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Study of POA-PVS-DBS Composite Films for the Development of Gas Sensor

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ABSTRACT

In the present investigation, the composite films of poly(o-anisidine)-polyvinylsulphonic acid-dodecylbenzenesulphonic acid (POA-PVS-DBS) were synthesized on silver electrode, using electrochemical polymerization technique. These synthesized composite films were characterized by electrochemical technique, conductivity measurement, UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM). The optimal film growth was achieved for synthesis of the poly(o-anisidine) composite films in the presence of polyvinylsulphonic acid-dodecylbenzenesulphonic acid (PVS-DBS). The synthesized POA-PVS-DBS composite films exhibit good electrochemical properties, conductivity with a uniform porous surface morphology which could be used for development of gas sensor.

Keywords: o-anisidine, galvanostatic method, composite film, gas sensor

I. INTRODUCTION

Among the polyaniline derivatives, o-anisidine has been extensively used because of their easy polymerization, high electrical conductivity, chemical stability and ability to form freestanding films. However, the role of structural & mechanical behavior of poly (o-anisidine) for its application to gas sensor is yet to be explored. The stability of polymer film depends on anion size. The anions play an important role during the electrosynthesis. The anions are small sized (inorganic) anions e.g., (Cl^-, NO_3^-, HSO_4^-), medium sized (mainly organic) anions e.g., p-toluenesulphonate (pTS) and large sized polymeric anions e.g., dodecyl benzene sulphonic acid (DBS), polyvinyl sulphonate (PVS) [1]. The POA film can be doped with small sized anion which can be incorporated into the film on oxidation. But, the polymer film formed with small anion has poor stability. To overcome this problem, the POA films needs to be synthesized with the large sized anion like polyvinyl sulphonate (PVS), p-toluene sulphonate (pTS), dodecyl benzene sulphonic acid (DBS) and their various combinations.

The conducting properties and surface morphology of the polymer film depends on the method of synthesis and various electrochemical process parameters such as, monomer, dopant and co-dopant concentration, type of co-dopant, synthesis temperature, pH of the reaction medium and applied current density during the

electrochemical polymerization [2-11]. Electrochemically synthesized conducting polymer films offers lot of advantages because it is very simple, low cost, carried out in a single compartment glass cell, reproducible and the synthesized films has desired thickness and uniformity [12-19]. By using electrochemical polymerization technique, thin films of conducting polymers of desired physical and chemical properties can be synthesized. Conducting polymers have extensively used in biosensors [20], electronic devices [21], electrochromic display devices [22], EMI shielding [23], light weight batteries [24], and electrochromic materials [25]. The basic issues related to electrochemical polymerization and characterization of substituted polyaniline to explore the possibility to utilizing these as alternatives of polyaniline in the technological oriented applications has been the focal point of research activity [26, 27].

It is reported that the large sized anions are not able to leave the polymer; it can result in a stable polymer film. The polymer synthesized with large sized anions causes the ions inserted into the films to maintain the charge neutrality during reduction, which is very useful for the gas sensing. The presence of polyelectrolyte in the polymerization solution results in increased growth rate, higher compactness and improved environmental stability of the synthesized film [28-30]. Few researchers had been studied the influence of large sized ions like PVS, pTS, DBS on the physical, chemical and electrical properties of various conducting polymers during their electrochemical synthesis [31-35]. The aim of the present research work is to study the influence of PVS-DBS combinations of co-dopants on the physical, chemical and electrical properties of electrochemically synthesized POA films so that it can be used for the gas sensing applications.

II. EXPERIMENTAL

The dopants polyvinyl sulfonic acid (PVS) (Aldrich), and dodecyl benzene sulfonic acid (DBS) (Loba Chemie) were used. All above dopants were obtained from Rankhem Ranbaxy New Delhi (INDIA). An aqueous solution of o-anisidine, dopant and co-dopants were prepared in distilled water. The o-anisidine monomer was distilled twice before use. The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop. The pH was adjusted by adding nitric acid (HNO_3) or sodium hydroxide (NaOH). The electropolymerization of o-anisidine was carried out by galvanostatic technique, in one compartment electrochemical cell on Silver electrode. The reference electrode was Ag/AgCl. All three electrodes were placed vertically in cell. An 80 ml solution was used for each reaction. The pH of the electrolyte was measured by a calibrated ELICO LI120 pH meter.

