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Plasma Polymerized Calixarene Thin Films and their Sensing Properties to Chloroform Vapors

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The production of calixarene thin films via double discharge plasma technique and their sensitivity towards chloroform vapor are presented here in. The calixarene thin film is fabricated for the first time by plasma polymerized technique. Each experiment carried out at room temperature, at 0.6 mbar operating pressure, 2.0 kV DC and 19 kV pulsed voltages. From the UV-vis spectra it is observed that the polyconjugated structure is established and the thin films highly possess the characteristic bands of the oligomer. The SPR results revealed that the films thickness is at the order of several nm and the refractive index range from 2.2 to 2.8. The QCM results show that the thin films are highly sensitive with a fast and reversible adsorption to chloroform. The typical response time was of a few seconds.

Keywords Calixarene; chloroform; double discharge; gas sensor; plasma polymerization

1. Introduction

Gas sensors are vital instruments due to their ability to sense invisible and odorless toxic gases. Gas sensors formed with polymers as active layer have received a great deal of interest with their advantages i.e., low cost synthesis, rapid measurement, and tunable physical and chemical properties, preferable to the conventional metal oxide sensors [1,2].

For synthesizing of thin active polymer layer for sensors, besides the wet processing like chemical and electrochemical methods, dry polymerization method is solvent free one that allows depositing polymer directly from the monomer and/or oligomer [3]. There are several techniques available for dry polymerization method such as physical vapor deposition, and plasma polymerization (PP). PP technique is a pin-hole free, room temperature process and can be used to deposit onto almost any substrate with thickness ranges from tens of angstroms to

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micrometers [4,5]. But it is difficult to predict the exact chemical structure of a deposited surface from plasma technique, because of the reactive species (e.g., radicals, ions, and electrons) present and polymerization process referred as an atomic process [6]. The molecular structure and properties of the plasma polymer depend on the monomer, gas phase composition, monomer flow rate, reactor pressure, plasma power and the geometry of the reactor.

The calixarenes are well known compounds with their flexible symmetric cone structures and frequently being used as ion and small molecule traps via host-guest interaction between the molecular cavity and guest molecule. The thin films of calixarenes and its derivatives have been produced via several techniques, such as Langmuir-Blodgett (LB), self-assembly, and spin-coating, and been demonstrated to form complexes with organic vapor molecules [7–10]. A systematic examination shows that the often-observed high symmetry of the host lattice normally reflects the shape and dynamics of molecular guests. Lattice distortions and disorder can be introduced by steric interactions between guest and host or inter-guest polar interactions [11]. Due to these interactions [11] and their multiplicity of options for several structural designs, calixarenes and their derivatives are having a great number of works in the sensor application area [12,13].

Herein, calix[8]arene (C8), and calix[4]arene (C4) thin films are synthesized for the first time by double discharge plasma technique (DDPT). The absorption behavior of C8, C4 oligomers and their thin films were characterized by UV-vis spectroscopy; the thickness and the refractive index of the films were studied by Surface Plasmon Resonance (SPR) Spectroscopy; and the kinetic response of the plasma polymerized calixarene thin films against chloroform vapor was investigated by Quartz Crystal Microbalance (QCM) technique. Since chloroform is widely used in industry and breathing (above 900 ppm) for a short time can cause dizziness, fatigue, and headache, and being toxic, it attracts most researchers to study reliable, selective and sensitive chloroform sensors. We found that the kinetic responses of the thin films to the chloroform vapor are almost fully reversible with a fast response and recovery times.

2. Experimental Details

The details of the experimental setup and the deposition procedure have been described elsewhere [14–16]. It consists of three cylindrical hollow electrodes $K_{1,2}$, A_1 , A_2 and two quartz tubes with 100 mm length and 30 mm internal diameter in between them (Fig. 1). While an ordinary low-pressure glow discharge is operating between hollow cathode and A_1 , a high pulsed voltage with a 5 Hz repetition rate

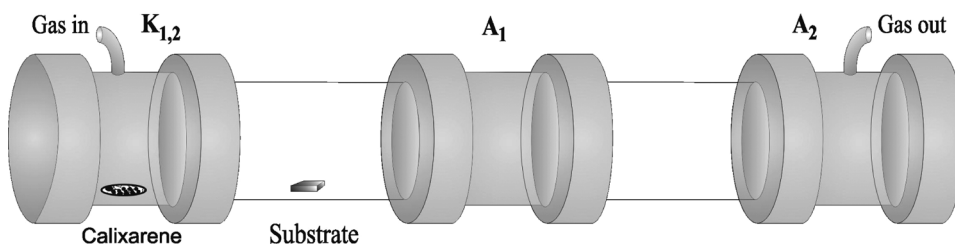


Figure 1. The calixarene and the substrate position in the DDPT device.

