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Mesoporous PdO/Pt/Al_2O_3 Film produced by Reverse-micro-emulsion and Its application for Methane Micro-sensor

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Liang Li *, Gengnan Li and Yuan Yuan

A simple, versatile and effective reverse micro-emulsion and pyrolysis protocol was presented for *in-situ* growth PdO/Pt loaded mesoporous Al_2O_3 film. Noble metal (oxide) nano-particles with narrow size distribution homogeneously dispersed throughout the Al_2O_3 support. Most importantly, the obtained worm-like catalyst network has both high specific area and highly crystalline, which is favorable for the application of methane catalytic combustion. When deposed on micro-heater and used as a sensor element, the resulting micro-sensor demonstrated a short T_{90} response time, relatively high signal output, high enough signal/noise ratio and extraordinarily low power consumption for methane detection.

Introduction

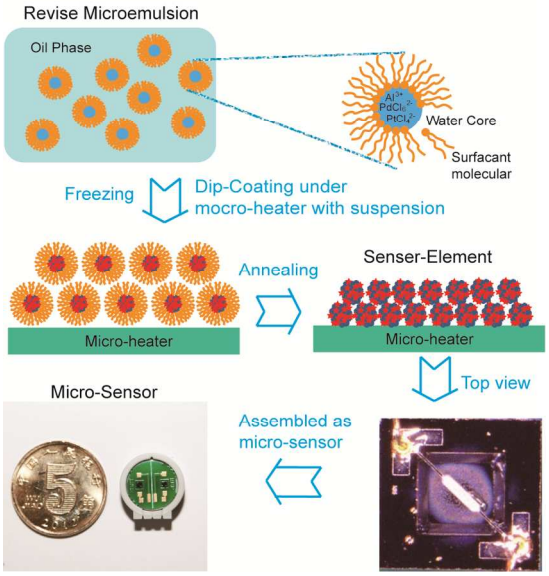
Methane, as a main component of natural gas, is widely used in industry and domestic life. The leakage may cause explosion and fire. The gas alarm or system monitoring methane concentrations thus is urgent and necessary especially under some special environment. Among various detection methods, the most commonly and widely used is the catalytic combustion technique.[1-11] Although traditional methane catalytic combustion sensor is portable, highly accurate and reliable so far, it has been found in practice that the power consumption and the size are still relatively high and not suitable for assembly in miniature sensor devices. Recently, with the rapid development of micro- electro- mechanical systems (MEMS), many micro- machining ways have been developed and used, which make the micromation, low power consumption and intelligence of sensors possible.[12-13]

For catalytic combustion gas sensors, there are two element strung onto the opposite arms of a balanced Wheatstone-bridge circuit. One is 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. The sensing mechanism of such gas sensors is based on the changes in the electrical resistance induced by the combustion reaction on the surface of the active-element, which is proportional to the amount of combustible gas present. Obviously, for the same catalytic system, the sensing behavior is associated with catalytic performance of the catalyst, which is closely related to its specific area and morphology.[14-17] Compared with the traditional catalytic combustion sensor, the heating area of a MEMS micro-heater chip is only about one percent of that in traditional. Thus, the control of the specific area and morphology for the catalyst is more essential in fabrication such micro-sensor.

It is well known that mesoporous materials possess high surface area and well defined pore structure which has been proven to be excellent in fabricating highly active catalyst or catalyst support. When combined with MEMS micro-heater, the loaded catalyst amount and contacted area between methane and the catalyst for the catalytic combustion micro-sensor could be greatly enhanced. However, as a main kind of catalyst for methane catalytic combustion sensor, noble metal (oxide) is difficult to form meso-structure directly. When loaded on other meso-porous matrix, or *in-situ* grown from precursor in the presence of reducing agents, they are usually accomplished in multi-steps which are not only time-consuming, but sometimes also not applicable for the preparation on the small are of a MEMS micro-heater. In the previous studies, we have reported that rhodium oxide can be formed uniformly mesoporous hybrid with Al_2O_3 in a large mole ratio range when P123 was used as template, and this hybrid can be easily deposed on micro-heater for methane detection.[18-19] Unfortunately, this protocol is only effective for rhodium system.[18] The fabrication of such a mesoporous film with high content of catalyst and controlled porosity by a simple and flexible method is still in challenge.