We have taken 0.2:0.4:0.1M (o-anisidine: PVS: DBS), 1.0 pH and 1mA/cm^2 applied current density at room temperatures during synthesis of POA films respectively. The deposited POA films were tested for conductivity, uniform and porous surface morphology. The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout reaction. The conductivity was measured by using four-probe technique. The optical absorption studies of these films were carried out in the wavelength range 300-900 nm using UV-visible spectrophotometer Shimadzu 1601. The FTIR spectrums were recorded using Shimadzu FTIR-8400 series, in the region 400-4000 cm^{-1}. The scanning electron micrographs were recorded using JEOL JSM-6360A Analytical system.

III. RESULTS AND DISCUSSION

Galvanostatic study of POA-PVS-DBS composite film

The potential-time curve recorded during the synthesis of POA-PVS-DBS film is shown in the Fig. 1. In fact, the behaviour of the galvanostatic synthesis overshoot during the first few seconds probably indicates the formation of dimmers and oligomers. After this, the potential remains constant suggesting that building up of the film proceeds according to the full thickness of the polymer.

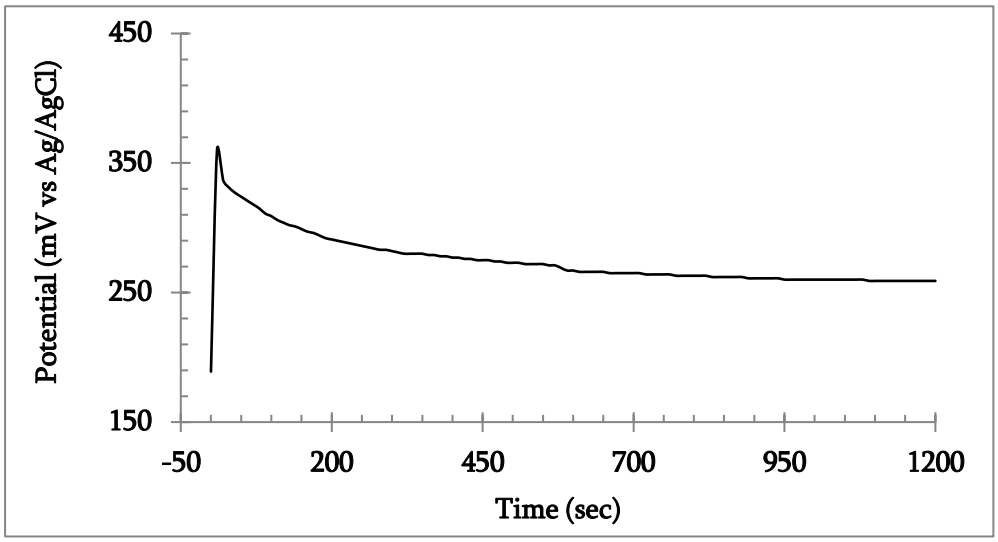

Figure. 1 Potential-time curve of POA-PVS-DBS film for 1.0 pH, 1mA/cm^2 current density a room temperature.

The POA films are galvanostatically synthesized with 0.2:0.4:0.1M (o-anisidine: PVS: DBS), 1.0 pH and 1mA/cm^2 applied current density at room temperature respectively. In order to have high conductivity, the polymerization potential should be minimum [03]. The polymerization potential 259 mV and conductivity 3.21 $\times 10^{-2}$ S/cm was recorded for PVS-DBS. It shows very good resemblance with polymerization potential recorded during the polymerization. This reveals that, the synthesized POA film with PVS-DBS co-dopants will have higher conductivity and provides more stable polymer matrix which is more advantageous for gas sensing.

UV-Visible study of POA-PVS-DBS composite film

The UV-visible spectra of synthesized POA film with PVS-DBS co-dopant is shown in the Fig.2. A green coloured film of PVS-DBS co-dopant shows a peak appearing at 300nm which is assigned to a $\Pi \rightarrow \Pi^*$ electronic transition between the valance and conduction bands of the polymer. It shows a strong peak appearing at 600nm, attributed to an intermolecular charge transfer excitation associated with quinide ring whereas a tail at 800nm indicates that the formation of emeraldine salt (ES) [27, 35].

