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Functionalized mesoporous silica films for gas sensing applications

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Abstract Mesoporous silica films prepared by sol gel process and argon plasma calcination have been used to form hybrids for gas sensing applications by entrapping sensitive materials in the porous network. Plasma calcination, a low temperature process, is employed to gel the sol instead of conventional thermal calcination. Polymers and surfactants are used as templates for generating the mesoporous structure upon removal by the plasma calcination. TEM, EDX and FT-IR are used to characterize the obtained films. To demonstrate the gas sensing property of the functionalized silica films, 10 MHz Quartz Crystal Microbalance (QCM) coated with β-cyclodextrin (β-CD) functionalized silica film is tested as a sensor for benzene vapor detection. The higher surface area of the mesoporous silica films could accommodate more receptor molecules (β-CD molecules) and subsequently more target analytes that enhance the QCM response. The sensitivity of the QCM is enhanced by depositing plasma calcined mesoporous sensing films on the electrodes.

Keywords Gas sensor · Mesoporous silica film · QCM · Plasma calcination

1 Introduction

In this study, we attempt to incorporate sol-gel based mesoporous silica films with the quartz sensor for enhanced gas sensing. Sol-gel technique is used to deposit porous films on the quartz sensor electrodes. By forming a porous network film on top of the quartz electrode, the available surface area for the host receptor molecules is drastically increased and therefore the sensitivity. Quartz crystal microbalance (QCM) is widely used for measuring small changes of mass deposited on the surface of the quartz crystal. Quartz crystal microbalance consists of a quartz disk, two of its sides deposited with metal electrodes. QCM can be used as sensors for chemical and biochemical analysis by depositing sensitive receptor molecules on its electrodes [1, 2]. The immobilized receptor molecules selectively capture the associated target analytes, thereby reducing the resonant frequency of the QCM. This frequency change is correlated to the target analytes concentration in the test chamber.

Mesoporous silica films are deposited on the QCM electrodes using plasma calcination. Compared to conventional thermal calcination, plasma calcination is more attractive due to the advantages such as low processing temperature and shorter processing time, which would favor the preparation of mesoporous films on quartz disks with no risks of altering the piezoelectric property of the quartz disk. Polyethylene glycol (PEG) is used as the pore generation template. CD is chosen as the receptor molecules as it can host a wide range of target analytes in its hydrophobic cavity. CD is chemically bonded to the silica matrix via covalent linkages. The sensing performance of the obtained hybrid material coating to benzene vapor is tested. Compared to the reported β-CD-QCM chiral sensors [3, 4] and gas sensors [5, 6], where the CD molecules were either physically adsorbed onto flat gold surface by spray coating/drop coating or chemically adsorbed on flat gold surface through thiol-based self assembly, our approach would be advantageous in terms of high sensitivity and high stability.

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2 Experimental

10 MHz, AT-cut QCM crystals with polished gold electrodes (diameter 5.1 mm) were purchased from International Crystal Manufacturer (ICM, Oklahoma US). All the chemicals used for preparing the silica films were purchased from Sigma-Aldrich. β-CD and dimethylformamide (DMF) were dried to completely remove the moisture content prior to use. The QCM disks were immersed in 3-Mercaptoproplytrimethoxy Silane (3-MPTMS) solution in ethanol for 4 h and then spin coated with PolyEthylene Glycol (PEG: MW = 400) doped Si sol (PEG/silica ~30 mol%). The samples were then treated on a hotplate at 80°C for 20 min and calcined in the Trion Plasma Reactor. The plasma calcined silica film prepared on QCM was first thiolated by an impregnation in 100 mM 3-MPTMS in ethanol for 4 h. The thiolated silica-QCM was then annealed on a hotplate at 80°C for 30 min, followed by impregnation with the purified alkenyl-β-CD for 4 h to form covalent linkages between the silica film and alkenyl-β-CD under the anti-Markovnikov reaction conditions [7]. QCM disk carrying β-CD functionalized silica film was introduced into a sealed gas chamber (approximately 8 L). The response to different concentrations of benzene (5–500 μL) was then monitored. In order to investigate the improved performance brought by the 3 dimensional mesoporous silica films, alkenyl-β-CD was directly immobilized on a planar QCM without introducing the silica film.

