Au-doped zinc oxide nanostructure sensors for detection and discrimination of volatile organic compounds

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Pure and 10% w/w Au-doped zinc oxide (ZnO) nanostructure sensors were produced and used as sensing devices in a portable electronic nose (E-nose). The nanosensors were prepared using thermal oxidation technique with sintering temperature at 700°C under oxygen atmosphere at a flow rate of 500 mL min^{-1}. The sensors were demonstrated to be sensitive to various volatile organic compounds (VOCs), especially ethanol vapour. The E-nose even with only two sensors was efficient to discriminate a number of selected VOCs. The Au-doped sensor shows a significant improvement of sensitivity. The portable E-nose can detect the difference between alcohol beverages and alcohol solutions and can distinguish the difference of white and red wines having the same percentage of alcohol.

Keywords: E-nose, Alcohol, Nanostructure, Gas sensor, Au-doped zinc oxide

Introduction

Electronic nose (E-nose) has recently become one of the most promising devices for quality control of food[1,2] and beverage,[3,4] environment protection[5] and public safety.[6] In principles, the E-nose combines an array of sensing elements with a data analysis system. Metal oxide semiconductors (MOX), such as ZnO, SnO_2 and TiO_2, are among the most popular sensing materials for E-nose. These sensors utilise the changes of electrical conductivity upon exposing to target gases. Doping these materials with some metal catalysts can enhance sensing properties. For examples, Gong *et al.*[7] reported an improvement in the sensitivity and selectivity of Cu-doped ZnO to CO. Shishiyan *et al.*[8] demonstrated that doping ZnO with Sn can increase the sensitivity of this gas sensor to NO_2. At present, most developments of selective MOX sensors are based on the ZnO thin films doped with different impurities such as Fe, Al, MnO_2, Bi, etc.[9–13] From the authors' point of view, Au is very interesting for doping in gas sensor since it is well known to be a good catalyst when they have particle size smaller than 10 nm.[14] The Au catalysts have been shown potentials for both selective and non-selective oxidation of hydrocarbons.[15–17] In addition, it was reported that Au-doped ZnO sensor exhibited and improvement of sensitivity toward ethanol.[18,19]

In this paper, the authors have produced and examined the gas sensing properties of undoped and Au-doped ZnO nanostructure sensors. These sensors were applied in E-nose for detection of volatile organic compounds (VOCs). It was shown that the E-nose having only two sensors can discriminate various kinds of samples.

Experimental

Preparation of ZnO and Au-doped ZnO nanostructure sensors

Pure and Au-doped ZnO nanostructure sensors were prepared using thermal oxidation technique. The oxidation was performed by heating zinc powder (purity 99·9%) and a mixture of zinc powder and 10 wt-%Au powder. Such mixtures were screened as a thick film onto an alumina substrate. The thick films were sintered at 700°C for 24 h under oxygen atmosphere with flow rate of 500 mL min^{-1}. The ZnO nanostructures were characterised using field emission scanning electron microscopy (FESEM). The FESEM images of ZnO and 10 wt-% of Au-doped ZnO nanostructure sensors on the alumina substrate are displayed in Fig. 1.

The wire-like or belt-like nanostructures outward from microparticle are observed. The diameter and length of ZnO nanostructures are within the range of 250–750 nm and 1·7–7·0 μm respectively. The sensors were simply fabricated by putting gold contact and heating coil underneath alumina substrate. The successfully produced ZnO and Au-doped ZnO nanostructure sensors are displayed in Fig. 2.

