



The properties of carbon nanotube on novel calixarene thin film

Amira Shakila Razali^{1,*}, Faridah Lisa Supian^{1,†}, Suriani Abu Bakar^{1,‡}, Tim H. Richardson^{2,§}, Noor Azyyati Azahari^{1,**}

¹*Department of Physic, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia.*

²*Department of Physic & Astronomy, University of Sheffield, Hounsfield Road, S3 7RH, United Kingdom.*

Abstract

This study focuses on the properties of carbon nanotube effect on novel calix[8]arene thin film as ion sensing application. The modification of calix[8]arene and carbon nanotube (CNT) were made by both components dissolved completely in chloroform (CHCl_3) for 12 hour sonication process, hence cutting off long carbon nanotubes structures and opening their ends [1]. By using spin coating techniques, the thin films were deposited on silicon substrate layer by layer. The morphology and composition of CNT-calix[8]arene have been characterized by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) and Raman Spectroscopy. UV-Visible spectrometer also studied in order to understand the behaviour in the molecular level. These supra-molecule material have high potential in the development of sensors to be applied in removing organic and inorganic contaminants from water to safe levels.

Keywords: Calix[8]arene; Carbon Nanotube; Modification.

1. Introduction

Water contamination by toxic compounds is one of the problems faced by the community in recent years. The contamination appears from the natural sources such as heavy metal in water and it can also turn up from the industrial effluents. Most of researches are unable to remove both organic and inorganic pollutant as well as toxic pollutant down to parts-per-billion level [2]. Hence, it is important to develop a sensor that can effectively remove a wide range of pollutants from water.

The application of carbon nanotubes in sensors has the potential of revolutionizing the sensors industry due to their inherent properties such as small size, high strength, high electrical and thermal conductivity [3,4]. Carbon nanotubes (CNTs) are hexagonal networks of carbon have diameter of a few nanometer and length up to 100 μm [5]. Carbon nanotubes consist of one or more graphene sheets rolled as cylinders [6].

*) For correspondence, E-mail: eirasya@yahoo.com.

†) For correspondence, E-mail: faridah.lisa@fsmt.upsi.edu.my.

‡) For correspondence, E-mail: absuraini@yahoo.com.

§) For correspondence, E-mail: t.richardson@Sheffield.ac.uk.

**) For correspondence, E-mail: azyyati_noor@yahoo.com.

Calixarene are cyclic oligomers formed via a phenol-formaldehyde condensation. They exist in a ‘cup’ like shape with a defined upper and lower rim and a central annulus as shown in Fig. 1. The rigid conformation enables calixarenes to act as host molecules as a result of their preformed cavities. By functionally modifying either the upper and lower rims, it is possible to prepare various derivatives with differing selectivities for various guest ions and small molecules [7].

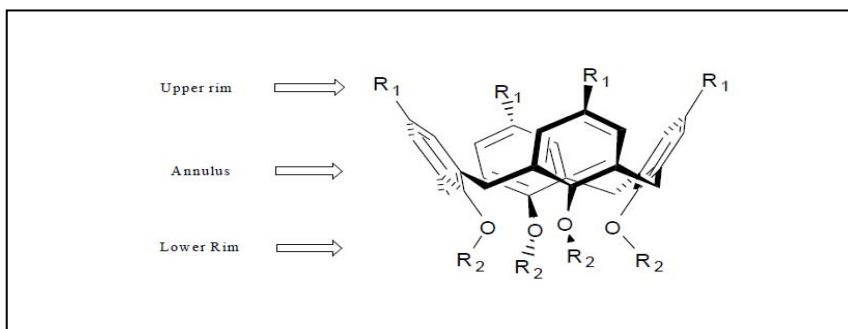


Fig. 1: Division of calix[4]arene (applicable to all the calixarene) [7].

The adsorption properties of the carbon nanotubes to a series of toxic agents, such as lead (II), cadmium (II) and lead (II) have been studied and tested for removing pollutants from water [8,9]. The results reported by Y. H. Li and Y. M. Zhao showed that carbon nanotubes are effective in removing these pollutants from water [10]. The combination of two materials, calixarene and carbon nanotubes are ideal material because this combination are useful in improving mechanical strength and the recovery of polymeric materials [2].

In this investigation, we use a type of calix[8]arene that were modified with carbon nanotube to achieve on the new properties as ion sensor application.

2. Experimental

In this study, calixarene has been selected as a base molecule and named as calix[8]arene. The chemical structure of calix[8]arene is shown in Fig. 2. The calix[8]arene could be dissolved in chloroform to give concentration of 0.2 mg ml^{-1} . The multiwalled carbon nanotube (MWCNTs) with outer diameter 10nm and 1-5 μm long were obtained from Advance Nanocarbon Sdn Bhd.

