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Synthesis and characterization of poly (O-anisidine) films under galvanostatic conditions by using ECP technique

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In the present study, the growth mechanism of poly (o-anisidine) (POA) with supporting electrolyte H_2SO_4 and HCL on platinum (Pt) substrate has been investigated. The POA films on Pt substrate have been synthesized by electrochemical polymerization (ECP) of o-anisidine under galvanostatic conditions from an aqueous solution with inorganic supporting electrolyte H_2SO_4 and HCL at temperature 29^0 C. We have optimized the monomer and supporting electrolyte concentrations, pH of the solution and applied current density for better conductivity, uniform and porous surface morphology of the synthesized POA film so that it can be used for biosensor applications. The uniform, thin, porous and strongly adherent dark green POA film was synthesized at 0.2 M monomer concentration, 1 M supporting electrolyte concentration (H_2SO_4 and HCL), 1.0 pH and 2 mA/cm^2 applied current density at temperature 29^0 C. The synthesized POA film was characterized by using electrochemical technique, UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and conductivity measurement. The synthesized POA films with optimized process parameters with supporting electrolyte H_2SO_4 and HCL were compared for their uniformity, adherence, conductivity and porosity. It was observed that, the synthesized POA film with H_2SO_4 supporting electrolyte provide better polymer matrix for immobilization of biocomponant.

Keywords: o-anisidine monomer, conducting polymer, electrochemical polymerization

1. INTRODUCTION

The need for new materials with potential properties has always been the driving power for the progress in several areas of the science and technology. There are so many new materials coming up for several technological oriented applications. The conducting polymer is one of the most promising new classes of materials, being used for several applications. The combination of electrical, chemical

and electrochemical properties of conducting polymers may lead them to be used in many technological applications [1-8]. We can synthesize thin films using conducting polymers for desired physical and chemical properties so that it can be used for specific applications [9-10]. The electrochemically synthesized conducting polymers offer lot of advantages because of their ease of preparation techniques and uniformity of the synthesized films [11-17].

One of the interesting features of the conducting polymer films is that we can produce grains of specific behaviour into the bulk material or on its surface regions, with possibility to build in side chain as well as the charged or neutral particles with the sensing behaviour [18]. These films could be deposited on various types of substrates with the wide choice of their molecular structure [19-20]. Conducting polymer films can be synthesized on a conductive surface form monomer solution [21-22]. Different methods are available for the synthesis of conducting polymers. However, the most widely used method is electrochemical polymerization (ECP). This method of synthesis is popular and preferred general method for synthesis of electrically conducting polymers because of its simplicity and reproducibility, and can be carried out in a single compartment glass cell [23-26].

The monomer, which is being used for deposition, should have good film formation ability with capacity of good adhesion to the supporting substrate. The deposited film should have the desired pore size and porosity to allow penetration (or diffusion) of analyte, being measured as well as it should be uniform with desired thickness. The polymer film surface should be energetic and should have swelling characteristics [27]. The conducting properties of the polymers are controlled by many factors including electrode material, supporting electrolyte, synthesis temperature, pH of the electrolyte, nature of the solvent, and applied current density. The value of the conductivity of the conducting polymers also depends on the synthesis and processing techniques. The electrochemical polymerization is a standard procedure (method) for the synthesis of the conducting polymers. This method has many experimental variables such as, electrode material, supporting electrolyte, synthesis temperature, pH of the electrolyte, nature of the solvent, applied current density which needs to be optimized for optimal results [28-30].

Many researchers have investigated the synthesis of POA. However, still it is essential to optimize the electrochemical process parameters so that it can be used for desired application. In the present investigation, we have optimized process parameters for the synthesis of POA film for biosensor applications. We took the monomer o-anisidine and conducting polymer POA was synthesized by electrochemical polymerization using galvanostatic method. We studied the influence of various parameters viz., concentration of monomer and electrolyte, applied current density, pH of the aqueous solution etc., on electrochemical polymerization of POA. The synthesized POA films with H_2SO_4 and HCL were characterized by using electrochemical technique, UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and conductivity measurement and compared for their uniformity, adherence, conductivity and porosity.

