

Characterization and optical properties of 1,5-diphenylcarbazide sensor thin film for sensing application

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Optical properties of 1,5-diphenylcarbazide sensor thin film have been investigated. In this project, The 1,5-diphenylcarbazide solution was prepared by dissolving powder form of 1,5-diphenylcarbazide with three types of solvent which were acetone, acetic acid and ethanol with 0.08 mol L⁻¹ molar concentration. It was then deposited on glass cover slip (substrate) using spin coating technique. The obtained thin film was confirmed and characterized by FTIR and AFM while the optical properties were evaluated by UV-VIS NIR spectroscopy. From the absorption edge studies, the values of the absorption coefficient and optical band gap have been found to be varies from 3.97 eV to 4.09 eV. From the experimental results, values of optical band gap are calculated and found to be dependent on the molar concentration of solution and type of solvents used.

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1. Introduction

1,5-diphenylcarbazide has been used as a reagent in the laboratory for many research areas especially in electrochemical studies, molecular studies and many more. Despite of the instrumental improvements of the last decades, the colorimetric techniques are still attractive from an analytical point of view since they are cheap, sensitive and easy to implement in routine laboratories [1]. In the other hand, Pflaum and Howick state that in the field of trace metal determinations, a plethora of organic colorimetric reagents are still widely employed [2]. One of organic colorimetric reagents that deserves a special attention is 1,5-diphenylcarbazide, which is commonly used in determination of trace metal.

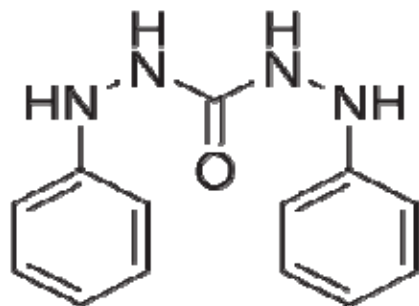


Fig 1. Molecular structure of 1,5-diphenylcarbazide (C₁₃H₁₄N₄O).

1,5-diphenylcarbazide (C₁₃H₁₄N₄O) has melting point in between of 173 – 176 degree Celcius and it have molecular weight of 242.28 gram per mole. The physical state is in solid form and usually appears in white or pink and odorless powder. Pure C₁₃H₁₄N₄O is stable and sensitive to the light. It can be easily soluble in hot alcohol, acetone, ethanol and glacial acetic acid. Furthermore, it is incompatible with oxidizing agent because it can be easily oxidized to diphenylcarbazone. However, through several decades later many questions regarding the mechanism of these reactions remain unexplained. The mechanism of oxidation of 1,5-diphenylcarbazide into diphenylcarbazone was recently studied by using electrochemical and spectrochemical techniques by Balt and Van Dalen in the year 1962 [3,4]. However, no confirmation of the possible intermediates was given probably due to the similarity between both of their properties. 1,5-diphenylcarbazide also can be considered as an importance substance to detect heavy metal ion especially in environmental pollution. Research done by Jaya and Ramakrishnan in the year 1982 had used 1,5-diphenylcarbazide to determine osmium using spectrophotometric method [5].

Research on thin film started in the 17th century but it seemed to be simply based on curiosity. In the 19th century, the scientific research is thought to have begun. Thin film is widely spread in development of optics, electronics and electron spectroscopy in the 20th century. Nowadays, the results of researches play the most important rules in advanced technology where thin films

are one of the most important tools for the preparation of novel materials.

Sensors in a thin film form provide a minimally importunate means of measuring surface parameters, such as strain or temperature in inimical environments. They are needed in engine system to evaluate advanced materials and components and to provide experimental verification of computational models. Some of the relevant characteristics of sensors are flexibility and elastically. They can be configured as single sensors or arranged in a matrix to fit different measuring surfaces. By selecting proper material and design will give novel sensors the ability to conform around highly contoured sites without wrinkling. An assortment of coatings can be applied to novel sensors.