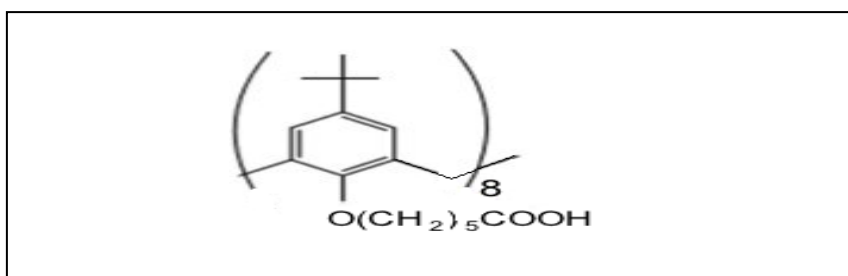


Fig. 2: The chemical structure of calix[8]arene molecule.

Calixarene modified carbon nanotube was prepared by dissolving 2 mg calix[8]arene powder in 10 ml of chloroform (CHCl_3) were ultrasonicated for one hour to be completely dissolved. Carbon nanotube (CNT) were added into calix[8]arene solution and also sonication process in 12 hours was applied into these mixture of solutions. The solution was kept in room temperature for 48 hour. The thin film of CNT-calix[8]arene were deposited layer by layer on silicon substrate (1x1) cm using spin coating technique. The spin speed of spin coating was 3000 rpm and acceleration time were 15.0 s and two thin films were done.

Surface pressure-area (π -A) isotherm were studied using Langmuir method, a solution of calix[8]arene in chloroform was prepared with a concentration of 0.2 mg ml^{-1} . The solution was spread on to water subphase with varying volume (50, 100, 150 and 200) μL . The UV-visible spectra of CNT-calix[8]arene were recorded in the ultraviolet and visible spectral region from 190 to 800 nm. JASCOV-570 model UV-Vis Spectrometer was in absorbance mode. Raman spectra were determined on a Renishaw inVia Raman Microscope in order to investigate the effect of calix[8]arene on carbon nanotube (CNT) crystallinity. High Resolution Field Emission Scanning Electron Microscope (FESEM) model Hitachi SU 8020 UHR was used in this experiment that enables to visualize the morphology of the surface.

3. Result and Discussion

3.1 π -A Isotherm

Isotherm graph of the calix[8]arene were obtained at the air-water interface by recording surface pressure as function of mean molecular area. These measurements were repeated several times using identical and different volume spreading (50, 100, 150 and 200) μL and result demonstrated good stability and reproducibility of the monolayer at the air-water interface.

Fig. 3 displays the isotherm of calix[8]arene with different volume spread. All solution exhibits solid phase when the surface pressure reached 20 mN/m. By extrapolating the steepest part of the graph to 0 mN/m at y axis, the mean molecular area can be deduced. The radius of calix[8]arene cavity was determined from isotherm and the cavity's radius is inversely proportional to spreading volume. The increasing spreading volume has affected the mean molecular area. This is most probably due to the orientation of the molecule are pack when the spreading volume was added into the through. The radius of calix[8]arene has been determine in Table 1.

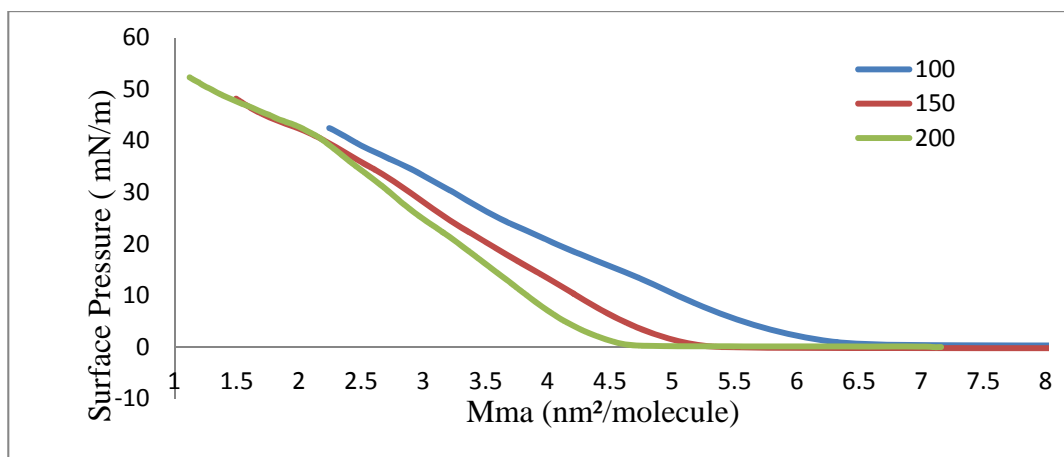


Fig. 3: Isotherm of Calix[8]arene with different volume spread with water.