Palladium/platinum system is one of the main noble metal catalytic systems for methane catalytic combustion reaction, in addition to the rhodium system.[14] In this report, a simple, versatile and effective reverse micro-emulsion and pyrolysis protocol was developed for *in-situ* growth mesoporous PdO/Pt loaded Al_2O_3 film on the MEMS micro-heater chip and used for the detection of methane gas (Scheme 1). Noble metal (oxide) nano-particles with narrow size distribution around 4 nm homogeneously dispersed throughout the Al_2O_3 support. Most importantly, the obtained worm-like catalyst network has both

high specific area and highly crystalline, which is favorable for catalytic combustion applications. The reverse micro-emulsion has been formerly a key technique to synthesize oxide nano-particle with controlled size and narrow size distribution.[20-22] It has been proved in this paper that this strategy is also feasible for mesoporous metal oxides film applications.



Scheme 1. Reverse micro-emulsion and pyrolysis protocol for fabricating $PdO/Pt/Al_2O_3$ porous film on MEMS micro-heater chip

Experiment Section

Chemicals and reagents

All chemicals used, such as aluminum isopropoxide, iso-propanol, poly (propylene glycol) - block - poly (ethylene glycol) – block – poly (propylene glycol) (P123) etc., were of analytical grade, and purchased from Sigma Chemical Co., Ltd without any further purification.

Synthesis of mesoporous Al_2O_3:

Aluminum isopropoxide (6.5 g) were dissolved in iso-propanol (125 ml). The solution was introduced into a prepared reverse micro-emulsion [15 g poly (propylene glycol) – block - poly (ethylene glycol) – block – poly (propylene glycol), 214.7 g pentanol, 65.2 g iso-octane]. After ageing and cooling at -5 ^oC for 24 h, the lower suspension was filtered and calcined at 500 ^oC for 1h.

Synthesis of mesoporous PdO and Pt loaded Al_2O_3 hybrid ($PdO/Pt/Al_2O_3$):

Aluminum isopropoxide (6.5 g) were dissolved in iso-propanol (125 ml). The solution was introduced into a prepared reverse micro-emulsion [15 g poly (propylene glycol) – block - poly (ethylene glycol) – block – poly (propylene glycol), 214.7 g pentanol, 65.2 g iso-octane and 12.8 g H_2O with K_2PtCl_6 and H_2PdCl_4 dissolved inside]. After ageing and cooling at -5 ^oC for 24h, the lower suspension was filtered and calcined at 500 ^oC for 1h.

Characterization of the materials:

X-ray diffraction (XRD) data were collected using a Bruk D8 Focus powder diffractometer with graphite mono chromatized Cu-Ka radiation (λ=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 fabrication and measurement:

A MEMS combustion-type sensor, employing mesoporous $PdO/Pt/Al_2O_3$ hybrid as a sensor materials and mesoporous alumina as a compensating materials was fabricated by spin-coating method. For active element (catalytic element), mesoporous $PdO/Pt/Al_2O_3$ hybrid suspension were dropped onto the MEMS micro-heater with integrated platinum electrodes. After spin-coating, the micro-heater was slowly and electrically heated up to 500 ^oC and then maintained at this temperature for 1 min to remove the template. This procedure was repeated 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 suspension 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

For $PdO/Pt/Al_2O_3$ catalytic system, It has been proved that optimal mole ratio of Pd/Pt is about 9/1 when used in methane catalytic combustion reaction, and thus applied in our micro-sensor.[23-25] In order to get stable and detectable output signal in such small heating area ($0.01mm^2$) of MEMS micro-heater, the surface coated catalytic materials were fabricated into mesoporous structure using revise micro-emulsion as precursor. Thus, the loaded catalyst amount and contacted area between methane and the catalyst could be greatly enhanced.

