

Deposition and Characterization of Poly (*O*-Anisidine)/TiO₂ Nanocomposite for Gas Sensing Application

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Abstract

The poly(*O*-anisidine) (POA) and Titanium dioxide POA (POA/TiO₂) composite thin film based for gas sensing application are synthesized. Pure POA and POA/TiO₂ composites with 20 wt% of TiO₂ were synthesized by chemical oxidative polymerization of *O*-anisidine using ammonium persulfate in acidic medium at 0–5°C. Thin films of POA and POA/TiO₂ composites were deposited on glass plate by dip coating method to prepare the chemiresistor sensor. The structural and optical properties of these composite films have been characterized by UV-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM) and FTIR spectroscopy. Finally, the response of these chemiresistor sensors for NH₃ gas was evaluated by monitoring the change in electrical resistance at room temperature. It was observed that the POA/TiO₂ composite thin film based chemiresistor sensors show a higher response as compared to pure POA sensor.

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Abbreviations: CSA, 10-camphor sulfonic acid; **EB**, emeraldine base; **ES**, emeraldine salt; **FTIR**, Fourier transform infrared spectroscopy; **HATR**, horizontally attenuated total reflectance; **PANI**, polyaniline; **POA**, poly(*O*-anisidine); **SEM**, scanning electron microscopy; **UGC**, University Grants Commission

INTRODUCTION

Polymers are amongst the most widely used materials in the modern world due to their diversified technological applications. The main advantage of these conducting polymers is that they exhibit conductivity ranging from insulator to conductor.^[1,2] Polyaniline has attracted a great interest due to its large field of applications like batteries^[3], protection of metals against corrosion,^[4,5] electrocatalysis,^[6,7] biosensors (analysis of ADN, proteins, and antipollution),^[8,9] electrochromism (flat-faced screens and diodes) and use in electronic components^[10–13].

Titanium dioxide is an important n-type semiconducting material, due to its excellent photocatalytic and electric properties. This material has been widely utilized as photocatalytic material^[14,15] and semiconducting electrode material for dye-sensitized solar cells.^[16,17] On the other hand, organic conducting polymer materials attracted widespread interest as functional device materials, due to their low cost, ease of processing, and compatibility with flexible substrates. Polyaniline (PANI), as a well-known conducting polymer, has attracted a considerable interest in recent years because of its good electric,

electrochemical, and optical properties and high stability^[18,19]. Also this conducting polymer shows the hole conducting properties. By considering the properties of TiO₂ and PANI, therefore, a nanocomposite of TiO₂ and PANI will give a new type of organic-inorganic p-n junction material that would be expected to have a potential application in the electronic and optical devices.

EXPERIMENTAL PROCEDURE

Materials

The *O*-anisidine hydrochloric acid (HCl) (35% concentrated), *O*-anisidine was used after double distillation. TiO₂ (99.9%) nanoparticles; with an average particle size of about 10–15 nm. Ammonium peroxide sulfate (APS) (99%), chloroform (99.9%) and ammonia solution (25% concentrated), and 10-camphor sulfonic acid (CSA).

Synthesis of POA and POA/TiO₂ Composite

Pure poly(*O*-anisidine) (POA) was synthesized by *in-situ* chemical oxidative polymerization method at 0–5°C, which has been reported elsewhere^[20,21]. The POA/TiO₂ composite was prepared by an *in-situ* chemical oxidation polymerization of *O*-anisidine using APS as an oxidant in presence of colloidal TiO₂ nanoparticles at 0–5°C in air. In a typical procedure, the TiO₂ nanoparticles were suspended in 1 M HCl solution and sonicated for 1 h to reduce aggregation of TiO₂ nanoparticles. The 0.1 M of *O*-anisidine was dissolved in 100 ml of 1 M HCl solution and then mixed with 10 ml of sonicated colloidal TiO₂ nanoparticles by further sonication for 30 min. The 100 ml of 1 M HCl solution containing the APS ((NH₄)₂S₂O₈) with an equal molar ratio to *O*-anisidine was then slowly added dropwise to well dispersed suspension mixture for 2 h with a continuous stirring at 0–5°C. After 3 h, a good degree of polymerization is achieved and the dark green precipitate was recovered. The solution was left in

undisturbed position for a night for the completion of chemical reaction. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 24 h. The composite powder thus obtained was conductive emeraldine salt (ES) form of POA/TiO₂. The POA/TiO₂ composites were synthesized using 20 wt% of TiO₂ with respect to *O*-anisidine monomer. For emeraldine base (EB), POA/TiO₂ (ES) powder was kept in 0.1 M ammonia solution and stirred for 6 h at room temperature. The precipitate was filtered and washed with deionized water until filtered solution became neutral and then dried in vacuum for 24 h to obtain emeraldine base POA/TiO₂ composite^[20].

