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Using highly selective mesoporous thin films to sense volatile organic compounds†

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Sensors based on mesoporous thin films of phenolic resin and silica, prepared on microinterdigitated electrodes through evaporation-induced self-assembly, exhibit excellent selectivity and reproducibility when sensing aromatic and polar volatile organic compounds, respectively. Moreover, the sensors displayed an ultra-fast response rate for the sensing experiments.

The rise in the levels of volatile organic compounds (VOCs) in the atmosphere is a by-product of waste organic solvents from increasing industrial activity.[1] Because many of these VOCs are harmful to human health, methods are required for their detection and for the prevention of related industrial accidents. The main kinds of volatile organic pollutants are alkanes, aromatic hydrocarbons, alkenes, esters, aldehydes, and ketones; the most common VOCs are formaldehyde, benzene, toluene, ethylbenzene, styrene, tetrachloroethene, MeOH, and acetone.

Gas sensors can be classified based on their operating principles—for example, electrochemical,[2a] piezoelectric,[2b–d] optical,[2e–g] and resistive[1,2h] sensors. In this study, we prepared novel resistive sensors to detect several common VOCs—benzene, toluene, xylene, MeOH, EtOH, formaldehyde, acetone, and $CHCl_3$—based on variations in the conductive properties of various mesoporous films after their interaction with these gases. The mesoporous thin film sensors displayed brilliant behavior with an ultra-fast response rate (time constant <1 min) compared with other kinds of VOCs sensors. We employed mesoporous silica and phenolic resin thin films as two different types of sensing layers for VOCs on these detection chips. The mesoporous silica–based sensing thin film was, as expected, sensitive toward polar VOCs because its hydrophilic surface presented silanol groups after sol–gel processing. In contrast, the mesoporous phenolic thin film exhibited more-selective gas sensing toward aromatic VOCs because of π–π interactions between its surface and the phenyl groups of these VOCs. Phenolic resin is a particularly attractive sensing material because its hydrophobicity means that it is barely affected by humidity.[3]

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To prepare the sensors (Scheme 1a), we first deposited Cr and Au onto a glass substrate through sputtering; we then manufactured a mask for subsequent exposure, developing, and etching processes to form the microinterdigitated electrode chip. Finally, we formed a sensing thin film of mesoporous phenolic resin or mesoporous silica on the microinterdigitated electrode through sequential evaporation-induced self-assembly (EISA), curing (for phenolic resin; phenolic/PEO-*b*-PCL = 1 : 1), sol–gel processing (for silica; TEOS/PEO-*b*-PCL = 5 : 1), and further calcination.[4] For measurement, we placed the sensing chip into a detector chamber and exhausted the air until the pressure reached approximately 5 torr at room temperature; employing a Wayne Kerr 4235 LCR meter, we adjusted the measurement conditions to a frequency of 10 kHz and a potential of 1 V. Next, we injected an individual organic solvent into the chamber and ensured the chamber pressure returned to 1 atm with air at the same time. We used computer software to record the data for subsequent analysis (Scheme 1b). In this study, we monitored the impedance (determined using the LCR meter) and time as parameters characterizing the performance of our sensors. We considered the difference in impedance ($R - R_0$) as the response and the sensitivity as the response divided by the initial impedance (R_0):