Portable electronic nose system

The diagram of portable E-nose system is shown in Fig. 3. It consists of three main parts:

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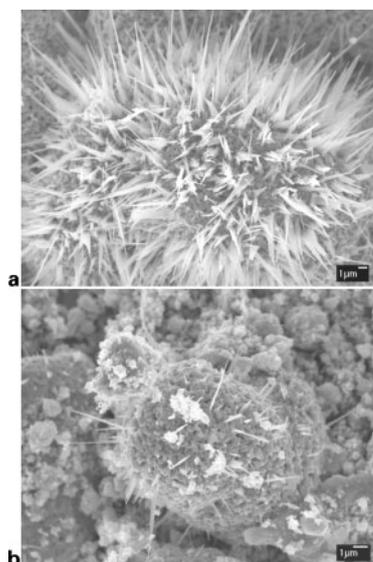
1 Image (FESEM) of *a* ZnO and *b* 10 wt-% Au-doped ZnO nanostructure

(i)   sensor chamber
(ii) air flow system
(iii) DAQ card and measurement circuit.

All parts were contained in a rectangular box with a dimension of $19\cdot5 \times 29\cdot5 \times 10$ cm³ respectively.

For the first part, the two nanostructure sensors were installed at the bottom of the chamber. The air carrying the odor molecules was introduced into the 150 mL of sensor chamber through a Teflon tube. The caliber is $\sim 2\cdot5$ mm. The sensor chamber also has an exhaust Teflon tube which has the same caliber. The second part consists of four electrically controlled solenoid valves, sample and reference glass containers, plastic pipes and flow controller. It is necessary for this type of measurement to switch between a reference and a sample glass in order to reduce the humidity effects.[20,21] Four electrically controlled solenoid valves were used to avoid mixing of the gas from the reference and the sample. Then, the gas from the reference or sample flows to the sensor chamber of which the flow rate was set at 2 L min⁻¹. Finally, in the measurement circuit, data acquisition was realised by a USB-DAQ-Card National Instruments NI USB-6008. The measurement program was written using LabVIEW.
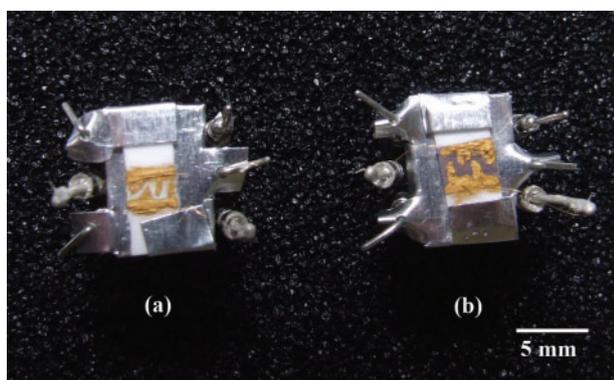
2 *a* ZnO and *b* 10 wt-% Au-doped ZnO nanostructure sensors used in portable electronic nose
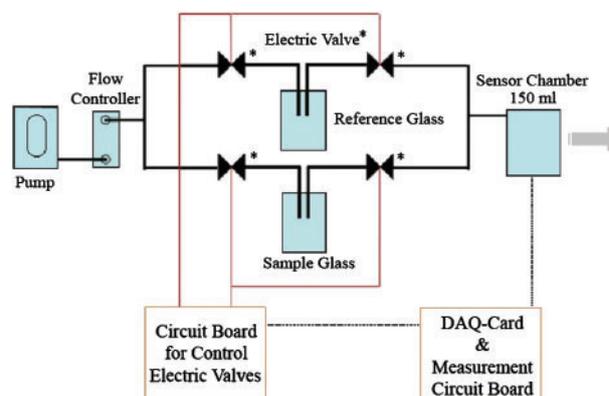
3 Schematic diagram of dynamic portable E-nose system

Noise correction

For data analyses, DC signal of each sensor was stored every 1 s. The noise or the standard deviation (SD) of signals from ZnO and Au-doped ZnO sensors is $0\cdot0224$ and $0\cdot0178$ V. To achieve high accuracy, RMS measurements with a low side lobe window[22] were employed to apply to the signals. The main lobe is centred at each frequency component of the time domain signal and the side lobes approach zero at

$$\Delta f = \frac{F_s}{N} \qquad (1)$$

where F_s is the frequency at which the acquired time domain signal was sampled. N is the number of points in the acquired time domain signal.