Thin Film Deposition

Normally POA composite in emeraldine salt (ES) form are not soluble directly in any organic solvent and it is difficult to process it in conducting form. Therefore, firstly POA (ES) and its composites were converted into emeraldine base (EB) form and then protonated with CSA to make it conducting processable solution for film casting. In a typical procedure; the 0.3 g of POA (EB) and the POA/TiO₂ (EB) composite powders were separately mixed with of CSA by grinding in a smooth agate mortar. The, POA/CSA and POA/TiO₂/CSA (with 20 wt% of TiO₂) mixtures were separately added in 30 ml chloroform to prepare the conducting solution. The solution preparation requires 4–5 days of continuous stirring to make the solution homogenous. Thin films of these prepared conducting homogenous solutions were deposited onto cleaned glass substrates using dip coating for 10 min. These sensor films were dried at 60°C in vacuum for 24 h^[22].

Characterization

The Ultra-violet-visible (UV-Vis) absorption spectra were recorded using a Hitachi-U-2000. The surface morphology

of the prepared thin films was investigated and evaluated by means of scanning electron microscopy (SEM) and E-DAX to characterize the surface morphology with a Leica Cambridge 440 Microscope (UK). Thickness measurement by Tolansky interferometer, conductivity measurement by Four Probe method, The FTIR transmission spectrum of coating was recorded in horizontally attenuated total reflectance (HATR) mode in the spectral range $4000\text{--}400\text{ cm}^{-1}$ using a Perkin Elmer spectrometer (1600 Series II, Perkin Elmer, USA). The NM_3 , sensing behavior of POA and POA/ TiO_2 nanocomposite films was analyzed by measuring the change of an electrical resistance of the films after NM_3 , exposure in air.

RESULTS AND DISCUSSIONS

Measurement of Yield after Synthesis

When chemical synthesis of poly (*O*-anisidine) (POA) is carried out as described, the weight of yield is 0.4140 gm. While chemical synthesis of poly (*O*-anisidine) incorporated with TiO_2 nanoparticles (i.e. POA/ TiO_2) carried out with as chemical oxidative the weight of

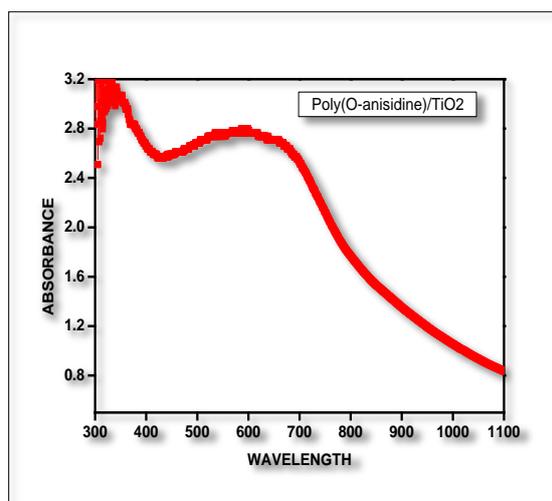
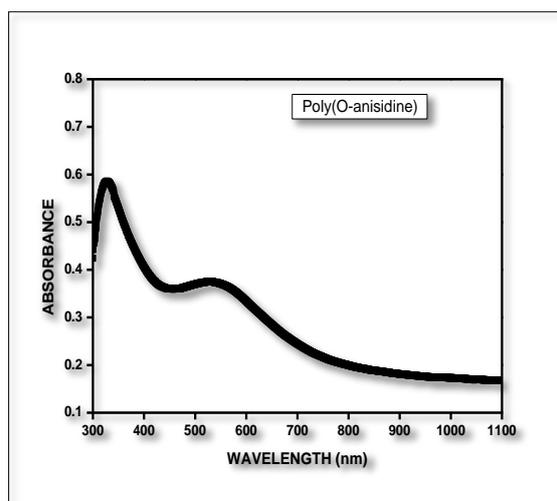
yield is 0.6286 gm. So from these results we conclude that incorporation of TiO_2 during synthesis improved the yield by an amount of 0.2146 gm.