The important of optical properties are absorption, refractive index, dispersion and transmission. Usually these properties are classified by the chemical composition and by melting process to a lesser degree and the subsequent thermal treatment. Basically, optics brings a lot of benefit into human life either in the field of technology or even in science field [6].

For optical materials in imaging or non-imaging optical system detailed knowledge of the wavelength dependent complex index of refraction is important for optical system design and performance. The optical absorption of UV light by the materials can contribute to optical degradation of the materials and reduced performance over time [7].

The optical properties of polymer are widely spread in the research area recently [8-12]. For instance, in the year 2009, Samuels *et al.* had studied the optical properties of various fluoropolymers, hydrocarbon polymers, and polyimides. It is useful for concentrator photovoltaic (CPV) system design of the geometrical optics and also provides insights into the system's optical absorption. When a light passes through compound, the molecules will absorb the light energy. Eventually, an electron is promoted from an occupied orbital to an unoccupied orbital. The transition that results from the absorption of light is known as the transition between electronic energy levels. The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole [13].

The absorption spectrum for an atom that absorb in ultraviolet sometimes consists of very sharp lines, as would be expected for a quantized process occurring between two discrete energy levels. The energy level diagram of isolated atoms consists with discrete energies. The optical transition between these level give rise to sharp lines in the absorption and emission spectra [13].

However for molecules, the ultraviolet absorption usually occurs over a wide range of wavelengths because there are many states of vibrational and rotational excitation. The rotational and vibrational levels are thus, superimposed on the electronic levels and give a combination of overlapping lines. This appears as a continuous absorption band. A molecule may therefore undergo electronic and vibrational-rotational excitation simultaneously [14]. Hence, it can be observed that a molecule usually consists of a broad band of

absorption centered near the wavelength of the major transition.

The application of 1,5-diphenylcarbazide for the analytic determination of metal species such as chromium, copper and mercury were firstly reported by Cazaneuve in the year 1900 [15]. By far, the reaction with chromium is received more attention since it has high sensitivity and selectivity. However, there is no work reported to link the relationship of optical properties of 1,5-diphenylcarbazide in determining the metal species. It is of interest to study the optical properties of 1,5-diphenylcarbazide thin film with solvents used which are acetic acid, acetone and ethanol.

2. Experimental

2.1. Chemical preparation

1,5-diphenylcarbazide with 242.85 g/mol molecular weight was purchased from BDH Chemicals LTD (Poole, England). The powder form of 1,5-diphenylcarbazide is dissolved with three types of solvent which are glacial acetic acid (R&M Marketing, Essex, UK), absolute ethanol (HmbG Chemicals, IL, USA) and acetone (HmbG Chemicals, IL, USA). The process has been carried out in room temperature. 1.0 g of 1,5-diphenylcarbazide have been prepared and dissolved it in 50 ml solvent. It was dissolved in glacial acetic acid, acetone and ethanol solution. The solution was stirred until 1,5-diphenylcarbazide dissolved. The solution is transferred into 50 ml volumetric flask until reach the mark point of volumetric flask.

2.2. Preparation of films

The glass cover slips were cleaned using acetone to clean off the dirt on the surface of glass laid. Then they were deposited with the analytical solution using spin process controller (Spin-3000 A, Midas System). Spin coating technique was used to produce a thin layer on the top of the glass [16,17]. Approximately 1 μ l of the solution was placed on the glass slip. The glass cover slip was spun at 4000 rev/min for 60 second using spin coating system [18-20]. After that, the glass cover slip was allowed to dry at room temperature for 3 minutes.

2.3. Characterization of sample

Morphological features and surface characteristics of sample were obtained from scanning electron microscopy (SEM) using JEOL JSM-6400 microscope (Tokyo, Japan). UV-VIS NIR spectrophotometer (UV-3600) from Shimadzu (Kyoto, Japan) was used to determine the absorbance of samples in the range of 200-900 nm. Accordingly, the predetermined electromagnetic radiation wavelengths for ultra-violet (UV) is between 300-400 nm, visible (VIS) is 400 to 765 nm and near infra-red (NIR)

are defined as 765 to 3200 nm. The Fourier transform spectroscopy (FTIR) spectra of the sample ranging from 400-4000 cm^{-1} were obtained on a Perkin-Elmer spectrophotometer (CA, USA).