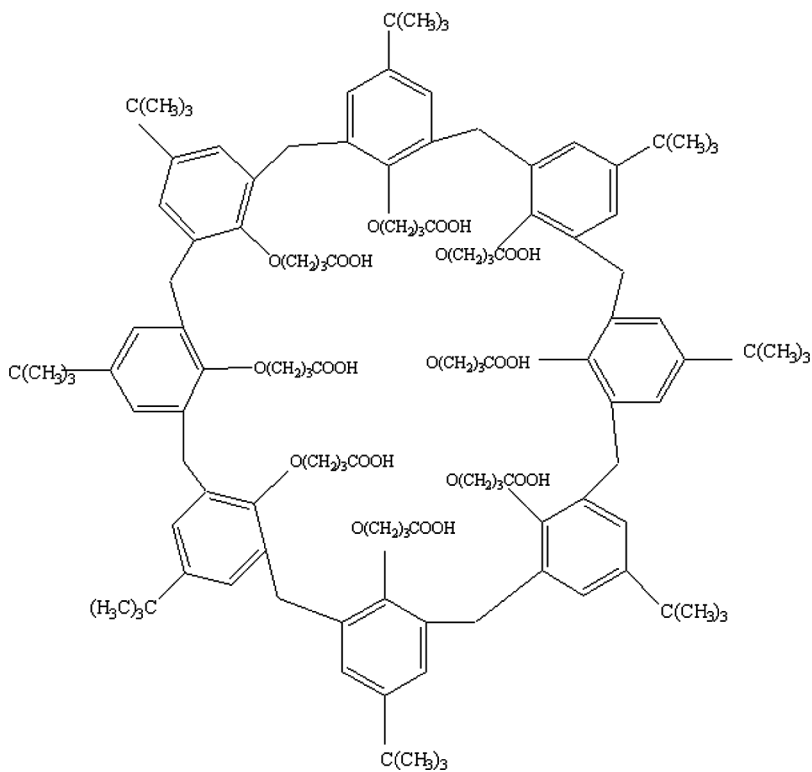


Figure 2. The Chemical structure of Calix[8]arene.

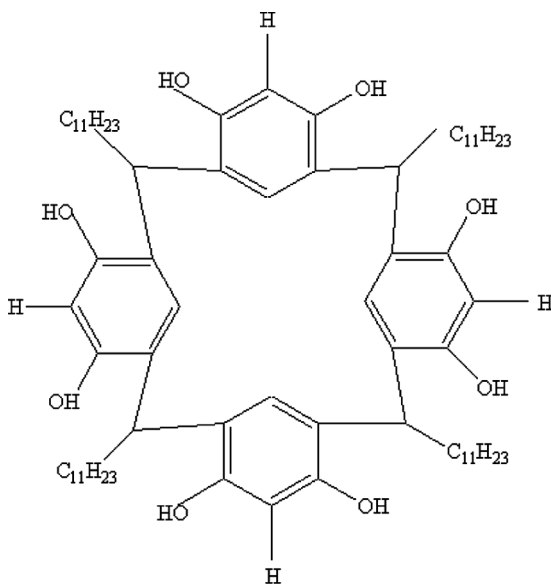


Figure 3. The Chemical structure of Calix[4]arene.

is applied to $K_{1,2}$ and A_2 . For specific values of current and pressure, a filamentary pulsed discharge with 2 mm diameter is formed along the symmetrical axis of the tube.

