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Synthesis, structural analysis, spectrophotometric measurements and semiconducting properties of 3-phenyl azo-4-hydroxycoumarin thin films

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ABSTRACT

3-phenyl azo-4-hydroxycoumarin, PAHC, compound was synthesized by reacting aniline diazonium salt with 4-hydroxy coumarin. The thin films of PAHC were prepared on the glass and quartz substrates by thermal evaporation technique under vacuum pressure 10^{-5} mbar. The structure of thin films was characterized using X-ray diffraction, XRD, and Fourier transformation infrared, FTIR, techniques. The XRD pattern for the pristine PAHC thin film showed nanocrystallites distributed in amorphous matrix. Annealing at 423 K improved the crystallinity of films and the crystallite size is in the range 23–36 nm. FTIR showed different vibrational modes, observed in infrared spectra of the powder, pristine and annealed thin films, were assigned to the molecular bonding structure of PAHC compound. The optical properties of PAHC thin films were investigated by the spectrophotometer measurements of the pristine and annealed PAHC films in the range 200–2100 nm. The refractive and absorption indices of the pristine and annealed PAHC films were calculated from measured transmittance and reflectance data. The results showed that the refractive and absorption indices of thin films are influenced with increasing annealing temperature. The direct allowed transitions were the most probable transition and the optical band gap was found to vary from 2.14 to 2.21 eV with increasing annealing temperature. The single oscillator model was applied in the normal region of dispersion spectrum to determine the dispersion parameters and it is noted that they are decreased with annealing temperature. The AC electrical conductivity, σ_{AC}, and the real and imaginary parts of dielectric constants measurements were investigated in temperature range 304–413 K and frequency range 0.1–100 kHz; they confirmed semiconductor behavior of the PAHC films.

1. Introduction

Organic semiconductors are very interesting area of current scientific research. There are many significant developments made in the synthesis, characterization and application oriented development of these materials. The electrical and optical properties of organic semiconductors are mainly responsible for the growing interest as an attractive area of research. The interest in the thin films of semiconductors is high as they show good luminescence, fluorescence and absorption properties at the nano-scale whereas there is no emission from them in their bulk form [1]. Further studies on organic semiconductors are very interesting because of their size dependent optical properties which can lead to many technologically important applications such as organic light emitting diode [2], integrated flash memory [3] and solar cell [4] devices. In the fastest growing field of the nanoscience and nanotechnology, the integration of optoelectronic devices with the nano- and micro-electronics which show efficient optical properties along with their integration in electronic technology is needed. Organic semiconductors are considered to be ideal candidates for optoelectronic applications of optical lighting and display applications because they show emission or absorption in the visible region [5].

Coumarins are a family of organic semiconductors which are manufactured from natural resources and others they were synthesized from molecular structure (1,2-benzopiron) [6]. Coumarins and their derivatives show absorption and fluorescence characteristics which could be enhanced by attaching of appropriate functional groups at suitable positions in the structure of coumarin which causes a change in mobility of electrons [7,8]. The

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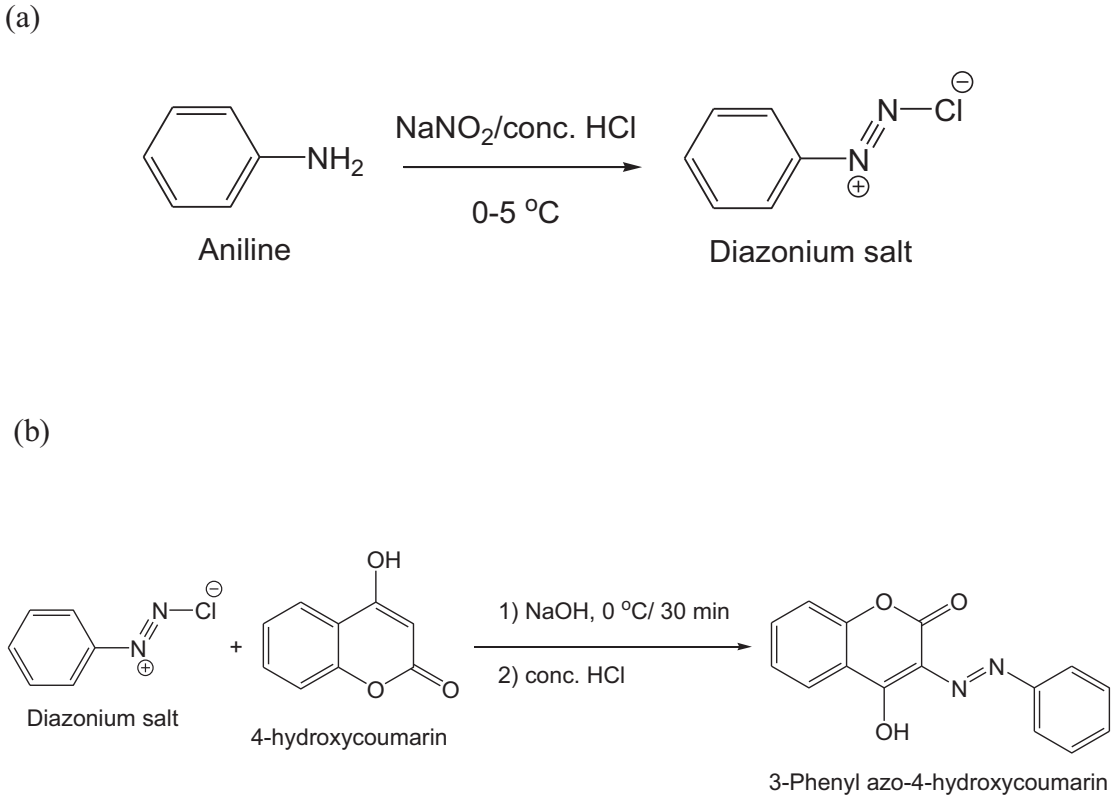
electron donor groups such as amino, hydroxyl situated at the position-7 in coumarin and heterocyclic electron acceptors such as benzothiazole and at the position-3 of benzoxazole should induce bathochromicity and shows strong fluorescence [7–9]. Coumarins were also employed as photo-controlled molecules opening and closing a silica pore, where from guest molecules are released, or in photodegradable polymers [10,11]. Coumarin dimers play an important role as photocleavable linker molecules for two-photon absorption controlled drug delivery [12]. The refractive index changes accompanying the photocleavage of the cyclobutane structure which may be used in optical and holographic recording [13].