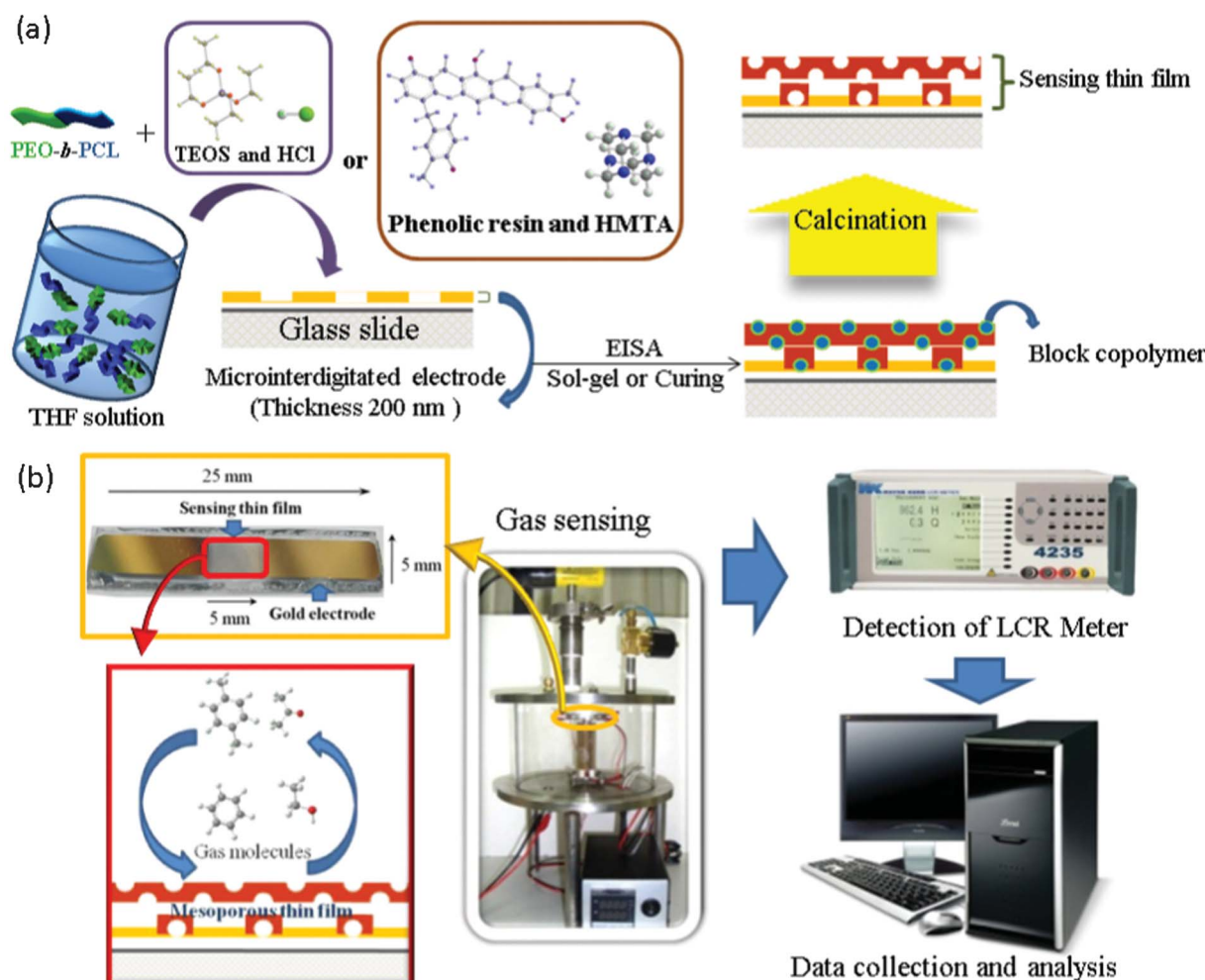$$\text{Sensitivity}(\%) = \frac{R - R_0}{R_0} \times 100\%$$

After normalization of the sensitivity, we considered the time required to reach 63% sensitivity as the time constant—that is, the time required to reach saturation of the vapor (Fig. 1). The efficiency of a sensor can be defined in terms of the time constant and the sensitivity. A lower time constant implies more-rapid sensing; a large change in sensitivity suggests a strong interaction between an organic vapor and a mesoporous sensing film. We used transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) to determine the structures of the mesoporous silica and phenolic resin films templated by double-crystalline amphiphilic PEO-*b*-PCL. The SAXS pattern of the mesoporous silica (Fig. S1a†) reveals the maximum intensity at a value of $q*$ of approximately 0.26 nm^{-1} (d = 24.1 nm), with higher-order reflections appearing at $3^{1/2}q*$ and $2q*$. The top-view TEM image in Fig. S1b† confirmed a hexagonal cylinder structure for the mesoporous thin film, revealing a highly ordered short-cylinder mesostructure consistent with what we had prepared previously.[4a] On the basis of the Broekoff–de Boer (BdB) sphere model, the mean pore size measured from the adsorption branch of the Brunauer–Emmett–Teller (BET) isotherm was as large