The chemical formula of C8 and C4 which were synthesized at the Institute of Bioscience and Technology, Cranfield University at Silsoe, Cranfield, UK, are shown in Figures 2 and 3, respectively. The calixarene powder was inserted at the cathode of the device as plasma precursors at an Ar carrying gas and the substrates were located in between $K_{1,2} - A_1$ as shown in Figure 1. Each experiment carried out at room temperature, at 0.6 mbar operating pressure, 2.0 kV DC and 19 kV pulsed voltages. Three different substrates were coated at the same plasma parameters; quartz glasses for UV-visible spectroscopic investigations, Au deposited glass for Surface Plasmon Resonance (SPR) and quartz crystal substrates for Quartz Crystal Microbalance (QCM) studies.

3. Results and Discussion

The UV-visible spectrum was recorded by Analytikjena Specord S600 spectrometer to investigate the absorption behavior of the calixarene's and the plasma polymerized thin films. The UV-vis spectra of C8 and C4 powders and the plasma polymerized thin films are given in Figure 4. The powder spectra of C8 and C4 were obtained in a chloroform solution and the thin films' were obtained from the films synthesized onto quartz glass substrates.

The dashed lines in Figure 4(a) and (b) indicate the spectra of C8 and C4 powder, respectively, obtained from a chloroform solution and the solid lines are the absorption spectra of the plasma polymerized thin films. The maximum absorption wavelengths (λ_{\max}) of the oligomer and the thin film of them almost resemble similar structure; however, the relative intensity of these peaks is differing from each other. We thought that the difference appear due to the high energy input, plasma polymerization involves monomer/oligomer fragmentation [6]. It is reported [17] that the linear as well as the cyclic oligomers have a pair of absorption maxima at 280 and 288 nm. In our case, those peaks overlaps with each other and observed at around 285 nm. Moreover, the polyconjugated structure is dedicated from the absorption edges of the synthesized C8 and C4 thin films that shift to higher wavelength values [18].

Surface Plasmon Resonance Spectrometer (BIOSUPLAR 6 Model) with a low power laser diode (630–670 nm) light source was employed to perform SPR measurements with an angular resolution of 0.003 degrees. A glass prism ($n = 1.62$) is mounted within a holder so as to be available for measurement in liquid or in air environments. Glass slides with the dimensions $20 \times 20 \times 1$ mm are coated on top by a very thin (~ 50 nm) homogeneous layer of gold. A transparent plastic flow cell was made in house to be allowing vapor measurements. The cell has two channels, with inlets and outlets connected to silicone tubes. The photodetector response was monitored as a function of time during periodic exposure of the sample to the organic vapor for at least 2 minutes; this was then allowed to recover after injection of dry air. WINSPALL software developed at the Max-Plank-Institute for Polymer Research, Germany was utilized for the fitting of SPR curves to determine thickness and refractive index values of the films.

The SPR spectra measured in air before and after polymer deposition on the bare gold layer for C8 and C4 are shown in Figure 5(a) and (b), respectively. As it is expected, the SPR curves of C8 and C4 become broader and the minimum