2. EXPERIMENTAL PART

The o-anisidine monomer was double distilled before use. Sulphuric (H_2SO_4) acid and HCL were used as supporting electrolyte. All above reagents were obtained from Rankhem Ranbaxy New

Delhi (INDIA). An aqueous solution of o-anisidine (99%) and various electrolyte concentrations were prepared in distilled water The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop [31]. The pH was adjusted by adding nitric acid or sodium hydroxide.

The electropolymerization of POA was carried out by galvanostatic technique, in one compartment electrochemical cell. Platinum rectangular sheet (20 mm × 40 mm × 0.25mm) was used as a counter electrode and another platinum rectangular sheet (20 mm × 10 mm × 0.25 mm) was used as a working 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 pH meter. We have varied the monomer concentrations (0.05 M, 0.1 M, 0.2 M, 0.3 M), supporting electrolyte concentrations (0.5 M, 1 M, 1.5 M), pH of the solution (0.5, 1, 2), and current density (0.5, 1, 2) mA/cm^2 during synthesis of POA.

The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout reaction. The optical absorption studies carried out the wavelength range 300 – 1100 nm using UV-visible spectrophotometer 1601. The FTIR spectra were recorded using Shimadzu FTIR-8400 series, using KBr pellets in the region between 400 - 4000 cm^{-1}. The scanning electron micrographs were recorded at various magnifications using JEOL JSM-6360 A Analytical SEM. The conductivity was measured by using four-probe technique (Model DRF-02 Owen 1038 - Optochem International, New Delhi).

3. RESULTS AND DISCUSSION

The chronopotentiograms recorded during electrochemical polymerization of POA at various concentrations of o-anisidine, 1M concentrations of supporting electrolyte, 2 mA/cm^2 current density at 1.0 pH are shown in Figure 1(a) and (b) for H_2SO_4 and HCL respectively. We have recorded lowest polymerization potential for 0.2M concentration of o-anisidine as compared with other concentrations.

The synthesized POA film with 0.2 M concentration of o-anisidine was uniform, thin and adherent. Similarly, we observed higher electrical conductivity of the synthesized POA film with 0.2 M concentration of anisidine as compared with other concentrations (Table 1). We have recorded lower polymerization potential with H_2SO_4 as compared with HCL for 0.2 M concentration of o-anisidine. However, we observed higher electrical conductivity of POA with H_2SO_4 than that of HCL (Table 1). We can observe different stages in the chronopotentiogram if the working electrode is not made up of inert material [32] (Figure 2). The first stage is usually referred as inductive time (or passivation time) for the ECP of OA, in which negative potential in the order of 500 mV can be recorded. The polymerizations do not occur during this stage. The second stage of the growth is related to the complete passivation of electrode surface in which the potential increases suddenly to a positive value. This may be considered as a complete passivation of electrode surface. When the complete passivation occurs the electrode will behaves like an inert surface. The third stage is electrochemical polymerization of OA; in which polymerization potential decreases sharply for shorter duration of time and eventually reached to a steady state where the polymerization of OA is suppose to occur.

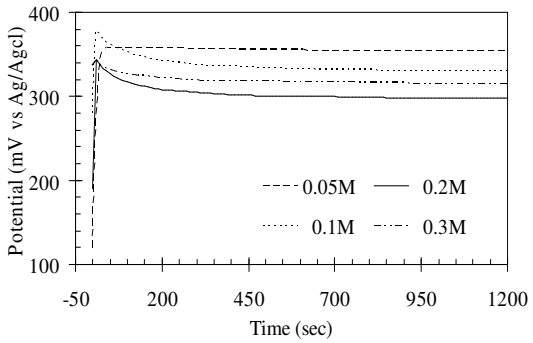

Figure 1. (a) The chronopotentiogram recorded during electrochemical polymerization of POA with various concentrations of o-anisidine, 1 M concentration of H_2SO_4, 2 mA/cm^2 current density, and 1.0 pH at temperature 29^0 C.