3. Result and discussion

3.1. Fourier transform infrared spectroscopy (FTIR) spectra

The Infrared spectrum is basically a plot of transmitted frequencies against intensity of the transmission. Frequencies appear as x-axis and in the units of inverse centimeters or known as wavenumbers. Meanwhile, intensities are plotted on the y-axis in percentage units. Moreover, infrared spectrum is useful in providing information about the presence or absence of specific functional groups in the compounds.

Fig. 2 shows that the presence of C-O-H bending that appears broad and weak peak at 1391.23 cm^{-1} , 1389.87 cm^{-1} , and 1392.32 cm^{-1} for sample acetic acid, acetone and ethanol respectively. Aromatic rings also presence between 900-690 cm^{-1} [21].

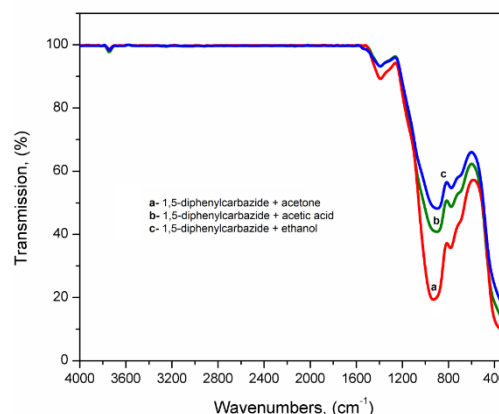


Fig 2. Infrared spectrum of 1,5-diphenylcarbazine with different solvents

From the infrared spectrum, the functional group that presences in the infrared spectrum are alkenes, alcohol and aromatic rings only. Ajay *et al.* study that reduction of carbonyl group in 1, 5-diphenylcarbazine occurs in the presence of alkali and acidic buffer solution [22]. This might be answering the absence of amides group in the infrared spectrum obtained in this research. Table 1 shows the band details that presence in the particular wavenumber.

Table 1. Band assignment at particular wavenumber

Sample	Wavenumber (cm^{-1})	Band Assignment
1,5-diphenylcarbazine + Acetic acid	1391.23 900.99	C-O-H bending vibrations Aromatics (out of plane bend) =C-H bending vibrations
1,5-diphenylcarbazine + Acetone	1389.87	C-O-H bending vibrations
1,5-diphenylcarbazine + Ethanol	1392.32 896.83 773.63	C-O-H bending vibrations Aromatics (out of plane bend) =C-H bending vibrations Alkenes (C=C) (out of planed bend)

3.2. Surface morphology study

Fig. 3 shows the sample thin film surface that obtained from scanning electron microscopy working in tapping mode.

Six measurements were performed on each sample at different positions on the surface in order to achieve statistical significance. The surface morphology of 1,5-diphenylcarbazine with acetone solution was the smoothest compared to other samples.