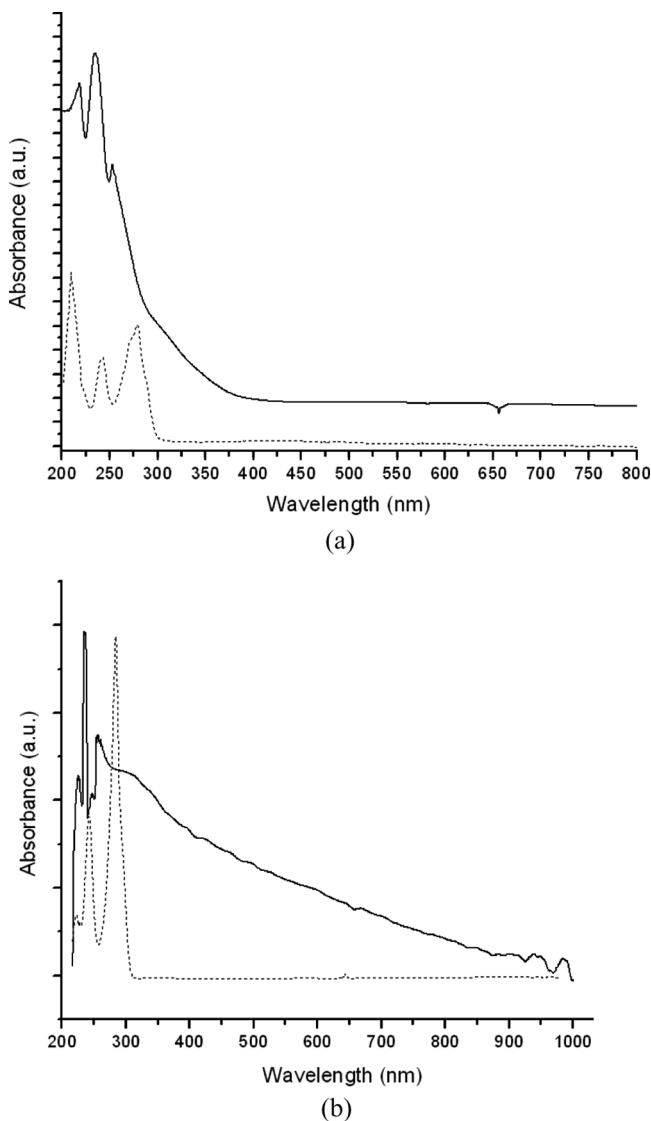
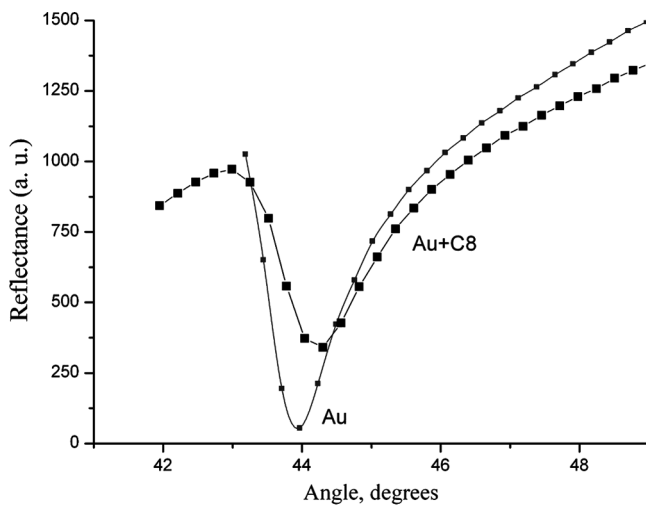


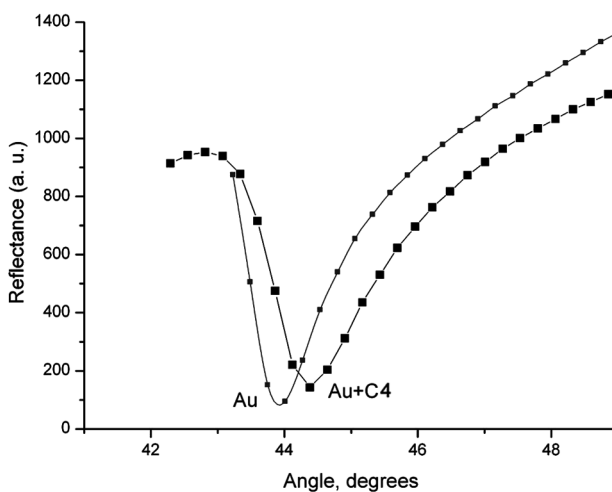
Figure 4. The UV-visible absorption spectra of (a) C8, and (b) C4, where the dashed lines indicate the spectra of powders in chloroform solution and the solid lines are the plasma polymerized thin films.

reflected intensity rises to a higher value. The film thickness and refractive index of C8 and C4 were calculated by fitting the SPR curves with a Fresnel formula algorithm by use of the Winspall software. It is found that the thickness of C8 and C4 are of about 8.0 and 7.9 nm, and the refractive indexes are 2.2 and 2.8, respectively.