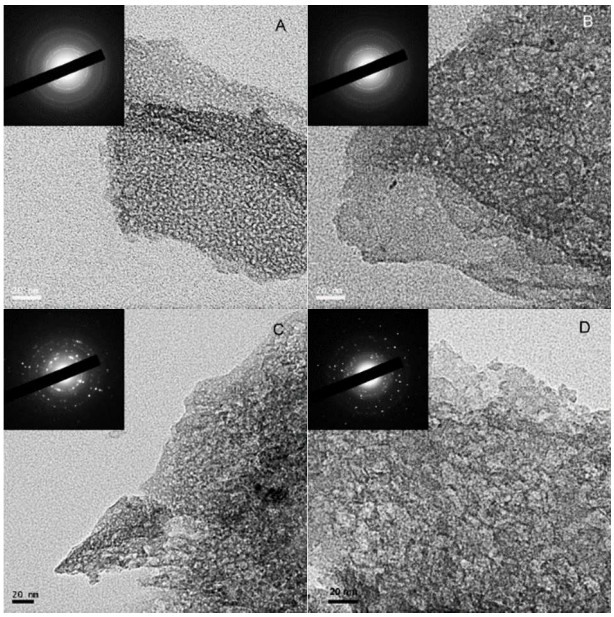


Figure 1 TEM images of mesoporous $PdO/Pt/Al_2O_3$ hybrids with different mole ratio of noble-metal/Al (a) 1/4, (b) 1/2, (c) 1/1, (d) 2/1

Figure 1 shows the transmission electron microscope (TEM) images for the synthesized PdO/Pt/Al_2O_3 materials with different noble metal/Al mole ratio from 1:4 to 2:1. All the samples show the characteristics of a worm-like architecture with metal nanoparticles uniformly dispersed throughout the porous support. There is not any large noble metal (oxide) visible either within or out of the meso-structure. The corresponding selected area electron diffraction patterns of the samples show a clear ring pattern, whereby the lattice constant measured agrees with the (101) (110) (112) plane of PdO and (111) plane of Pt. The lattice spacing of the particles determined through HRTEM analysis (Figure 2) match well with that of (200) (111) crystal planes of Pt and (110) (101) crystal planes of PdO, respectively. Surprisingly, there is no Al_2O_3 nanoparticle distinguishable in the image, this may due to the much lower diffraction contrast or relative lower crystallinity when compared with noble metal (oxide). The noble metal (oxide) nano-crystals show a narrow particle size distribution with an average of 4 -5 nm.

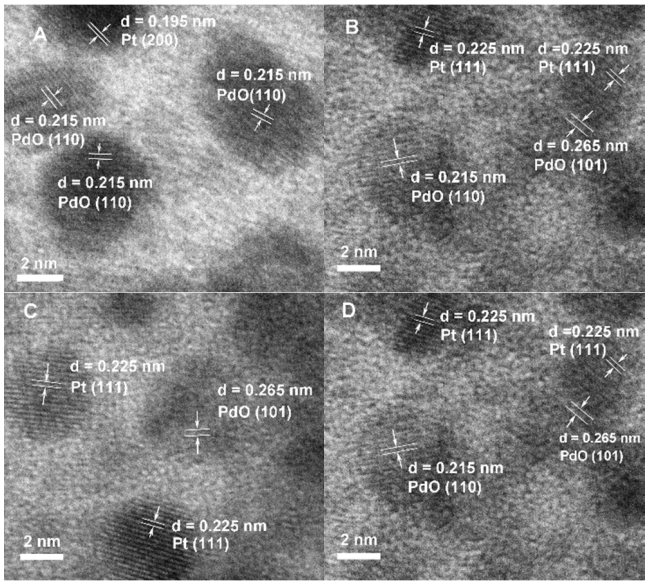


Figure 2 HRTEM images of mesoporous PdO/Pt/Al_2O_3 hybrid with different mole ratio of noble-metal/Al (a) 1/4, (b) 1/2, (c) 1/1, (d) 2/1