Table 1: Mean molecular area and radius of calix[8]arene

Volume (μL)	Mean molecule area, Mma (nm^2)	Radius (nm)
100	5.465	1.319
150	4.678	1.220
200	4.430	1.187

3.2 Field Emission Scanning Microscope (FESEM) & Energy dispersive X-ray (EDX)

High resolution field emission scanning microscope (FE-SEM) enables to visualise the morphology of the surface. Fig. 4a and 4b show the morphology of carbon nanotube without calix[8]arene and within calix[8]arene. The formation of calix[8]arene on the exterior walls of the carbon nanotube can be seen from the feSEM micrographs, shown in Fig. 4b. This formation of calix[8]arene on the outer walls of carbon nanotube was supported by using energy dispersive x-ray (EDX) as shown in Fig. 4c. The presence of the peak for oxygen, $K_{\alpha}=0.525$ KeV indicated that the calixarene had been successfully incorporated with carbon nanotube into the thin film.

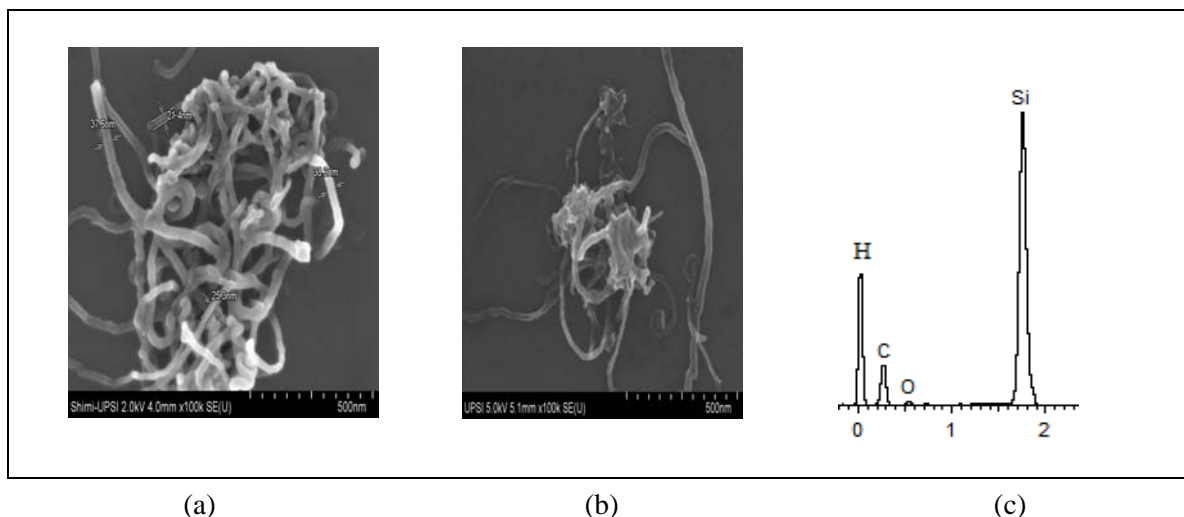


Fig. 4: The high-resolution field emission scanning microscope (FESEM) of carbon nanotube (a) without calix[8]arene (b) within calix[8]arene and (c) EDX analysis of CNT-calix[8]arene.

3.3 Raman Spectroscopy

Raman spectroscopy was used to confirm the interactions between calix[8]arene molecule and carbon nanotube as shown in Fig. 5. Raman spectrum of carbon nanotubes without calix[8]arene exhibits normal two peak at 1588.45 cm^{-1} for graphite (G) peak and 1363.74 cm^{-1} for defect (D) peaks. The ratio of the intensities of these peaks, I_D/I_G was determined to be 0.78. Raman spectrum done on CNT-calix[8]arene shows that G and D peak have been shifted to higher wave number of 1605.78 cm^{-1} and 1387.92 cm^{-1} respectively. This evidence that prove the presence of both calix[8]arene and carbon nanotubes in thin film.