Thickness Measurement by Tolansky Interferometer

The films of poly(*o*-anisidine) and that of POA/ TiO_2 deposited on plane clean glass plate. The thickness of these films was measured by Tolansky method and it was observed that the film thickness is also affected by incorporation of TiO_2 , means it reduces the film thickness

Conductivity Measurement by Four Probe Method

In comparison to pure POA the conductivity of 20 wt% POA/ TiO_2 composite thin film has found to be increased from 0.44×10^{-5} to 3×10^{-5} S/cm. This may be attributed to that the doping of TiO_2 nanoparticles within POA matrix form a more efficient network for charge transport between different molecular chains of POA, thus enhancing the conductivity of composite.



Ultraviolet–Visible (UV–Vis) Spectroscopy

Fig. 1. (a) UV–Visible Absorption Spectrum of Pure Poly(*O*-Anisidine) Coating; (b) UV–Visible Absorption Spectrum of POA/ TiO_2 Composite Coating.

Figures 1(a) and 1(b) show the UV-vis absorption spectra of pure POA and

POA/ TiO_2 composite thin films respectively deposited on the clean glass

substrate. The UV-vis absorption spectra for CSA doped POA and POA/TiO₂ composites thin films exhibit two absorption bands at 330 and 560 nm. The bands at 330 and 560 nm are attributed to the p-p* and polaron-p* transition in the conducting POA. Specially; it is observed that for POA/TiO₂ composite thin films, the absorption intensity increases with TiO₂. It may be due to the good absorption property of TiO₂ nanoparticles. In addition, it can be noted that there are some shifts in the peaks for POA/TiO₂ composites thin films as compared to the pure POA thin film. It may be due to that the encapsulation of TiO₂ nanoparticles has the effect on the doping of conducting POA or coordinate complex formation between TiO₂ nanoparticles and POA chains.

FTIR Characterization of POA and POA/TiO₂ Films

The FTIR spectrum of the POA coatings is shown in Figure 2(a). This spectrum exhibits the following spectral features: a broad band at ~3258 cm⁻¹ due to the

characteristic N-H stretching vibration suggests the presence of -NH- groups in *O*-anisidine units; the band at ~1515 cm⁻¹ is an indicative of stretching vibrations in quinoid (Q) rings; the band ~1484 cm⁻¹ represents the stretching vibrations of the benzoid (B) rings; the presence of Q and B bands clearly show that the POA coating is composed of amine and imine units; the bands at 1246 cm⁻¹ are attributed to the presence of carbonyl groups of salicylate in the POA coating; the band at ~1458 cm⁻¹ is assigned to the C-N stretching vibrations in quinoidimine units; the bands at 1115, 1021 and 847 cm⁻¹ are attributed to the 1-4 substitution on the benzene ring; the band at ~1170 cm⁻¹ is considered as a measure of the degree of delocalization of the electrons on POA and is referred to as the electronic like band and the bands between 800-700 cm⁻¹ reveals the occurrence of the 1-3 substitutions. Thus, the FTIR spectroscopic study indicates that the electrochemical polymerization of *O*-anisidine has occurred and results into the formation of POA.