In the experiment, N is 1000 samples. After using mathematical correction, the SD becomes $0\cdot0049$ V for ZnO sensor and $0\cdot0016$ V for Au-doped ZnO sensors resulting in a signal to noise ratio of about 44 and 65 dB respectively.

Results and discussion
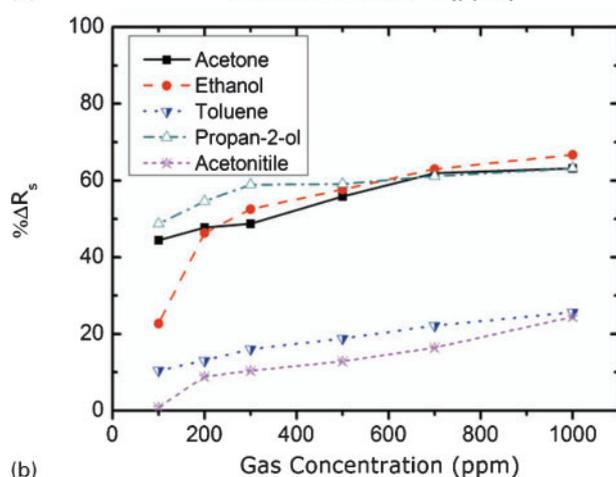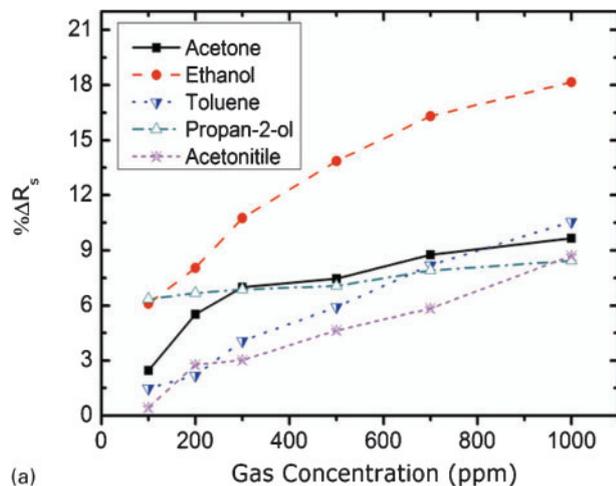
Sensor responses on VOCs

To compare sensitivity of two sensors on different VOCs, it is better to calculate the percentage change of resistance ($\%\Delta R_s$) via

$$\%\Delta R_s = \left| \frac{\overline{R}_{sam} - \overline{R}_o}{\overline{R}_0} \right| \times 100 \qquad (2)$$

where $\overline{R}_{sam}$ and $\overline{R}_0$ are the mean sensor resistance in the presence and absence of the testing gas respectively.

Figure 4 shows the sensor responses of pure and Au-doped ZnO to acetone, ethanol, toluene, propan-2-ol, acetonitile.