Scheme 1 (a) Preparation of mesoporous thin film sensors for the (b) sensing of VOCs.

as 19.8 nm (Fig. S1c†). Fig. S1d–f† display the SAXS pattern, TEM image, and BET isotherm of the gyroid-type mesoporous phenolic resin. Fig. S1d† reveals a set of Bragg reflections with approximate relative values of q of $6^{1/2}q^*$, $24^{1/2}q^*$, $38^{1/2}q^*$, and $50^{1/2}q^*$, corresponding to a gyroid ($Ia\bar{3}d$) structure. The TEM image in Fig. 2e reveals that the gyroid structure of the mesoporous phenolic resin had a high degree of periodicity over large domains. The mean pore size

measured, from the adsorption branch of isotherm in Fig. S1f†, was 13.9 nm. We tested the mesoporous silica sensor for eight kinds of common VOCs: benzene, toluene, xylene, MeOH, EtOH, formaldehyde, acetone, and $CHCl_3$. All of these VOCs could be sensed within 1 min, suggesting that the mesoporous silica sensing chip displayed excellent sensing efficiency. Fig. 2a reveals that the mesoporous silica thin film had relatively higher sensitivity toward MeOH, EtOH, formaldehyde, acetone, and $CHCl_3$, suggesting a key role for hydrogen bonding interaction between these polar VOCs and the silanol groups on the silica walls;[5] the mesoporous silica sensor was
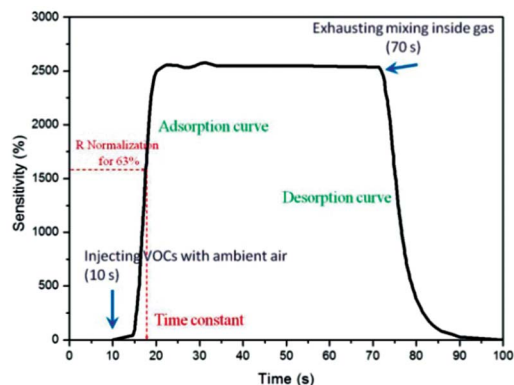

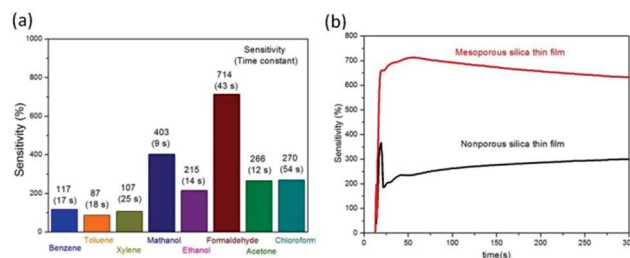**Fig. 1** Performance curve of the gas sensor.

Fig. 2 (a) Sensitivity of mesoporous silica chips toward various VOCs, each at a concentration of 16 ppm. (b) Temporal sensitivities of mesoporous and non-porous silica sensors toward formaldehyde vapor (16 ppm).

less sensitive toward the hydrophobic VOCs benzene, toluene, and xylene. Relative to their corresponding non-porous materials, mesoporous materials have ultralarge surface areas;[6] indeed, the sensitivity of our mesoporous silica thin film was approximately 3.5 times higher than that a non-porous silica thin film (Fig. 2b).

