Camphor Sulfonic acid Protonated Poly (2, 5-dimethoxyaniline) - Cadmium sulfide blend thin film for Ammonia gas Sensing Application

Maggie Dayana. A, Victor Williams Rayar

Abstract: Poly (2, 5-dimethoxyaniline) and Cadmium sulfide nanocomposite blend have been prepared by low cost, feasible oxidative polymerization method. Poly (2, 5-dimethoxyaniline) has been protonated with Camphor sulfonic acid. nanocomposite blend thin films were obtained by blending with CdS into Poly (2, 5-dimethoxyaniline) for different weight percentage by dip coating. The structural, morphological, optical characterizations of pristine Poly (2, 5-dimethoxyaniline) and nanocomposite blend thin films were analyzed. The XRD pattern shows that the crystallinity of the blend film increases with increasing CdS concentration. FESEM images shows porous blend film. The UV-Vis and Photoluminescence spectra analysis shows the extension of conjugation length with decreasing band gap with increasing CdS concentration. The presence of functional groups were studied from FTIR spectra. The CSA protonated Poly (2, 5-dimethoxyaniline) – Cadmium sulfide blend films have been investigated as ammonia gas.

Keywords: ammonia sensor, Cadmium sulfide Camphor sulfonic acid, m-cresol, Poly (2, 5-dimethoxyaniline), thin film

1. INTRODUCTION

Ammonia gas is one of the most widely produced industrial chemicals. It is lighter than air and will rise up in the presence of high humidity. If the concentration of ammonia gas increases more than 50 ppm (parts per million) in air or 35 ppm in water causes harmful effects. NH3 is a part of the nitrogen cycle and is produced in soil from bacterial processes. Ammonia is also produced naturally from decomposition of organic matter, including plants, animals and animal wastes. Low energy density compared to hydrocarbon fuels and its toxicity are the main disadvantages of ammonia gas. [1] Great deal of efforts have been taken in recent years in order to monitor the trace level of ammonia gas by fabricating many types of gas sensors based on organic polymers, inorganic metal oxides and organic – inorganic (hybrid). Conducting polymers with zinc oxide, titanium oxide, silicon oxide, tin oxide, tungsten oxide, cadmium sulfide, reduced graphene oxide so on have been far reported as ammonia gas sensor[2],[3].

Among the conducting polymers Polyaniline is one of the well-known polymer with excellent sensing response [4]. But limited work has been reported on the sensing response of Polyaniline derivatives. Poly (2, 5-dimethoxyaniline) (PDMA) is a substituted derivative of Polyaniline. It has features like two methoxy groups at para and meta position in the benzene ring, where this functional group is an electron donating in nature, p type conjugate polymer, solubility in organic solvents, similar conductivity value of Polyaniline.[5] In this report, for the first time ammonia gas sensing performance of Camphor sulfonic acid protonated Poly (2, 5-dimethoxyaniline) / CdS nanocomposite blend thin film have been discussed. To the best of our knowledge no work so far published on Camphor sulfonic acid protonated Poly (2, 5-dimethoxyaniline) / CdS nanocomposite blend thin film and that is the driven force to explore the sensing response of Polyaniline derivative. In this work Poly (2, 5-dimethoxyaniline) (PDMA) has been polymerized by chemical oxidative technique with APS as an oxidant. PDMA then protonated with CSA with a known ratio of 1:0.5. To this protonated polymer, cadmium sulfide of three different weight ratio was doped. This blend film was characterized by UV spectrophotometer, FTIR spectrometer, X-RAY diffraction, Photoluminence, FESEM. The blend thin film was fabricated as an ammonia gas sensor and its response to ammonia gas was performed.

II. EXPERIMENTAL PROCEDE

A. Synthesis of CdS nanoparticles

Cadmium chloride (CdCl2) and Sodium sulfide (Na2S) of same molar ratio were taken in two different beakers and dissolved in 50ml deionized water separately. Cadmium chloride solution was stirred continuously for 1 hr, to this solution sodium sulfide was added in drops. This precursor solution was stirred continuously for 5hrs. After 5hrs, the precursor solution slowly turns into dark yellow precipitate indicating the formation of CdS nano particles.