QCM technique was employed to study the kinetic response of the plasma polymerized calixarene thin films against chloroform vapor. The QCM is a well-known and widely used device in sensor applications due to eliminating the sophisticated preparation of samples and expensive off-site analysis. The QCM measurements



(a)



(b)

Figure 5. The SPR spectra measured in air before and after polymer deposition on the gold layer for (a) C8 and (b) C4.

were performed at room temperature using an in-house designed oscillating circuit [19] and standard quartz crystal with a nominal resonance frequency of 10 MHz. Figure 6(a) and (b) show the kinetic response of C8 and C4 thin films against chloroform vapor. The variation of the frequency changes was monitored as a function of time when the sample was periodically exposed to the chloroform for at least 5 minutes and was allowed to recover after the injection of dry air. The plasma polymerized thin films show a response to chloroform vapor with a fast, reproducible and reversible response after flushing the gas cell with fresh air. While the frequency increase of C8 is more regular than that of C4 when the concentration of chloroform increased, the response of C8 to saturated chloroform exposures is larger than C4 one with recovery times of the order of a few seconds when the gas cell is flushed

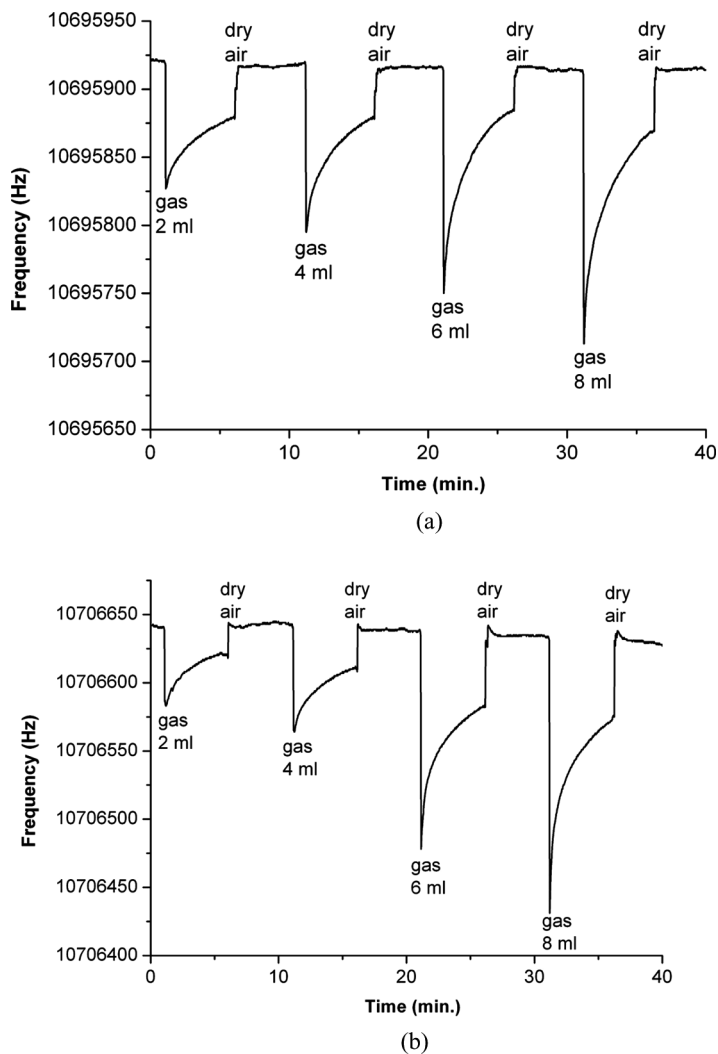


Figure 6. The kinetic responses of (a) C8 and (b) C4 thin films to chloroform vapor with increasing concentration.

with dry air. We thought that an in-situ Fourier Transform Infrared Spectroscopy (FTIR) is essential to investigate the mechanism of chloroform adsorption on the thin films.

4. Conclusion

We presented the plasma polymerized calix[8]arene and calix[4]arene thin films deposited by double discharge plasma technique on three different substrate at the same plasma parameters. The UV-vis spectra revealed that the thin films highly possess the characteristic bands of the oligomer, and the polyconjugated structure is obtained upon the deposition. The SPR measurements showed that the deposited film thickness is at the order of nm's with refractive indexes 2.2 and 2.8 for C8 and

C4 respectively. The kinetic response of QCM revealed that both thin films are significantly sensitive to chloroform vapor with a fast, large and reversible response and both responses depend on the concentration of chloroform.

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