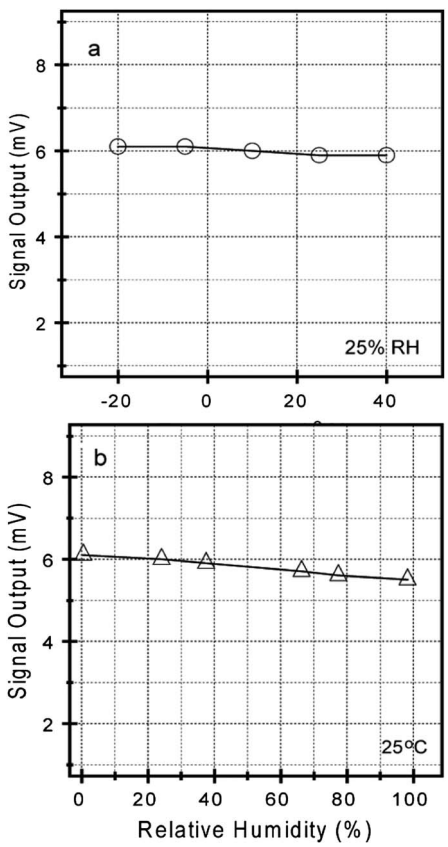

Fig. 8 Effect of the temperature (a) and relative humidity (b) on the signal output of the sensor (methane concentration: 50% LEL).

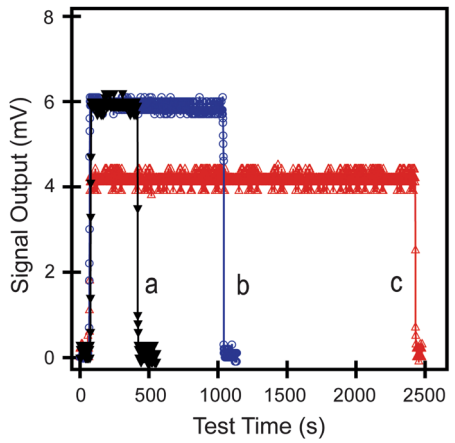

Fig. 9 Response of the sensor (methane concentration: 50%LEL) before (A) and under (B) the exposure to 100 ppm H_2S, and the response under the exposure to 100ppm H_2S mixed with 50%LEL methane (C).

response to 50% LEL methane in the humidity range of 0.5%–98% RH. The responses are also plotted against the relative humidity with respect to the saturated vapour pressure at 25 °C. The voltage output linearly and slightly decreased with the increase in humidity, but the voltage output variation is not as strong as that of traditional catalytic combustion sensor.[12,18] Only 9.8% sensitivity lost from 0% to 98% RH. All these indicate that the mesoporous hybrid Rh_2O_3/Al_2O_3 film based MEMS sensor has a strong ability against the change of the environment.

As methane detecting equipment, the catalytic combustion sensor is often used in hostile environment. Catalyst poisoning or performance degradation can occur when combustible sensor are exposed to certain substances. Among them, the most commonly encountered are sulfur containing compounds. Fig. 9 shows the effect of typical poison H_2S on the performance of MEMS sensors. It clearly indicates that a 40 min exposure to 100 ppm H_2S mixed in 50% LEL methane does not cause any change in sensitivity and response time. In our MEMS sensor, the catalyst consists of a low-density mesoporous structure and has a large surface area. This highly porous structure ensures the quick recovery of the sensor even if some of the active sites of the catalysts were poisoned when exposured under poisoning environment.

Conclusions

A one-pot approach has been developed for the synthesis of an uniform mesoporous rhodium oxide/alumina hybrid following a facile method using P123 as template. Such hybrid nanomaterials display high dispersions of both the noble metal oxide and alumina in a broad scope of Rh/Al mole ratio up to 8 : 1. Their interesting porosity properties make them attractive materials for catalytic applications. After coated on a MEMS micro-heater and assembled as methane catalytic combustion sensor, it demonstrated a very short T_{90} response time of less than 9 s for all the methane concentrations, a high signal output of about 3.1 mV for pre-alarm 10% LEL methane concentration, high enough signal noise ratio in practical detecting, and, even more importantly, a low power consumption of 25 mW, which was about one fifth of that of a traditional LEL sensor.

Acknowledgements

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18 In general, the power consumption of single element of traditional commercial LEL sensor is about 120 mW and the response based on rhodium catalyst is about 25 mV for 50% LEL methane. 12%–15% sensitivity loss from 0% to 80% RH.
19 T90: Time needed to reach 90% of the highest signal.