B. Synthesis of Poly (2, 5-dimethoxyaniline)

An aqueous solution of APS in 1M HCl was taken in a beaker. This aqueous solution was added drop by drop to the monomer DMA and 1M HCl in a beaker which was maintained in an ice bath of ~ 0° - 5° C. Polymerization was indicated by the change of color of the reaction mixture from brown (DMA) into dark green solution thereby representing Emeralide Salt (ES) of PDMA and this solution was stirred for another 5hours.
C. Synthesis of CSA protonated Poly (2, 5-dimethoxyaniline)/ CdS nanocomposite blend thin film

The as prepared PDMA of known weight was taken in three different beakers. To this three beakers CdS nanoparticles of three weight percentage (25%, 50% and 75%) were added. This blend was treated with 1M NH4 OH solution by stirring for 2hrs to obtain the Emeraldine Base (EB) form of PDMA. The solution was filtered by Whatman paper and washed with diethyl ether till the filtrate become colorless. The obtained deep blue color precipitate forms the EB- PDMA/CdS blend which was dried in open hot air condition for an hour.

The EB - PDMA / CdS nano composite was redoped by grinding with Camphor sulfonic acid (CSA) of 0.5 weight percentage with EB - PDMA using smooth agate mortar to obtain the protonated green color Emeraldine Salt (ES) PDMA/ CdS nano composite. A small quantity of CSA protonated PDMA / CdS nano composite of each weight percentage was taken separately and 2ml of m-cresol added to the mixture and ultra sonicated for half an hour.

Pre cleaned glass substrate was dipped in each solution and withdrawal time was maintained constant to get a uniform CSA protonated PDMA / CdS nano composite thin film. The substrate was dried by keeping on a hot open air for 1 hour. As formed thin films are marked as CP, CPC1, CPC2 and CPC3 respectively.

III. RESULT AND DISCUSSION

A. XRD Analysis

Figure 1 shows the XRD pattern of pristine PDMA (EB), CSA protonated PDMA (ES), CdS nanoparticles, PDMA (EB)/CdS.

XRD pattern of PDMA which is the EB form shows the amorphous nature without definite and sharp peaks.

PDMA / CSA which is the protonated PDMA shows peaks at 10.62°,23.77°, 27.42° are (010),(200),(122) due to PDMA [6]. The peak at 27° attributed to the distance between the ring planes of benzene ring [7] and the peak at 33° ascribe the periodicity perpendicular to the polymer chain [8]. A small peak at 15.52°, 17.52° and 19.22° belongs to CSA[9]. The peaks at 24.62°, 26.32, 28.02°, 43.82°, and 51.79° shows the cubic phase of CdS[10].

PDMA/CdS pattern shows the presence of CdS in the polymer matrix. Intensity and crystallinity of PDMA increases with the increasing ratio of CdS and with CdS size decreasing. The mean particle size of CdS was calculated using scherrer equation and found to be 19.57nm. The increase of crystallinity may be due to the replication of Benzenoid and Quinoid rings in PDMA [11].

Figure 1. The XRD pattern of PDMA (EB), PDMA/CSA (ES) and CdS blend PDMA with weight percentage 25% (CPC 1), 50% (CPC 2), 75% (CPC 3)

B. Surface Morphology

The surface morphology of CSA protonated PDMA- CdS blend films with weight percentage 25% (CPC 1), 50% (CPC 2), 75% (CPC 3) are shown in figure 2. The FESEM images shows that the blend films have an effective morphology with the increase of CdS concentration. The blend films showed transformation to porous surface. These pores influence large surface area which enhance adsorption and desportion of the target gas. The highly porous CPC3 blend thin film shows better sensing performance.
C. UV – VIS spectra analysis

The UV-VIS absorption spectra of PDMA, CdS, CdS blend PDMA with weight percentage 25% (CPC 1), 50% (CPC 2), 75% (CPC 3) are shown in the figure 3. The blend films have an absorption bands around 330nm is attributed to the π – π* transition of the benzenoid ring[11]. The highly CdS blend film shows a peak at 445nm which is due to polaron - π* transition and confirms the polymer PDMA in conducting form [12]. A broad hump around 800nm attributes to π – polaron transition [13]. The impact on conjugation length of the hybrid films were depend on the CdS ratio which can be observed in the spectra. For the weight percentage 50% the peak remains to be at 395nm as in 25% this may be a reason of poor interaction of CdS with PDMA. But for the 75% a hump around 453nm is appeared and this red shift confirms the effective expansion of conjugation length. The absorption hump at 500nm of the CdS thin film may be due to small size CdS nanoparticles[14]. The cause for peaks with red shift and increasing intensity may be due to the strong bonding of PDMA – CSA with CdS nanoparticles and due to expanded structure of PDMA molecule by m-cresol which are initially of coil like confirmation[15]. The large red shift of polaron band to - π* band of 50nm is due to excitonic coupling. From the peaks, π – π* transition also shows red shift which may be due to interaction with CdS and due to excitonic coupling of π electrons with CdS nano particles[16].