Next, we employed our mesoporous phenolic sensor for the detection of the same eight VOCs. Fig. 3a reveals the high sensitivity and selectivity of this sensor towards aromatic VOCs, with a ratio of impedance difference as high as 278% per ppm. Because phenolic resin is a benzene-based material, we expected it to interact with the phenyl groups of the aromatic VOCs through π–π interactions, thereby promoting the sorption of these vapors into the mesoporous thin film on the device surface, leading to decreased impedance. The sensing chip exhibited an ultrafast response rate (time constant: <17 s) because of the high surface area of its sensing mesoporous thin film. Reproducibility is an important parameter affecting the reusability of a stable sensor. As indicated in Fig. 3b, the response of our mesoporous phenolic sensor was rapid and reversible. The impedance changes upon exposure to 100 ppm benzene remained quite constant over five successive response–recovery cycles of 100 s. Together, the data in Fig. 3a and 3b characterize a mesoporous phenolic thin film sensor exhibiting high sensitivity, selectivity, and reproducibility. The surface area and pore volume of a mesoporous

material strongly affect its sensing efficiency, because the operating principle behind VOC sensing was the change in conductivity upon diffusion of the organic vapor into contact with the surface of the mesoporous sensing thin film. The sensitivity of our mesoporous thin film sensor was approximately 1.5 times greater than that of the corresponding non-porous thin film sensor (Fig. 3c); in addition, the time constant of the mesoporous thin film sensor was approximately half that of the non-porous material. These values confirm that the high surface area and porosity of the mesoporous phenolic thin film did indeed improve both the sensitivity and the time constant of its sensor.

In conclusion, we have prepared two types of mesoporous thin film sensors that exhibit remarkable efficiency for the sensing of VOCs. Our mesoporous silica sensor was selective for polar VOCs, due to the presence of silanol groups on the silica; in contrast, our mesoporous phenolic resin sensor was more sensitive toward aromatic VOCs, due to π–π interactions between the phenyl groups of the VOCs and those on the surface of the phenolic resin. Furthermore, the mesoporous thin film sensors also showed unique performance at an ultra-low time constant based on the high surface area of mesoporous thin films, which means we can detect harmful VOCs more effectively. For designing an ideal VOCs sensor, the humidity effect is considered a challenge; therefore, how to improve the sensing of hydrophilic VOCs is an important topic for the future, for example, to utilize surface modification and change the surface properties of mesoporous silica thin film sensors.

Fig. 3 (a) Sensitivity of mesoporous phenolic resin chips toward various VOCs, each at a concentration of 16 ppm. (b) Response of the mesoporous phenolic sensor to repeated dosing with benzene vapor at 100 ppm. (c) Temporal sensitivities of mesoporous and non-porous phenolic sensors.

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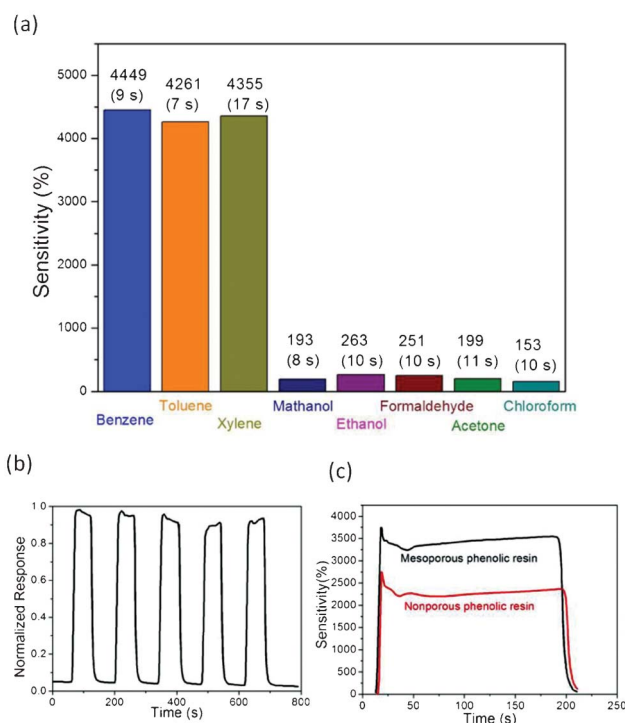6 M. Tiemann, *Chem.–Eur. J.*, 2007, **13**, 8376–8388.