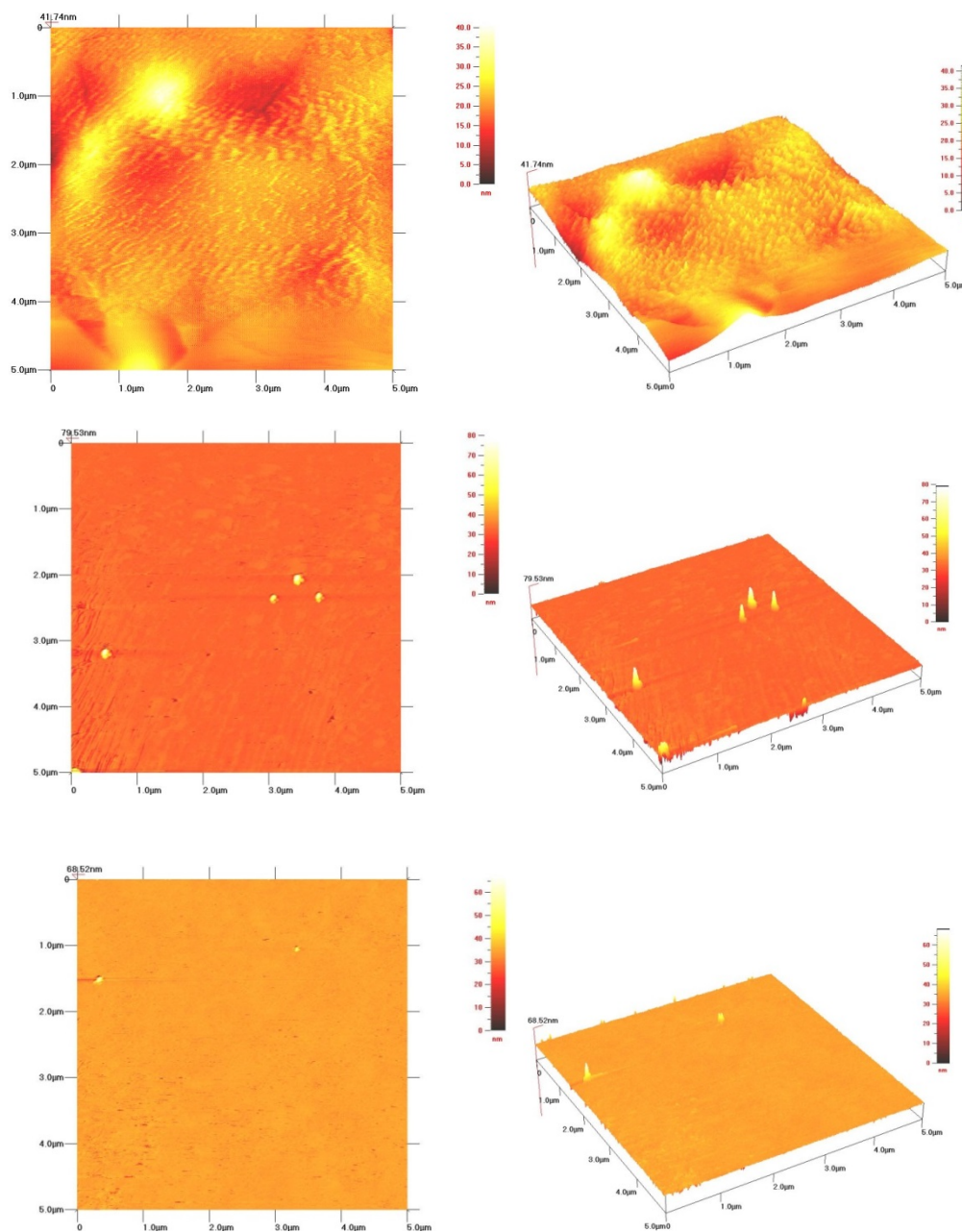


Fig 3. SEM images (2D and 3D) of 1,5-diphenylcarbazide with acetic acid (a), acetone (b) and ethanol (c) solution

This may be due to the high evaporation rate of acetone, which might give effect to the surface morphology. The surface roughness obtained for acetic acid, acetone, and ethanol were 6.2 nm, 3.4 nm, and 5.7 nm, respectively. The roughness implies that a smoothing mechanism by surface diffusion. This result proves that the use of acetone can improve the surface of the thin film [23,24].

3.3. UV-VIS NIR studies

3.3.1 Relationship between Absorbance (A) and Wavelength (λ)

The absorbance (A) of a sample is defined by Tauc [25]:

$$A = \log_{10} \frac{I}{I_0} \quad (1)$$

where I is the transmitted light intensity and I_0 is the intensity of the light before it enters the sample or incident light intensity. The optical absorption spectrum of a compound is shown in the graph as a plot of the light absorbed by the compounds against wavelength. In the graph, the absorption maxima (λ_{\max}) in the region of the spectrum can be determined.