Using the fundamental law the optical band gap have been determined,

\[ \alpha = A \left( E_g - h\nu \right)^n \]

Where \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy in eV, \( A \) is the proportionality constant, \( n = \frac{1}{2} \) for direct transition and \( n = 2 \) for indirect transition. A linear graph have been drawn by plotting \( \left( ah\nu \right)^n \) vs. \( h\nu \) for N values and by the extrapolation of the linear part, the optical band gap has been found. The optical band gap of Emeraldine base Poly (2,5-dimethoxyaniline), Emeraldine salt Poly (2,5-dimethoxyaniline), Poly(2,5-dimethoxyaniline)/ CdS and three weight percentage of CdS with CSA protonated Poly(2,5-dimethoxyaniline) 25% (CPC 1), 50% (CPC 2), 75% (CPC 3) are tabulated in the Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical Band Gap (eV)</th>
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<tbody>
<tr>
<td>PDMA EB</td>
<td>4.08</td>
</tr>
<tr>
<td>PDMA ES</td>
<td>3.09</td>
</tr>
<tr>
<td>PDMA CdS</td>
<td>4.03</td>
</tr>
<tr>
<td>CPC 1</td>
<td>3.22</td>
</tr>
<tr>
<td>CPC2</td>
<td>2.53</td>
</tr>
<tr>
<td>CPC3</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Table-1. Optical Band Gap of Emeraldine base Poly (2, 5-dimethoxyaniline), Emeraldine salt Poly (2, 5-dimethoxyaniline), Poly (2, 5-dimethoxyaniline)/ CdS and three weight percentage of CdS with CSA protonated Poly (2, 5-dimethoxyaniline) 25% (CPC 1), 50% (CPC 2), 75% (CPC 3)
From the above discussion the thin film CPC3 shows lower Optical band gap and therefore it is considered to be the optimized ratio for better conductivity. This sample exhibit enhanced conductivity which may be due to the presence of maximum number of carriers due to protonation by CSA. The intensified conductivity of the blend thin film is attributed due to the generation of polarons or bipolarons in the composite structure[17].

D. Photoluminescence

The Photoluminescence spectra for PDMA, CSA protonated PDMA, CSA protonated PDMA – CdS blend with weight ratio 25% (CPC 1), 50% (CPC 2), 75% (CPC 3) respectively is shown in figure 5. The samples were excited with the excitation wavelength of 300nm.

Pure PDMA shows band at 361nm, and very small emission peak at 484nm. The CSA protonated PDMA – CdS blend thin film shows peak around 493nm, 519nm, 408nm and 362nm. These peaks showed red shift as the CdS concentration increases indicating the bonding of CdS with N-H of PDMA chains.

There are increase and decrease of emission peaks which can be observed in blend films. The presence of CdS in the polymer matrix increases the size of PDMA which decreases the PL intensity due to decrease of defect states in the polaronic band and that induces large transitions from the polaronic band to π band. The increase in intensity of PL due to higher extent of π–π conjugation. As mentioned in UV-Vis spectra analysis, the CPC3 shows red shift due to expansion of π–π conjugation. This extension accompanied with regular arrangement to benzenoid and quinoid units in the blend film leading to the formation of singlet exciton. As the conjugation length increases the formation of exciton increases. Since the conjugate polymers cannot generate the spin flip which is necessary for an optical transitions but the formed singlet exciton are accountable for photoluminescence emission[18].

![Figure 5. The Photoluminescence spectra for PDMA, CSA protonated PDMA, CSA protonated PDMA – CdS blend with weight percentage 25% (CPC 1), 50% (CPC 2), 75% (CPC 3) ](image)