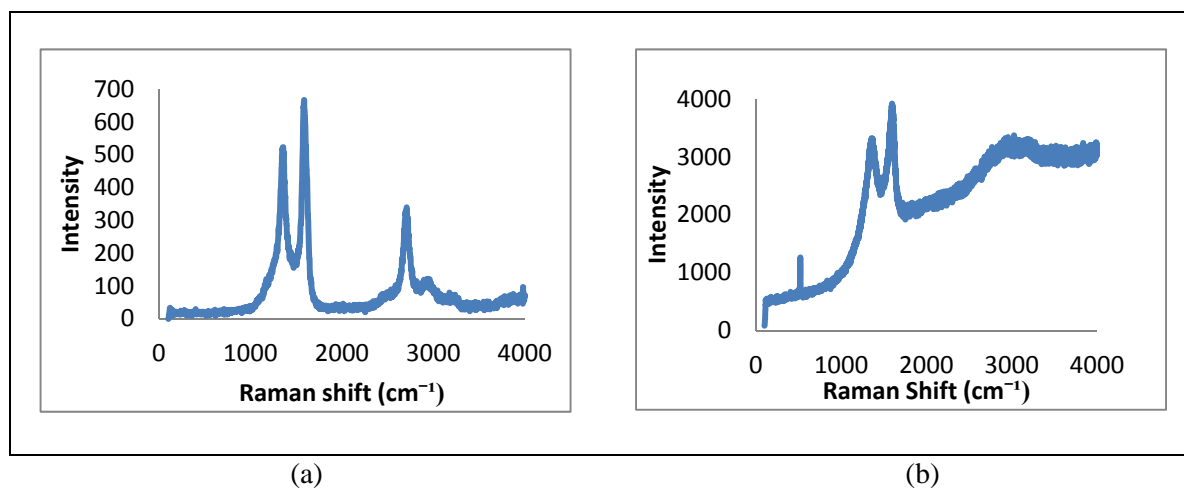


Fig. 5: Raman spectra of carbon nanotube (a) without calix[8]arene (b) within calix[8]arene.

3.4 UV-Visible Spectroscopy

The UV-Vis spectra of calix[8]arene and CNT-calix[8]arene are shown in Fig. 6. The absorption spectra exhibits a peak at 212 nm of calix[8]arene and it attributed to π - π^* transition. The general shape of the absorption spectra is same for calix[8]arene within carbon nanotube or without carbon nanotube. But in CNT-calix[8]arene, the absorption peak are shifted to 210 nm. A similar observation on carbon nanotubes modified calixarene has also been reported by Maria Ignat [11]. This blue shift indicates the presence of interactions between carbon nanotubes and calix[8]arene on external surface.

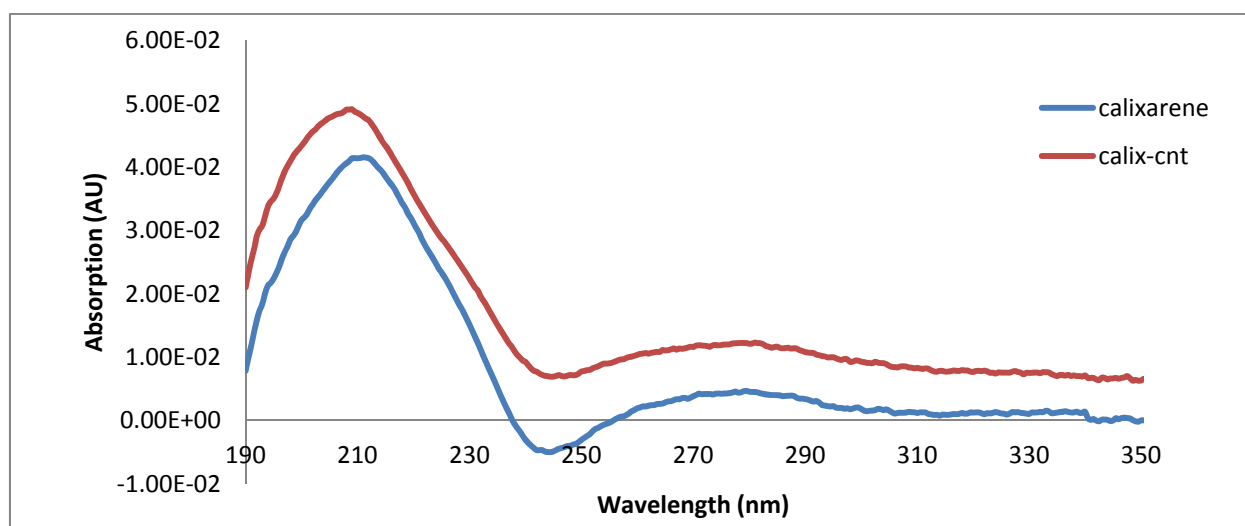


Fig. 6: UV-Vis spectra of calix[8]arene and CNT-calix[8]arene.

4. Conclusion

The properties of carbon nanotube on novel calixarene thin film by using spin coating method have been investigated using isotherm graph, UV-Vis spectra, Raman spectra and FESEM. Π -A isotherm have explained that the size of calix[8]arene molecule. The Π -A isotherm shifted to the left with increasing the volume spread and the optimum size of calix[8]arene is 4.43 nm² in 200 μ L at 0.2 mg/ml concentration. From Raman spectra, the combination of two compounds, calix[8]arene and carbon nanotube were shifted to higher wave number in Raman spectra from 1588.45 cm⁻¹ to 1605.78 cm⁻¹ that prove the presence of calix[8]arene in carbon nanotubes. UV-Vis result explain that CNT-calix[8]arene is shifted to 210 nm indicate the interaction between calix[8]arene and carbon nanotubes.

Acknowledgments

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