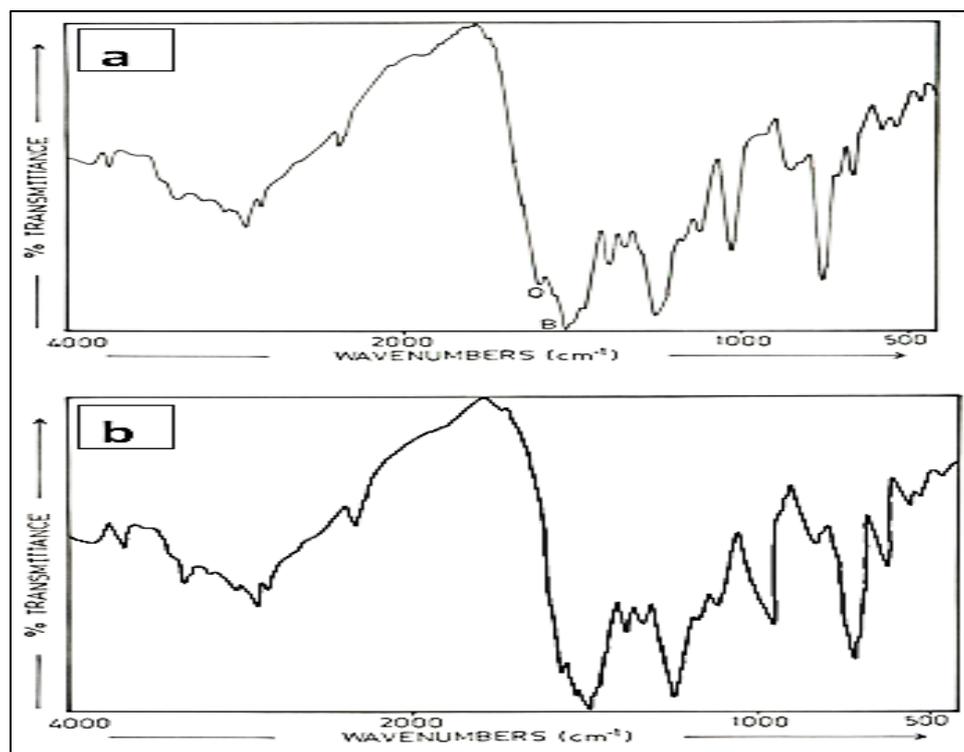


Fig. 2. FTIR Spectrum of (a) POA and (b) POA/TiO₂ Composite Coating.

The FTIR spectrum of the POA coatings is shown in Figure 2(b). For POA/TiO₂ nanocomposite, the IR spectrum is almost identical to that of pure POA, but all bands shift slightly, indicating that some interaction exists between POA and nano-TiO₂. In addition, the absorption band at 1408 cm⁻¹ can be assigned to the in-plane bending vibration of O–H on the surface of TiO₂.^[23]

SEM Characterization

The surface morphology of the pure POA and POA/TiO₂ nanocomposite coatings

synthesized by chemical synthesis were characterized by SEM. The surface morphology of the pure POA coating as shown in Figure 3(a) is relatively rough and it is characterized by the presence of the pores in the coating. Figure 3(b) shows that the surface morphology of the POA/TiO₂ nanocomposite coating is uniform, featureless and pore-free. It seems that the pores present in the pure POA coating are filled up by TiO₂ nanoparticles.

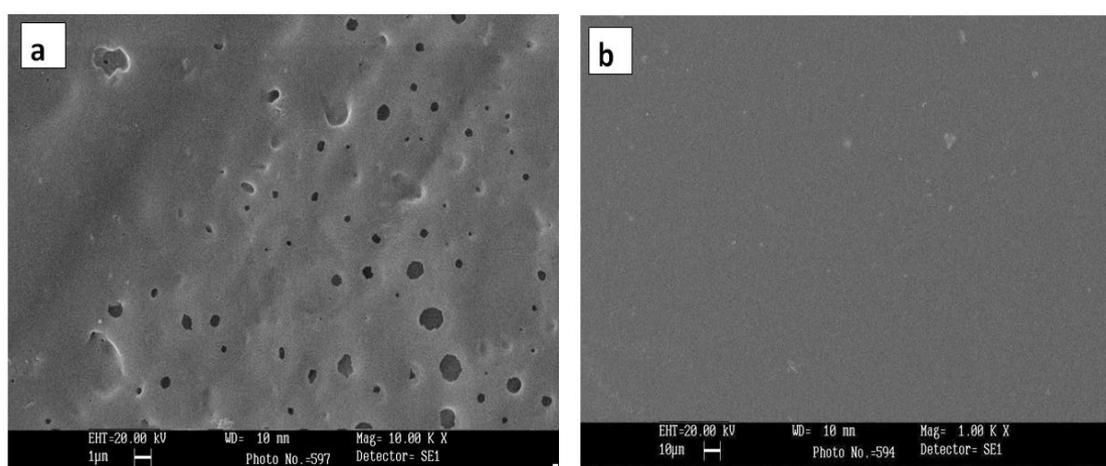


Fig. 3. Scanning Electron Micrographs of (a) POA and (b) POA/TiO₂ Thin Films.

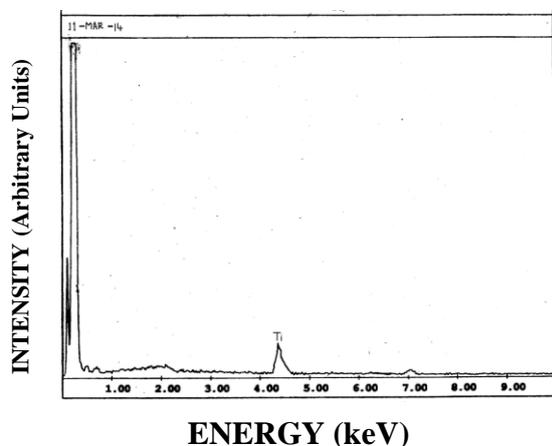


Fig. 4. E-DAX Analysis of the POA/TiO₂ Coating.