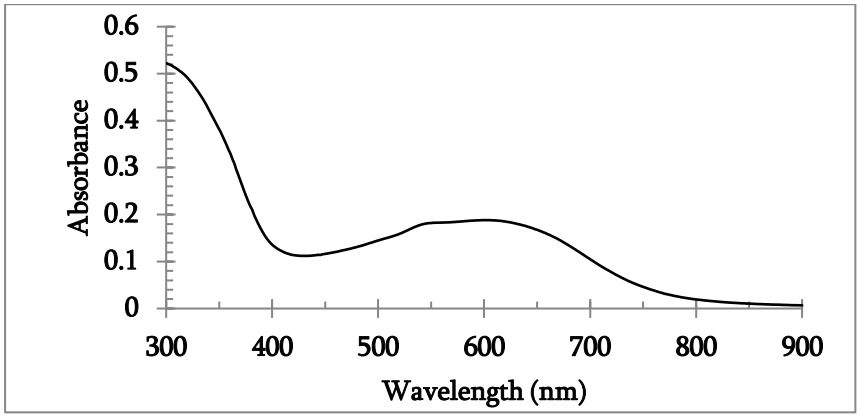

Figure 2. UV-visible spectra of POA film with PVS-DBS co-dopants.

FTIR study of POA-PVS-DBScomposite film

The FTIR assignments of POA film with PVS-DBS co-dopant are given below.

The characteristic band at 3435.0 cm^{-1} arises mainly from N-H stretching and the bands at 1656.7 cm^{-1} arises from C=N group while the bands at 952.8 cm^{-1} arises from O-C=O. The characteristic band at 1423.4 cm^{-1} arises mainly from C-O group whereas the bands at 1315.4 cm^{-1} arises from C-H stretching. Thus, FTIR assignments results confirm the structure of POA film [35].

SEM study of POA-PVS-DBScomposite film

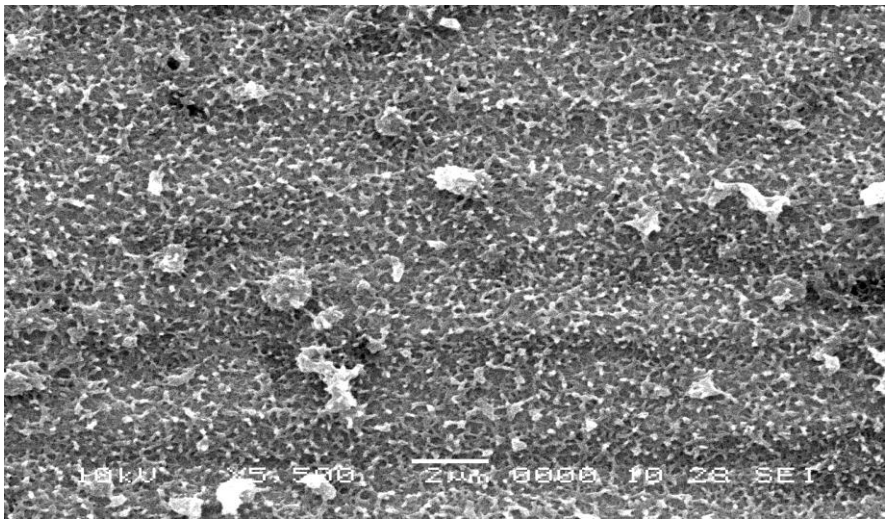

Figure 3. SEM picture of synthesized POA film with PVS-DBS co-dopant.

The surface morphology of the POA film using scanning electron microscope synthesized with PVS-DBS co-dopant is shown in the Fig.3. It shows the sponge like structure with whitish and blackish colours clearly indicate the presence and effect of PVS-DBS co-dopants. The POA film doped with PVS-DBS co-dopants shows a sponge like matrix with excellent porosity which is advantageous for gas sensing.

IV. CONCLUSION

The POA films with PVS-DBS co-dopant have been successfully synthesized. The conductivity of the POA film synthesized with PVS-DBS co-dopants was found to be 3.21×10^{-2} S/cm. The UV-visible spectra show the systematic changes with the conductivity. The FTIR spectra confirm the formation of POA in the presence of PVS-DBS co-dopants. The POA-PVS-DBS composite films show good electrochemical properties, conductivity as well as uniform and porous polymer surface morphology which is more advantageous for gas sensing.

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