Hydroxycoumarins and their derivatives possess many remarkable properties; they are well known for their high sensitivity as excellent lasing properties in the blue–green region [14] and application as luminescent colorants for bio-substrates, fluorescent whiteners for polyster and polymide fabrics [15] and photoprotective compound used as a sunscreen component [16]. The electronic structure of hydroxycoumarins, including their UV light absorption ability, has become the subject of much interest. Absorption spectra of hydroxycoumarins and their derivatives have been studied [17,18]. Three main absorption bands of coumarins have assigned to $\pi \rightarrow \pi^*$ transitions in the long wavelength region. The first absorption band of hydroxycoumarins belongs to transition from HOMO → LUMO which is localized on the carbon atoms of the phenyl ring and the lactone ethylene bond. The second transition band is due to (HOMO − 1) → LUMO transition and the third band belongs to the transition HOMO → (LUMO + 1) [17,18]. The intensity, shape and position of these bands depends on the type of solvent, for example the maximum positions of electronic absorption for coumarins derivatives in ethanol are very close to those in cyclohexane [18]. 4-Hydroxycoumarin derivatives were studied by spectral methods: electronic absorption spectroscopy [19], IR spectroscopy [20] and X-ray crystal analysis [21]. The knowledge of absorption and fluorescence characteristics of these compounds with different substituents under varying condition of solvents [22], temperatures [23] and pH [24] are important for understanding the operation of tunable dye lasers at maximum efficiency. The electronic absorption and emission spectra as well as fluorescence quantum yield of 3-(benzothiazol-2-yl)-7-hydroxycoumarin (BTHC) were measured in different solvents and are affected by solvent polarity. BTHC acts as good laser dye upon pumping with nitrogen laser (λ_{max} = 337 nm) in ethanol and gives laser emission with maxima at 508 and 522 nm [25]. Effect of solvents of varying polarities on absorption and fluorescence spectra and dipole moment of laser dye: 7-diethylamino-3-thenoylcoumarin has been investigated. A bathochromic shift observed in absorption and emission spectra with increasing solvent polarity, which implied that the involved transition is $\pi \rightarrow \pi^*$ [26]. Although, several reports have been emerged on the physical properties of coumarins [17–26], the optical and electrical transport properties of many 4-hydroxycoumarin derivatives have not yet been systematically studied, in our research efforts focus on the study of structural formation, optical constants, dispersion parameters and semiconducting behavior of 3-phenyl azo-4-hydroxycoumarin, PAHC, thin films and influence of the annealing temperature on their structural, optical and electrical properties.

2. Experimental details

2.1. Synthesis of 3-phenyl azo-4-hydroxycoumarin

The chemicals used in the present work were obtained from Sigma–Aldrich Co. and used as received without any further purification or treatment. The synthetic procedure route



Scheme 1. Mechanism of synthesis of 3-phenyl azo-4-hydroxycoumarin, PAHC: (a) formation of diazonium salt and (b) coupling reaction of diazonium salt with 4-hydroxycoumarin.