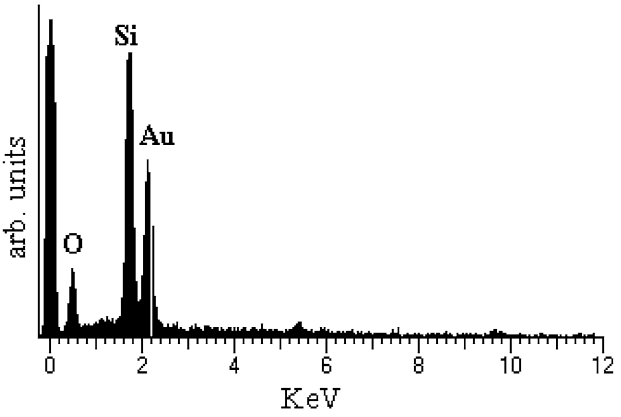

Fig. 2 EDX spectrum of the plasma calcined silica film

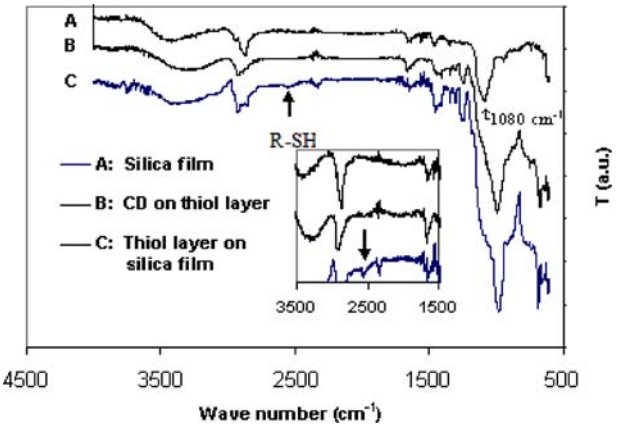

Fig. 3 FT-IR spectrum of the plasma calcined silica film

3 Results and discussion

Figure 1 shows the TEM image of the plasma calcined silica film. The mesoporous structure of the plasma calcined silica film can be seen from the TEM image with pores in the order of few nanometers. These colloidal pores in conjunction with the textural pores enhance the surface area of the silica film in order to accommodate more receptors molecules. The obtained silica film was first silanized with 3-MPTMS to introduce thiol groups on the surface. Alkenyl-β-CD molecules are then covalently bonded to the thiolated silica matrix through propyl thioether linkage.