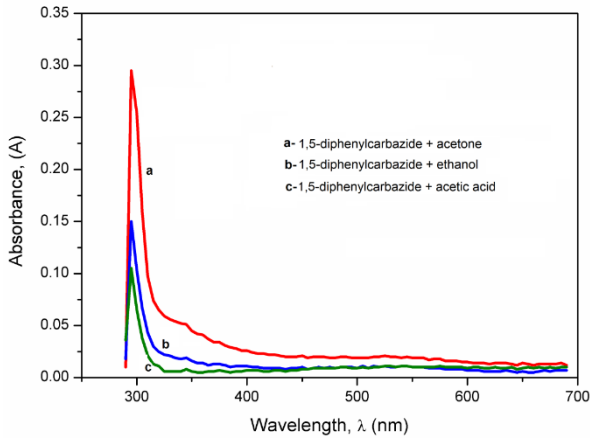


Fig 4. Optical absorbance spectra for 1,5-diphenylcarbazine with different solvents

Fig. 4 shows the optical absorption spectra for 1,5-diphenylcarbazine solutions with molar concentration of 0.08 mol L^{-1} . As we can see from the graph, the absorption edge is sharply defined at the 295 nm (λ_{max}). Lampman *et al.* said that two bands of medium intensity with λ_{max} above 200 nm generally indicate the presence of an aromatic system [13]. This is proved because the molecular structure of 1,5-diphenylcarbazine contains aromatic system. Acetic acid has the absorption value of 0.105 meanwhile the absorption value for sample acetone and ethanol is 0.295 and 0.150 respectively. The lowest value of absorption intensity was attributed to the acetic acid as it is a strongest polar solvent, which has a smaller difference in electronegativity. The polarity of the solvent can be arranged into the increasing of polarity, (i.e., acetone < ethanol < acetic acid). The intensity of absorbance is related to the dipole of the bond. It was observed that the smaller difference in electronegativity of bonded atoms has a smaller dipole moment, hence, the absorbance intensity becomes lower. Furthermore, the absorption edge of the acetic acid had shifted to the longer wavelength when the solvent was changed to the acetone solution. Such red shift was probably due to the impact of polar solvents, where, it can stabilize the excited state more than the ground state as the excited state is more polar than the ground state.

3.3.2. Relationship between the optical transition and photon energy

When molecule in the compound is exposed to the electromagnetic radiation or called as light, it may absorb a photon thus increasing its energy by an amount equal of the photon. The photon energy values can be obtained using the formula:

$$\hbar\omega = \frac{h}{2\pi} (2\pi f) = \frac{hc}{\lambda} = hv \quad (2)$$

The relation between the optical band gap, absorption coefficient and energy ($h\nu$) of the incident photon given by Tauc [25,26]:

$$\alpha h\nu = B(h\nu - E_{\text{opt}})^n \quad (3)$$

where $h\nu$ is the photon energy, h is Planck's constant, α is the absorption coefficient, E_{opt} is the optical energy gap, B is constant, for direct transitions $n = 1/2$.