E. Fourier Transform Spectra Analysis

The FTIR spectrum of PDMA (EB), PDMA/CSA (ES) and CdS doped PDMA blend with weight percentage 25%, 50% and 75% are shown in the figure 6. The peaks at 1619cm⁻¹, 1575 cm⁻¹,1479 cm⁻¹, 1634 cm⁻¹,1564 cm⁻¹,1511 cm¹,1621 cm¹,1537 cm⁻¹,1484 cm⁻¹, 1614 cm¹,1578 cm¹,1485 cm¹, 1620 cm¹, 1546 cm¹, 1438 cm¹ are due to C = O stretching vibration of Quinodic (Q) and Benzoind ring (B) which are observed in pure PDMA, PDMA–CdS, CSA protonated PDMA – CdS blend thin film for the ratio 1:1:0.5, 1:1:1 and 1:1:2 respectively. Also the peaks at 1445 cm⁻¹, 1463 cm⁻¹, 1411 cm⁻¹, 1412 cm⁻¹, 1438 cm⁻¹ and 1140 cm⁻¹, 1144 cm⁻¹, 1169 cm⁻¹, 1183 cm⁻¹, 1187 cm⁻¹ are attributed to C-N stretching vibration of QBQ, QBB & BBQ and N=Q=N stretching vibration for pure PDMA, PDMA–CdS, CSA protonated PDMA – CdS blend thin film for the ratio 1:1:0.5, 1:1:1 and 1:1:2 respectively. C-N stretching vibration of a secondary aromatic amine strengthened by protonation of PDMA showed peaks at 1303 cm⁻¹, 1309 cm⁻¹, 1286 cm⁻¹, 1324 cm⁻¹ for CSA protonated PDMA and CSA protonated PDMA – CdS blend thin film for three different weight ratio[19]. These peaks are absent in pure PDMA thin film. The peaks observed at 1184 cm⁻¹, 1193 cm⁻¹, 1183 cm⁻¹ confirms the presences of methoxy group in all the samples[20]. The peaks at 1038 cm⁻¹, 1060 cm⁻¹, 1058 cm⁻¹, 1069 cm⁻¹ are due to CSA/ SO³⁻ observed in CSA protonated PDMA – CdS blend thin film[21]. Due to Cd-S stretching the peaks at 651 cm⁻¹, 617 cm⁻¹, 616 cm⁻¹ and 773 cm⁻¹, 773 cm⁻¹, 769 cm⁻¹ are observed for CdS protonated PDMA – CdS blend thin film for the ratio 1:1:0.5, 1:1:1 and 1:1:2 respectively[22]. The Cd-S stretching band shows shift due the interaction with PDMA-CdS. Shift in Q and B bands may be due to difference in the protonation level and oxidation level or the change in stability of the conjugation system.

![Figure 6. The FTIR spectrum of PDMA (EB), PDMA/CSA (ES) and CdS doped PDMA blend with three weight percentage 25% (CPC 1), 50% (CPC 2) and 75% (CPC3) ](image)
From the structural, morphological, optical and electrical analysis of CSA protonated PDMA-CdS blend revealed that the blend film with weight percentage of 75% showed enhanced behavior which is useful for gas sensing applications.

NH3 is a reducing gas. From the response curve it can be studied that even for a lower concentration of ammonia of NH3 can be detected with CSA protonated PDMA/CdS blend thin films. Particularly the weight percentage of 75% (CPC3) shows a significant response when compared to other two weight percentage. This increasing response due to high surface roughness caused by merging of nanoparticles into polymer matrix leading to the adsorption of gas molecules effectively. Adsorbing electrons from NH3 gas results in maximum change in resistance of the sensor.[23]. The increasing response may be due to high surface area, porosity of the blend films also. Highly porous and uniform distribution of pores enhance the best sensing performance. The blend film CPC3 shows fast response and recovery rapidly after cutting off the NH3 gas. This shows that the porous film improves the adsorption and desorption speed to target gas molecules during sensing process[24][25]. Low porous CPC1 and CPC2 showed long response and recovery time due to less adsorption and desorption of gas molecules. During the exposure of different concentration of NH3 gas, the resistances increases accordingly showing the response of blend layers. The increase of sensitivity is about 50% for CPC3 when compared to CPC1 and CPC2 and also stable sensing performance.

Thus the CSA protonated PDMA-CdS blend film has been optimized for CdS weight ratio and weight percentage 1:1:2 was investigated for ammonia sensing performance.

REFERENCE


AUTHOR’S PROFILE

First Author Pursuing PhD from Bharathidasan University, Tiruchirappalli, India. Completed M.Sc., M.Phil. Research area of interest are Polymer thin films, Organic / Inorganic blend thin films, Solar cells and Sensors

Second Author Dr. Victor Williams Rayar was Professor of Physics at St. Joseph’s college(Autonomous), Tiruchirappalli, India, with 36 years of teaching experience. He got his PhD in thin film Physics He was heading the department of Electronics and Physics. Three of his research students have completed their PhD degree and three more are about to complete their PhD degree in thin film physics. He has published more than twenty five research articles in reputed International Journals. He has attended many National and International conferences and delivered invited talks. He has specialised himself in thin film physics, solar energy and instrumentation techniques.