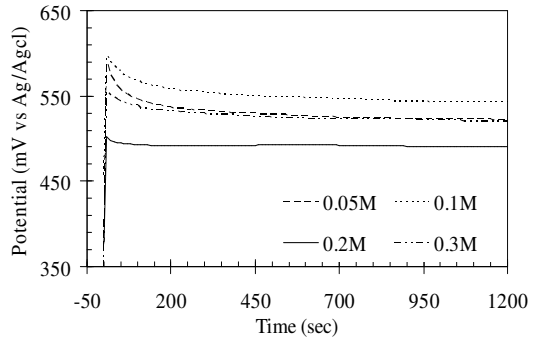

Figure 1. (b) The chronopotentiogram recorded during electrochemical polymerization of POA with various concentrations of o-anisidine, 1 M concentration of HCL, 2 mA/cm^2 current density, 1.0 pH at temperature 29^0 C.

Table 1. The conductivity of POA film for different concentrations of OA and 1 M of H_2SO_4 and HCl.

Sr. No.	o-anisidine conc. (in molar)	Conductivity of POA-H_2SO_4 films (S/cm)	Conductivity of POA-HCl films (S/cm)
1	0.05	1.72	0.40
2	0.1	1.78	0.33
3	0.2	1.91	0.66
4	0.3	1.85	0.50

In our case since we have used platinum an inert material for working electrode, we have recorded only second and third stage. The second stage where the growth is related to the complete passivation of electrode surface in which the potential increases suddenly to a positive value and third stage in the chronopotentiogram, in which the polymerization potential decreases sharply for shorter duration of time in the beginning and eventually reached to a steady state where polymerization of OA has been takes place. The conducting polymers are being used in biosensors because they provide stable and porous matrix for the entrapment of biocomponant and it facilitate the electron transfer process. The matrix with higher conductivity will be more useful for electron transfer process. We

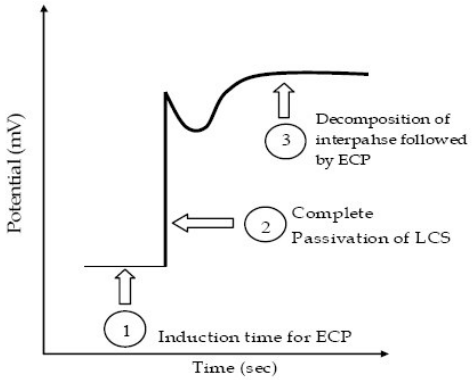

Figure 2. Schematic representation of the three distinct growth stages of ECP.

have also investigated the influence of concentration of supporting electrolyte with 0.2 M concentration of OA. We have synthesized POA films with 0.5M, 1M, 1.5 M concentrations of supporting electrolytes H_2SO_4 and HCL. The chronopotentiograms recorded during electrochemical polymerization of POA with various concentrations of H_2SO_4 and HCL, 0.2 M concentration of monomer, and 2 mA/cm^2 current density at 1.0 pH is as shown in Figure 3(a) for H_2SO_4 and (b) for HCL. We have recorded lowest polymerization potential for 1M concentration of H_2SO_4 as well as HCL.

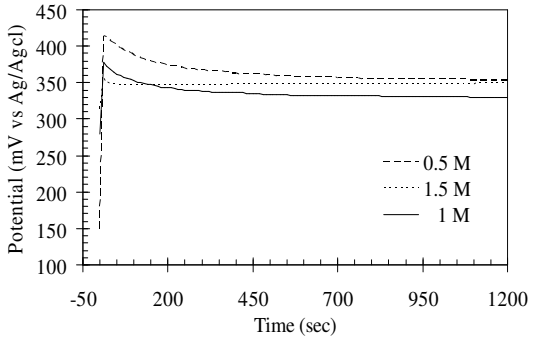

Figure 3. (a) The chronopotentiogram recorded during electrochemical polymerization of POA with various concentrations of H_2SO_4, 0.2 M concentration of monomer, and 2mA/cm^2 current density, 1.0 pH at temperature 29^0 C.