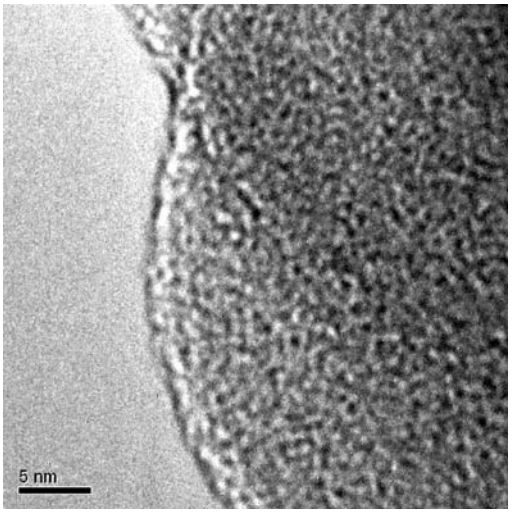

Fig. 1 TEM image of plasma calcined silica film

Figure 2 shows the EDX spectrum of the plasma calcined silica film obtained using JOEL SEM JSM 5600 system. The presence of silica film on the QCM is confirmed by the Si and O peaks. Figure 3 shows the FT-IR plot of the plasma calcined silica film obtained using Perkin-Elmer Spectrum 2000. The sharp peak at ~1080 cm^{-1} (Curve A) corresponds to Si—O—Si bonds and the removal of organic template (PEG) from the silica film could be confirmed by the absence of peaks at C—H range at ~2900 cm^{-1} (Curve A). The establishment of the covalent bond between the purified alkenyl-β-CD and the thiol functionalized silica film could be understood from the FT-IR plot shown in Fig. 3. The small peak at ~2540 cm^{-1} (SH stretching) [8, 9] in the curve C, corresponding to thiolated silica film, proves the presence of thiol group (R-SH) on the silica matrix. The inset in Fig. 3 clearly shows the absence of peak at 2540 cm^{-1} in curve B

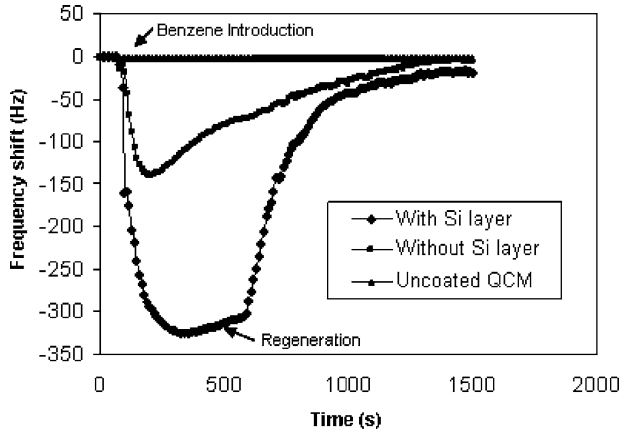

Fig. 4 QCM response to 500 μL of benzene in 8 L chamber

(corresponding to CD functionalized silica film), confirming that the hydrogen atom belonging to the thiol group has reacted with the modified CD, establishing the covalent bond between the silica film and the modified CD.

4 Sensor response

Figure 4 shows the response of the β-CD-QCM and β-CD/silica-QCM to 500 μL benzene in 8 L chamber. It can be seen that the β-CD functionalized QCM with mesoporous silica film (β-CD/silica-QCM) exhibits a higher frequency response to the target analytes when compared to β-CD functionalized flat QCM without mesoporous silica film (β-CD-QCM). This is because more β-CD molecules are incorporated in the mesoporous silica network, hence the number of bonding sites for the apolar benzene molecules is increased, which leads to a higher frequency shift. Quantitatively, at this test concentration, QCM incorporated with mesoporous silica film adsorbs approximately three times the benzene molecules that are adsorbed by the QCM without the porous network. As a result, the QCM with the silica layer shows a higher sensitivity, i.e., frequency shift/ppm benzene, than that of the flat QCM developed in this study and reported in a previous study [6]. A frequency shift of $\sim$0.3 Hz per ppm benzene is obtained in the concentration range up to 300 ppm. Figure 4 shows that there is almost no frequency change when the uncoated QCM is introduced to 500 μL benzene in the gas chamber, which confirms that frequency shifts obtained earlier are only due to the interaction between the target analyte (benzene) and the CD functionalized silica film. Since benzene is volatile, sensor regeneration is achieved by opening the chamber outlet.

5 Conclusion

Mesoporous silica films have been successfully prepared on the QCM through sol gel process in combination with argon plasma treatment. β-CD has been incorporated in the silica network through covalent linkages as a sensing material for detecting benzene vapors. QCM coated with β-CD functionalized mesoporous silica films exhibits higher frequency response to benzene vapors when compared to β-CD modified flat QCM. Further studies will focus on incorporating different receptor molecules in the porous network for various chemical sensing and bio-sensing and also on analyzing the influence of pressure, temperature, and moisture on the sensors response.

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