From Fig. 4, it indicates that the sensor responses of both sensors work linearly with gas concentration. At the same concentration, the sensor response of Au-doped ZnO sensor on all VOCs is higher than that of ZnO sensor. The Au in ZnO enhances the adsorption reaction between the VOCs and the adsorbed oxygen ion on the crystal surface with a negative charge. The species of oxygen ion previously determined to be O^{2-}.[23] At the grain boundaries, the surface density of the negatively charged oxygen decreases immediately and abundantly. Therefore, the changing of resistance of Au-doped ZnO sensor is much more than that of ZnO sensor. Moreover, such ZnO nanosensor shows the strong
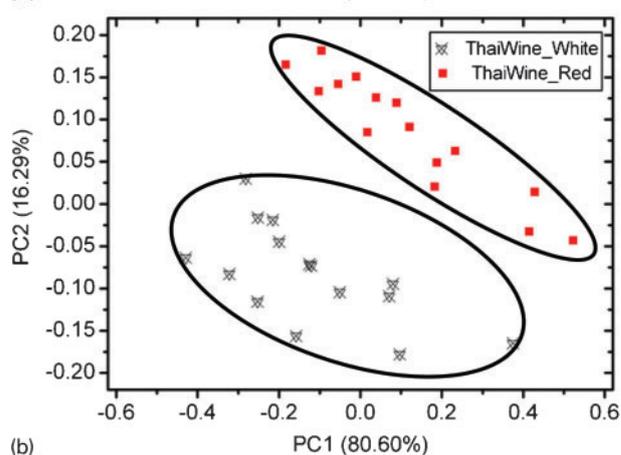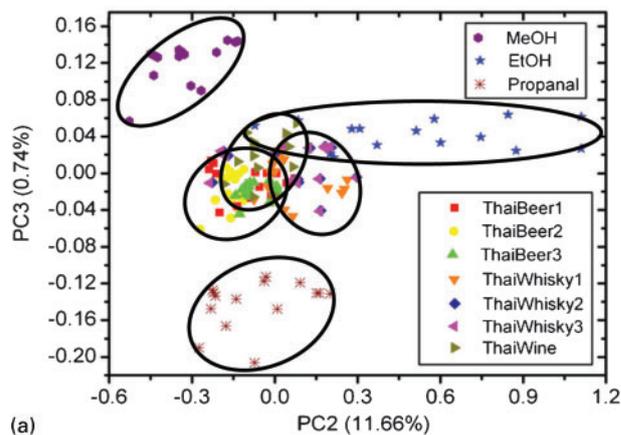
4 Sensor response of *a* ZnO and *b* 10 wt-% Au-doped ZnO sensors to concentrations of VOCs

5 Results of PCA for discriminate of *a* alcohols and *b* typical Thai wines

response on ethanol. Therefore, it is suitable to employ in detecting alcoholic solution and beverages.

Detection and discrimination of alcohol samples

Because such sensors could well respond to alcohol. The ethanol, methanol, propanol and various Thai beer, Thai wine and Thai whiskey samples were measured using the E-nose based on two nanosensors. The data were introduced into the principle component analysis (PCA) for recognition and discrimination of samples. The PCA method can be used for dimensionality reduction of a dataset while retaining those characteristics of the dataset that contribute most to its variance. The input data can be the percentage change of every sensor or only some sensors for multiple measurements of different samples. However, in this E-nose, there are only two sensors. It means that the dataset only has two dimensions. Feature extraction techniques need to be applied to raw data for selecting the appropriate data and for increasing the dimension. The last 10 samples of each sensor before and after switching to another line were averaged. The difference of both values was used. Another feature can be extracted from the range of decay times. The difference of slope for the sample measurement was also used. Therefore, one experiment can give four different sensor output features.

Figure 5 shows two-dimensional PCA results for discrimination of alcohols. In Fig. 5*a*, it can be observed that the E-nose based on two nanosensors

can discriminate quite well between the ethanol, methanol and propanol with PC2 of 11·66% and PC3 of 0·74%. Thai alcoholic beverage sample points locate around the ethanol sample points because alcoholic beverages have the contents of ethanol. However, in the case of Thai wines having the same percentage of alcohol (12·5% alcohol by volume), the E-nose can clearly discriminate the white and red wines as shown in Fig. 5*b* with PC1 of 80·60% and PC2 16·29%. The discrimination of white and red wines even with the same alcohol amount indicates that the E-nose is sensitive to other vapour ingredients apart from alcohols as well.

Conclusions

Pure and 10 wt-% Au-doped ZnO nanostructure sensors were successfully produced by using thermal oxidation technique. Doping 10 wt-%Au could improve the sensitivity of gas sensors on VOCs. The responses of the sensors are linear with gas concentrations varying from 100 to 1000 ppm. Therefore, it can be used for predicting the gas concentrations of unknown VOCs. In the real applications, only two sensors can be installed in the E-nose which is sufficiently efficient to detect and discriminate various different alcohol beverages. This E-nose can then be employed for quality control in the beverage industry. These elementary results are promising for further applications of this E-nose which can be further enhanced by using a higher number of ZnO sensors at various Au-doping percentages.

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