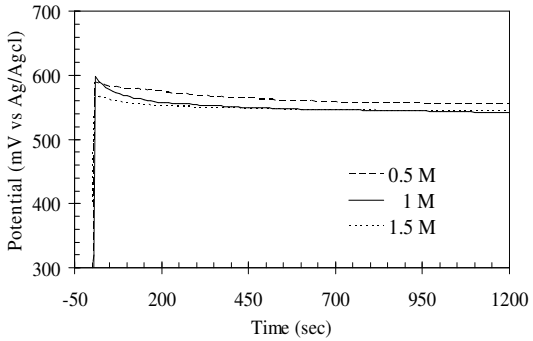

Figure 3. (b) The chronopotentiogram recorded during electrochemical polymerization of POA with various concentrations of HCL, 0.2 M concentration of monomer, 2 mA/cm^2 current density , 1.0 pH at temperature 29^0 C

This indicates that the synthesized POA films have highest conductivity for 1 M concentration of H_2SO_4 and HCL as compared with other concentrations. Similarly, synthesized POA films with 1 M concentration of H_2SO_4 and HCL were uniform, stable, porous and adherent to the surface. However, the polymerization potential recorded during synthesis of POA with 1M concentration of H_2SO_4 was lower as compared with 1 M concentration of HCL, which indicates that the synthesized POA film with H_2SO_4 will be more conducting than that of HCL.

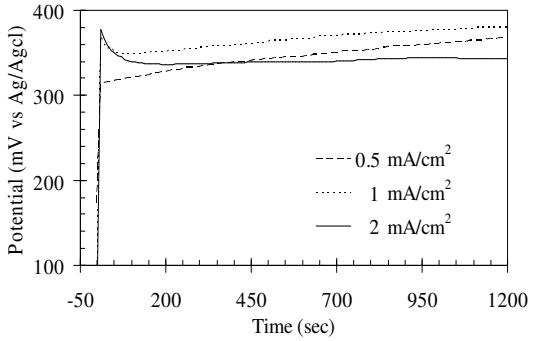

Figure 4. (a) The chronopotentiogram recorded during electrochemical polymerization of POA with various current densities, 0.2 M concentration of monomer, 1 M concentration of H_2SO_4, 1.0 pH at temperature 29^0 C.

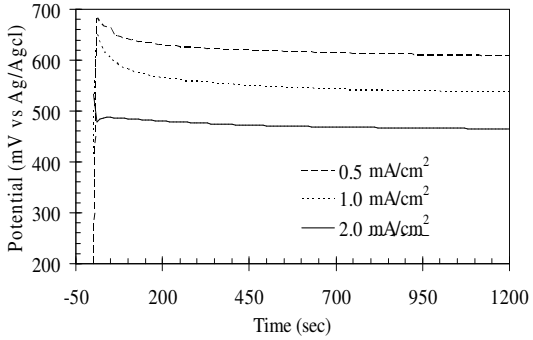

Figure 4. (b) The chronopotentiogram recorded during electrochemical polymerization of POA with various current densities, 0.2 M concentration of monomer, 1 M concentration of HCL, 1.0 pH at temperature 29^0 C.

We have also investigated the influence of applied current density and pH. We have carried out ECP of OA with various current densities (0.5, 1, 2 mA/cm^2) at different pH (0.5, 1 and 2). The chronopotentiograms recorded during synthesis of POA for H_2SO_4 and HCL at various current densities are shown in Figures 4(a) and (b) respectively. Similarly, the chronopotentiogram recorded during synthesis of POA for H_2SO_4 and HCL at various pH are shown in Figures 5(a) and (b) respectively.