E-DAX Characterization

The E-DAX analysis of the POA/TiO₂ coating was also performed to confirm the

incorporation of the TiO₂-nanoparticles in the POA matrix as shown in Figure 4. Interestingly, the signal due to the Ti is clearly detected in the E-DAX spectrum as shown in Figure 4, which proves that the TiO₂-nanoparticles are incorporated in the POA matrix.

NH₃ GAS-SENSING PROPERTIES OF POA AND POA/TiO₂ FILMS

POA/TiO₂ nanocomposite thin film layer when exposed to NH₃ gas of different concentrations. The specially fabricated gas sensing apparatus is used for this work, and a certain amount of NH₃ gas was injected into the test chamber after the resistance reached a steady value in clean air. Gas exposure time was 150 sec for each pulse of NH₃ gas and the chamber

was purged with clean air for ca 200 sec after each pulse to allow the surface of the sensitive film to regain atmospheric condition. The measurement was processed at room temperature. Dynamic responses of the sensors based on POA and POA/TiO₂ thin films fabricated at room temperature. It can be seen that the resistance of both sensors increases dramatically after exposed to NH₃ gas. POA nanocomposite thin films contact with NH₃ by gas injection, which may be due to the surface adsorption effect, and the chemisorptions leads to the formation of ammonium. However, the interaction process between the thin film and the adsorbed gas is a dynamical process. Thus, when the thin film is exposed to NH₃ gas, the adsorption and desorption processes will simultaneously occur, and the thinner the films, the quicker the gas desorption. Then, the resistance attains a stable value when dynamic equilibrium is attained. The gas response is defined as $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$, where R_{air} is the resistance of sensor in air and R_{gas} is the steady resistance of sensor in the presence of a tested gas. The response values of all the samples are plotted as a function of NH₃ concentration in Figure 5, indicating a highly linear characteristic and the highest response value for the sensor composed of the POA/TiO₂ as compared to POA.

Table 1. Response Time (T_1) and Recovery Time (T_2) of Sensors Based on POA and PANI/TiO₂ Thin Films Prepared at RT Exposed to NH₃.

Concentration of NH ₃ (ppm)	POA		POA/TiO ₂	
	T_1	T_2	T_1	T_2
30	10	86	4	68
60	8	69	4	49
90	9	57	3	41
120	8	46	5	30
150	9	33	4	18
180	8	16	5	9

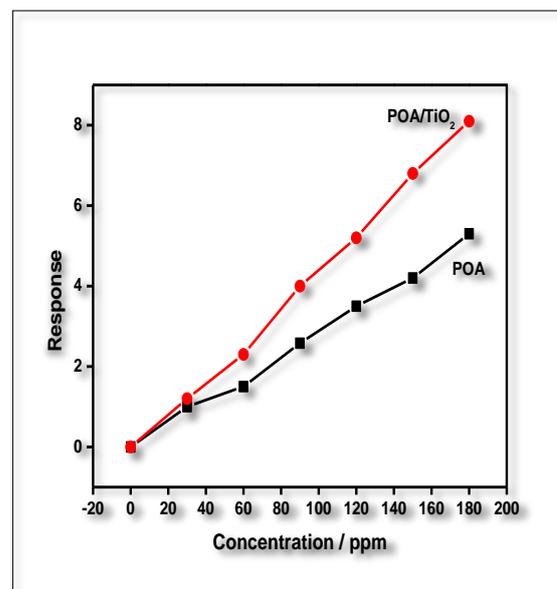


Fig. 5. Responses of the (a) POA (b) POA/TiO₂ in NH₃ of Different Concentration.

CONCLUSIONS

- The POA and POA/TiO₂ composite was prepared by an *in-situ* chemical oxidation polymerization of *O*-anisidine using APS as an oxidant in presence of colloidal TiO₂ nanoparticles at 0–5°C in air.
- Thin films of these prepared conducting homogenous solutions were deposited onto cleaned glass substrates using dip coating.
- The resulting coatings were characterized by FTIR, SEM, UV–Visible and E-DAX.
- These thin films were exposed to NH₃ gas, POA/TiO₂ nano composite coating shows quicker gas desorption as compared to POA films.

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