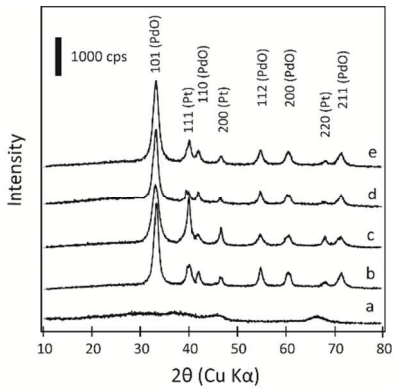


Figure 3 Wide angle XRD pattern of mesoporous PdO/Pt/Al_2O_3 hybrid with different mole ratio of noble-metal /Al (a) 0/1, (b) 1/4, (c) 1/2, (d) 1/1, (e) 2/1

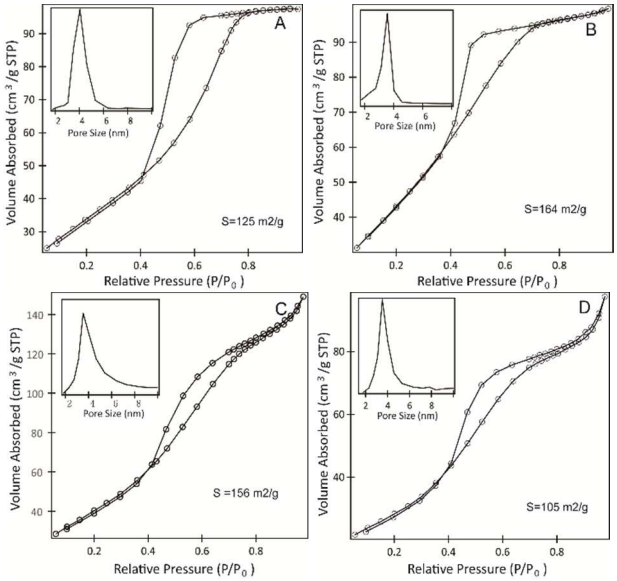


Figure 4 N_2 adsorption-desorption isotherms and corresponding pore size distributions of mesoporous PdO/Pt/Al_2O_3 hybrid with different mole ratio of noble-metal/Al: (a) 1/4, (b) 1/2, (c) 1/1, (d) 2/1

Figure 3 presents the X-ray diffraction (XRD) data for these meso-porous structured catalytic materials. There is not any diffraction peaks in the small angle range indicating the disordered pore arrangement. The peaks at 2θ value of 33°, 42°, 54°, 61° and 71°can be assigned as (101), (110), (112), (200) and (202) diffractions of PdO crystal (PDF no. 43-1024), additional two reflection peaks at 2θ value of 40° and 46°can be readily assigned as (111) and (200) diffraction of platinum (PDF no. 04-0802), suggesting the nano-crystallized state of Pt and PdO. From the full width at half-maximum of the (110) diffraction peak of PdO and (111) diffraction peak of Pt, the calculated crystallite size of noble metal (oxide) are only about 4 nm, corresponding well with that of TEM analysis.

The N_2 adsorption isotherms and corresponding pore size distributions of the synthesized hybrids are shown in Figure 4. In all the cases, the isotherms are type IV suggesting meso-porous structure and the appearance of H4 hysteresis loops indicate the formation of very narrow slit-like meso-pores. The specific areas of the hybrids are expected to be substantially lower than that of the pure meso-porous alumina at increased noble metal content. The corresponding specific surface area and the pore size of the hybrids can also be found in Figure 4. Although the hybrids have a much higher noble metal content, the materials still have much higher specific area, narrow pore distribution and much large pore volume compared with that synthesized by other method.[18] Meanwhile, the average pore sizes are all at about 4 nm. It seems that the noble-metal/Al mole ratio hardly affects the pore size of the final materials. It can be expected that the synthesized mesoporous structured PdO/Pt/Al_2O_3 materials are more suitable for the methane catalytic combustion reaction.