We have recorded lowest polymerization potential for the synthesis of POA films at 2 mA/cm^2 current density and 1.0 pH as compared to other current densities and pH for both H_2SO_4 as well as HCL, which indicate higher conductivity. The synthesized films at current density 2 mA/cm^2 and pH 1.0 were uniform and adhesive as compared to other current densities and pH. The chronopotentiograms recorded during electrochemical polymerization of POA with optimized process parameters (viz., 0.2M concentration of monomer, 1M concentration of electrolyte, 2 mA/cm^2 current

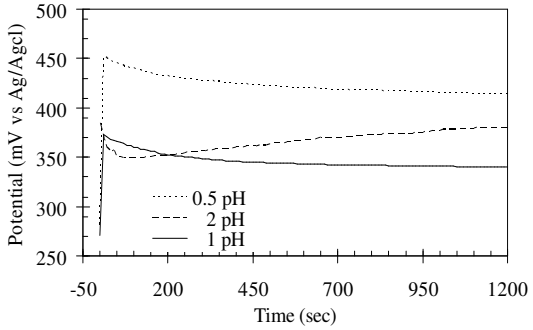

Figure 5. (a) The chronopotentiogram recorded during electrochemical polymerization of POA with various pH, 0.2 M concentration of monomer, 1M concentration of H_2SO_4, 2.0 mA/cm^2 current density at temperature 29^0 C.

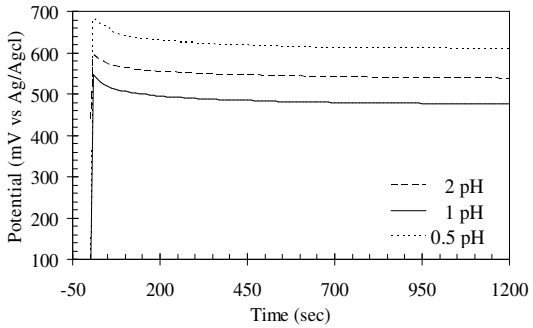

Figure 5. (b) The chronopotentiogram recorded during electrochemical polymerization of POA with various pH, 0.2 M concentration of monomer, 1 M concentration of HCL, 2.0 mA/cm^2 current density at temperature 29^0 C.

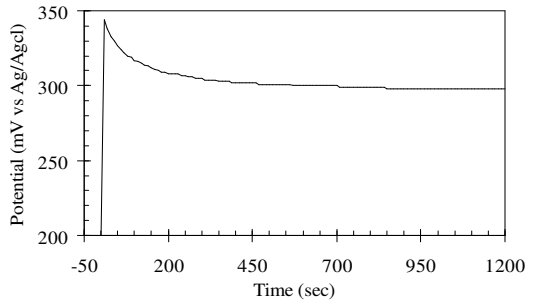

Figure 6. (a) The chronopotentiogram recorded during electrochemical polymerization of POA with optimized process parameters (viz., 0.2 M concentration of monomer, 1M concentration of H_2SO_4 (electrolyte), 2 mA/cm^2 current density, and 1.0 pH) at temperature 29^0 C.

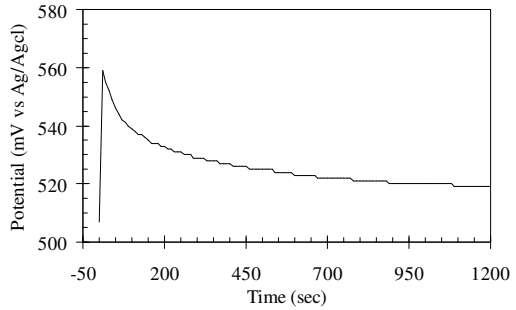

Figure 6. (b) The chronopotentiogram recorded during electrochemical polymerization of POA with optimized process parameters (viz., 0.2 M concentration of monomer, 1 M concentration of HCL (electrolyte), 2 mA/cm^2 current density, and 1.0 pH) at temperature 29^0 C.

density, and 1.0 pH) at temperature 29^0 C for H_2SO_4 and HCL are shown in Figures 6(a) and (b) respectively. It can be seen from Figures 6(a) and (b) the polymerization potential for H_2SO_4 is lower as compared with HCL, which indicate that the synthesized POA film with H_2SO_4 will have higher conductivity.