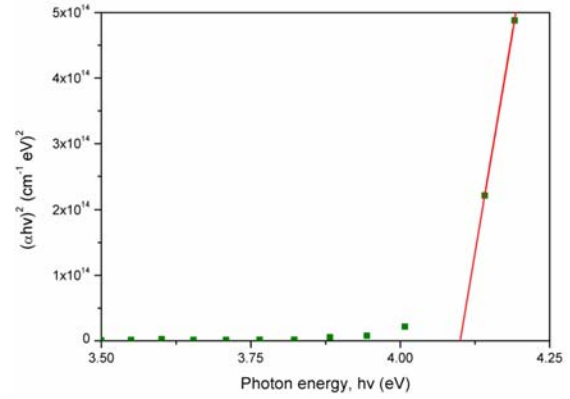


Fig 5. Optical band gap of 1,5-diphenylcarbazine dissolved in acetic acid

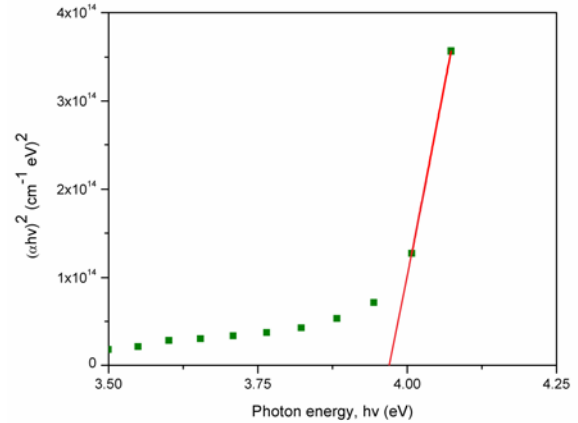


Fig 6. Optical band gap 1,5-diphenylcarbazine dissolved in acetone

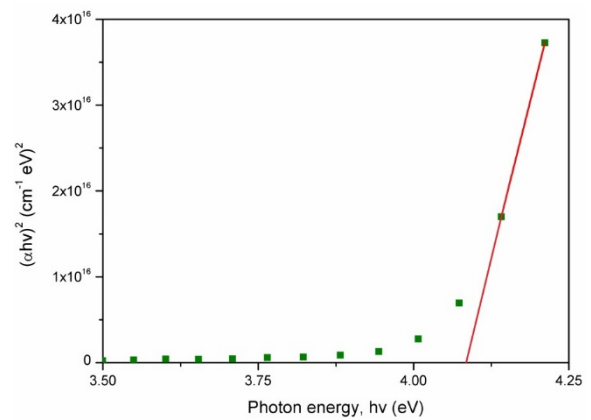


Fig 7. Optical band gap 1,5-diphenylcarbazine dissolved in ethanol

From all these graphs, the variations of optical band gap energies were experimentally obtained from the linear

fitting of the graph [27,28]. The value of energy band gap obtained varies with the type of solvent used. The energy band gap obtained is 4.09 eV, 3.97 eV, and 4.08 eV for sample acetic acid, acetone and ethanol respectively. It can be found that the range of optical band gap obtained in this study is between 3.97 eV to 4.09 eV [29,30]. Due to the variation value of optical band gap gained, it can be noticed that the choice of the solvent to be used in ultraviolet spectroscopy is quite important because it affects the absorption spectrum. It was observed that the acetone is a less polar solvent than acetic acid and ethanol, therefore, it tends to absorb the electronegativity, hence, providing the greater absorbance value and lowest value of energy band gap.

4. Conclusion

The optical properties of 1,5-diphenylcarbazide have been studied. The FTIR analysis shows that the functional group that presences in the infrared spectrum are alkenes, alcohol and aromatic rings. The morphology studies of 1,5-diphenylcarbazide is found to be varying with the presence of different type of solvent used. The surface of the sample is smooth when 1,5-diphenylcarbazide dissolved in ethanol. When dissolve in acetic acid and acetone, there is few pores presence, and the surface is found to be rough and unevenly distributed. The solution is said to have high surface tension and viscosity that lead to the rough surface. From the theoretical fitting of the experimental absorption coefficients for all samples, the optical band gap is found to be between 3.97 eV to 4.09 eV. This range of optical band gap is between insulator and semiconductor where the band gap for insulator is more than 4 eV while for semiconductor less than 3 eV. Apart from that, it was deduced the film that is suitable for sensing application is 1,5-diphenylcarbazide thin film with the solvent of acetone. This thin film has shown the best absorbance and energy band gap, which could be used as metal ions sensing material.

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