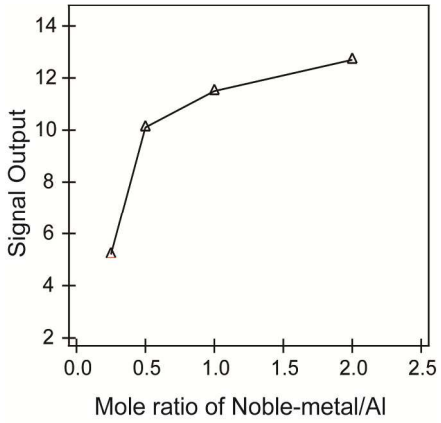


Figure 5 Responses of the MEMS sensor based on PdO/Pt/Al_2O_3 hybrids with different mole ratio. (25 °C, 25% RH, 2 vol% methane or 50% of the lower explosion limit, 50% LEL)

The catalytic efficiency and gas sensor properties of the meso-structured PdO/Pt/Al_2O_3 materials were evaluated after coated as catalyst on micro-heater and then assembled as MEMS methane catalytic combustion sensors, employing mesoporous alumina as compensating material. Figure 5 shows the response signals of MEMS sensors with different noble metal/Al mole ratio for 2 vol% (corresponding to 50% of the lower explosion limit, 50% LEL) methane concentration at working temperature of 400 °C. It clearly shows that the output single increases with the increase of noble metal content due to the higher content of catalyst. However, when mole ratio of noble metal/Al reached to 1/2, slight increase in response signal was observed, which also means the slight increase of the oxidized methane per unite time within the catalytic element. In general, for methane catalytic combustion sensor, the larger content of catalyst, the stronger output signals. However, the MEMS sensor with noble metal/Al =1/2 has high enough response signal of 10.1 mV for methane dictating when compared with that using Rh_2O_3 as catalyst (6 mV).[19] Thus, this mole ratio was selected for further investigation after considering synthetically from the factors of the cost and intensity of signal output, respectively. Thanks to the porous catalyst structure and high content of noble metal content, only about 1% heating area reaches the 25% signal output as compared with the traditional methane catalytic combustion sensor.[14,26]

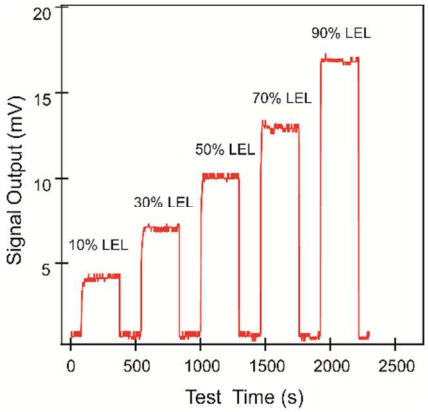


Figure 6 Sensor responses to the methane inputs of different concentrations (25 °C, 25% RH)

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} (Time needed to reach 90% of the highest signal) response time must be less than 15 s.[14] For the fabricated MEMS sensor with mole ratio of noble-metal/Al =1/2, the response magnitudes at different concentrations of methane were further recorded at the working temperature of 400 °C (Figure 7). The sensor shows a fast response and decay toward the methane exposure and insulation at all methane concentrations. The signal output increased linearly with increasing the methane concentration. The T_{90} response time lies between 3–10 s at all methane concentrations. The signal output is about 4.3 mV for 10% LEL methane concentration, the signal noise ratio is high enough for detecting when assembled in an instrument.

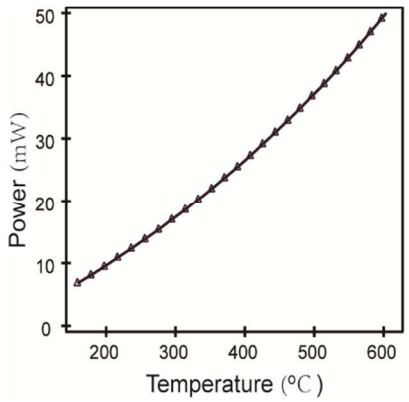


Figure 7 Power consumption of the micro-heater as a function of working temperature of the gas sensor

The power consumption of such micro-sensor can be calculated from the resistance of micro-heater under a given potential. The resistance of Pt micro-heater in the sensor device is temperature dependent. Thus, the working temperature T (°C) can be determined by the resistance R of the micro-heater, or

$$T = T_0 + (R-R_0)/\alpha R_0$$

where α is the temperature coefficient of Pt resistance, R_0 is the original resistance at room temperature T_0 (25 °C). Obviously, by measuring the resistance of the micro-heater under a given potential, the temperature T in the device can be calculated. Figure 7 depicts the heating power consumption as a function of the temperature of the sensor, showing a nearly linear relation. At the working temperature T = 400 °C, power consumption of the micro-heater is only about 25 mW, which is about 5 times lower than that of commercial methane catalytic combustion sensor. [14]