The optical absorption spectrum of synthesized POA films with optimized parameters for H_2SO_4 and HCL are shown in Figures 7(a) and (b). The spectrums were recorded in DMSO solution. It was recorded using UV-visible spectrophotometer 1601.All spectra were recorded in the wavelength range of 300- 1100nm. The shoulder is appearing at 414nm and peak is appearing at about 894nm for H_2SO_4 whereas for HCL the shoulder is appearing at 412nm and peak appearing at about 898nm corresponds to the formation of ES phase irrespective of the inorganic supporting electrolyte. It shows very good resemblance with earlier reported work [33-34].

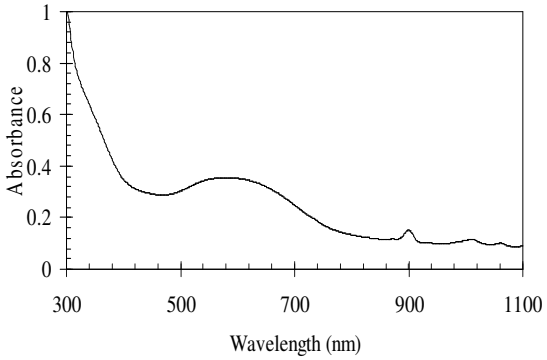

Figure 7. (a) The optical absorption spectrum of synthesized POA - H_2SO_4 film with optimized process parameters.

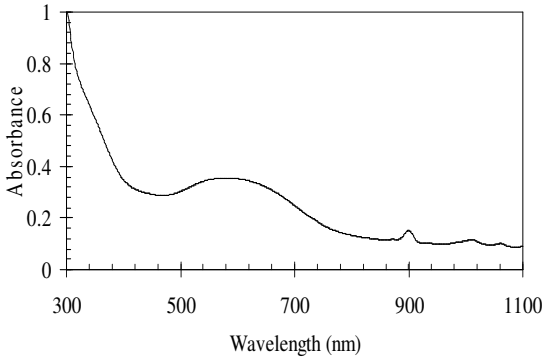

Figure 7. (b) The optical absorption spectrum of synthesized POA - HCL film with optimized process parameters.

The FTIR spectroscopy was used for structural characterization of synthesized POA films. The FTIR spectrum of synthesized POA films with the optimized process parameters for H_2SO_4 and HCL are as shown in Figures 8(a) and (b) respectively. It was recorded in the wave number range 4000-400 cm^{-1} on the Testscan Shimadzu FTIR-8400. The peak at 3444.6 cm^{-1} corresponds to the N-H stretching vibrations. The strong bands at 1660.6 cm^{-1} represents the presence of carbonyl group C=O. The presence of duplex peaks at 1411.8 cm^{-1} corresponds to C-O group. The bands at 954.7 cm^{-1} represents the O-C=O in the plane deformation. The band at 528.5 cm^{-1} represents the C-C-O in plane deformation. The strong bands at 1660.6 cm^{-1} indicates the presence of stretching vibrations in qunide

-ring whereas the band at 1411.8 cm^{-1}represents the stretching vibrations of benzoid-ring. It shows very good resemblance with earlier reported work [32]. The comparison is shown in Table 2.

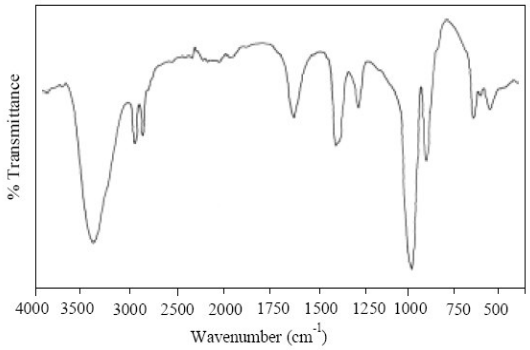

Figure 8. **(a)** The FTIR spectrum of synthesized POA - H_2SO_4 film with optimized process parameters.

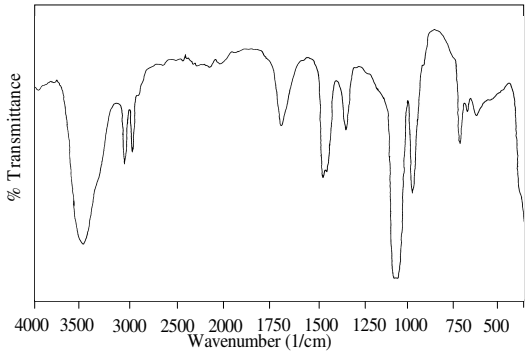

Figure 8. (b) The FTIR spectrum of synthesized POA - HCL film with optimized process parameters.

Table 2. Comparison of FTIR-bands of POA with H_2SO_4 and HCl as supporting electrolytes.

Observed Peaks (cm^{-1})		Functional groups
POA : H_2SO_4	POA : HCl	
3444.6	3436.9	N-H stretching vibrations
1660.6	1658.7	Presence of carbonyl group C=O
1411.8	1433.0 & 1413.7	Corresponds to C-O group
954.7	954.7	O-C=O in the plane deformation
528.5	613.3	C-C-O in plane deformation
1660.6	1658.7	Stretching vibrations in quinoid-ring
1411.8	1433.0	Stretching vibrations of benzoid-ring

The scanning electron micrographs of synthesized POA films with optimized process parameters for H_2SO_4 and HCL are shown in Figures 9(a) and (b) respectively. Scanning electron micrographs were recorded using JEOL JSM-6360 A Analytical SEM.

It shows very good resemblance with earlier reported work [35-36]. It can be seen from Figures 9(a) and (b) that, the synthesized POA film with H_2SO_4 shows excellent surface morphology with very good porosity which is suitable for immobilization of biocomponant.

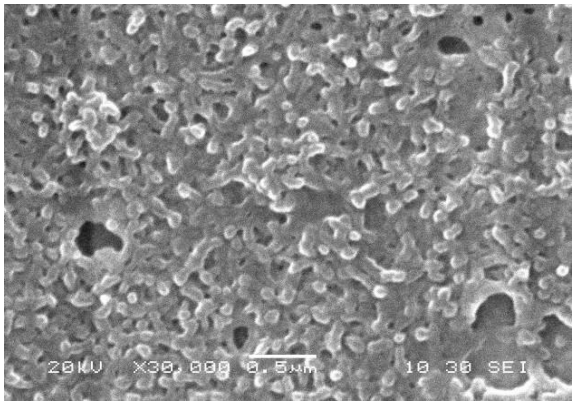

Figure 9. **(a)** The scanning electron micrograph of synthesized POA - H_2SO_4 film with optimized process parameters.

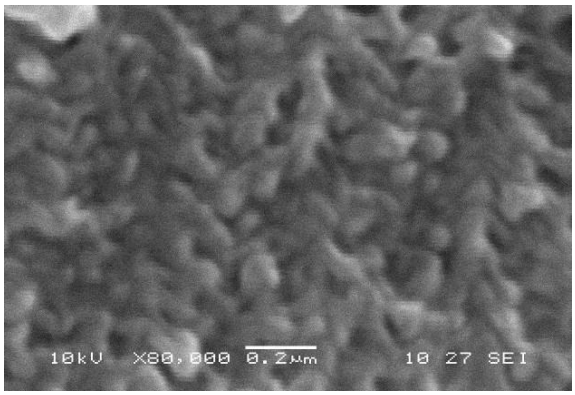

Figure 9(b) The scanning electron micrograph of synthesized POA - HCL film with optimized process parameters.

4. CONCLUSIONS

We have optimized the process parameters for the synthesis of the poly (o-anisidine) POA thin films. The synthesized POA film with 0.2 M monomer concentration, 1M supporting electrolyte concentration (H_2SO_4), 1.0 pH, and 2 mA/cm^2 applied current density at temperature 29^0 C are excellent combination for the synthesis POA film. The characterization of POA film Viz., UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy

(SEM) and electrical conductivity reveals that the synthesized POA film with H_2SO_4 supporting electrolyte provide a uniform, stable, porous matrix with higher conductivity.

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