To check the applicability for practical use, the influences of ambient temperature and humidity on the sensing performance were also investigated. The operating temperature and humidity range is the span of ambient temperatures and humidity given by their upper and lower extremes. Figure 8A dipicts the influence of ambient temperature on the responses to 50% LEL methane in the range of -20– 40 °C at the humidity of 25% RH. The measurement error is about 1.2% mV and it equals to 0.02% methane concentration. The variation in sensor response is negligible under the given temperature range. The voltage output errors by varied temperature has been well compensated by compensating element (meso-structured alumina film coated MEMS micro-heater), which had

been pre-incorporated directly into the MEMS sensor. Figure 8B shows the influence of humidity on the sensor peak 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 vapor pressure at 25 °C. The signal 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. Only 5% sensitivity lost from 0% to 98% RH. All these indicate that the mesoporous PdO/Pt/Al_2O_3 film based MEMS sensor has a strong ability against the change of the environment.

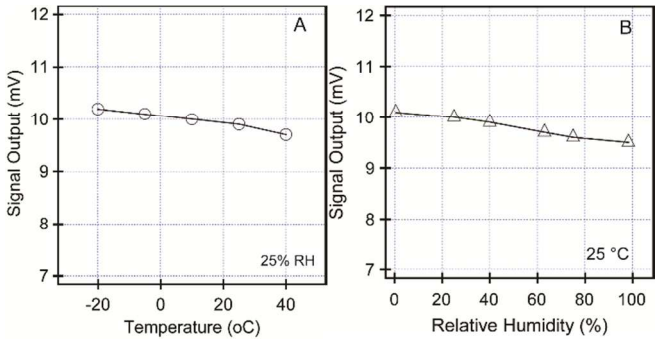


Figure 8 Effect of the temperature (A) and relative humidity (B) on the signal output of the sensor (methane concentration: 50%LEL)

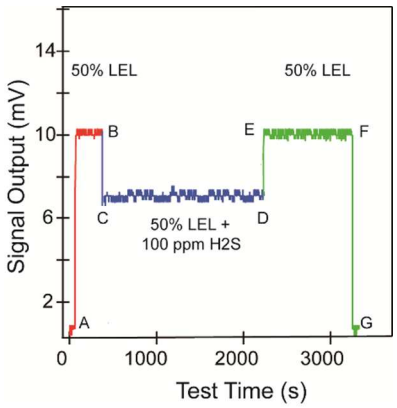


Figure 9 Response of the sensor (methane concentration: 50%LEL) before (A-B) and after (E-F) the exposure to 100 ppm H_2S, and the response under the exposure to 100ppm H_2S mixed with 50%LEL methane (C-D).

Generally, catalyst poisoning or performance degradation can occur when combustible sensor are exposed to certain substances. As methane detecting equipment, the catalytic combustion sensor is often used in hostile environment. Among them, the most commonly encountered are sulfur containing compounds. Figure 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 exposure under poisoning environment.

Conclusions

A simple and versatile reverse micro-emulsion and pyrolysis protocol has been developed for growth PdO/Pt loaded mesoporous Al_2O_3 film. The interesting porosity properties and narrow noble metal (oxide) particle distribution make it attractive material for catalytic applications. When 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 4.3 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 for that of traditional.

Acknowledgements

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Notes and references

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

E-mail: liliang@ecust.edu.cn; Tel: 021-64252599; Fax: 021-64250740.

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26 In general, the power consumption of single element of traditional commercial LEL sensor is about 120 mW and the response based on PdO/Pt catalyst is about 40 mV for 50% LEL methane. 12%– 15% sensitivity loss from 0% to 80% RH.

Graphical Abstract

The worm-like PdO/Pt/Al_2O_3 film on the MEMS micro-heater has both high specific area and crystalline, which is favorable for catalytic combustion applications.