Optical Sensor for Detecting 2,4-Dinitrotoluene based on Polyaniline

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Abstract: This paper reports the use of in-situ polymerization method as a simple route for fabricating low-cost, highly sensitive 2, 4-Dinitrotoluene (2, 4-DNT) sensor made of polyaniline (PANI) coatings on glass substrates. The 2, 4-DNT sensing capabilities of the polyaniline film were studied using UV visible absorption spectroscopy. A significant change was observed in the absorption spectra of the film after it was exposed to different concentrations of 2, 4-DNT, in the range 0.5 mM-100 mM.

Keywords: Polyaniline (PANI), 2, 4-Dinitrotoluene (2, 4-DNT), UV-Visible spectroscopy

I. INTRODUCTION

In the recent times, we have witnessed a colossal interest in the research and development activity aimed at realization of sensors for the detection of explosive compounds. Such security and environmental needs have generated major demands for effective and innovative field-deployable devices for detecting organic explosives in a sensitive, reliable, and cost-effective manner. Because of its potential harm as a concealed weapon, 2, 4, 6-trinitrotoluene (TNT) has become a target analyte of high interest for chemical sensor devices including its precursor, the one-nitro-group-less analog, 2, 4-dinitrotoluene (2,4-DNT) Many studies have been reported in the literature for the detection of 2, 4-DNT, based on electrical and optical methods [1-3]. In the present work, we have fabricated 2, 4-DNT sensor based on a polymer (polyaniline) as sensing layer on a glass substrate.

Polyaniline (PANI) is an extensively investigated polymer and intrigued the scientific community due to its concomitant chemical, electrical and optical properties. It is regarded as one of the most promising conducting polymer, with high potential in commercial applications. The potential areas of application includes secondary batteries, photovoltaic devices, micro-electronic devices, memory device, biological sensors, gas sensors etc. [4-5]. The various techniques used to deposit the PANI films are electrochemical polymerization, spin coating, Langmuir-Blodgett technique, in- situ polymerization technique among others [6-9]. In-situ polymerization technique allows for an easier realization of the industrial processing of PANI with controllable sizes and morphologies.

The goal of the present investigation is to produce a reliable and sensitive 2, 4-DNT sensor, functional at room temperature. The room temperature operation is an important criterion to achieve intrinsically safe performance, in potentially hazardous situations. Other challenge for the realization of PANI based economical sensors, is the cost of production. Therefore, in this work, we have fabricated a cost effective 2, 4-Dinitrotoluene (2, 4-DNT) sensor based on polyaniline, using in situ polymerization technique and investigated its room temperature sensing behavior.

Materials and Method

APS (ammonium persulphate), HCl (Thomas Baker -hydrochloric acid) and 2, 4-Dinitrotoluene (Thomas Baker -2, 4-DNT,) were used as received. Aniline (Thomas Baker) was purified by vacuum distillation prior to use. Double distilled water was used in the experiment. Glass slides cut into desired size, were used as substrates. We have prepared the sensor using in situ polymerization technique. This technique allows the deposition of thin PANI film, on any substrate (here glass), demonstrating the method's adaptability, as schematically shown in Figure.1. The polymerization on the glass was performed for 20 minutes. The glass substrate drawn out from the reaction vessel, 20 minutes after the reaction was initiated gives a greenish appearance. The films were then washed with copious amount of distilled water, to remove the residual moieties.

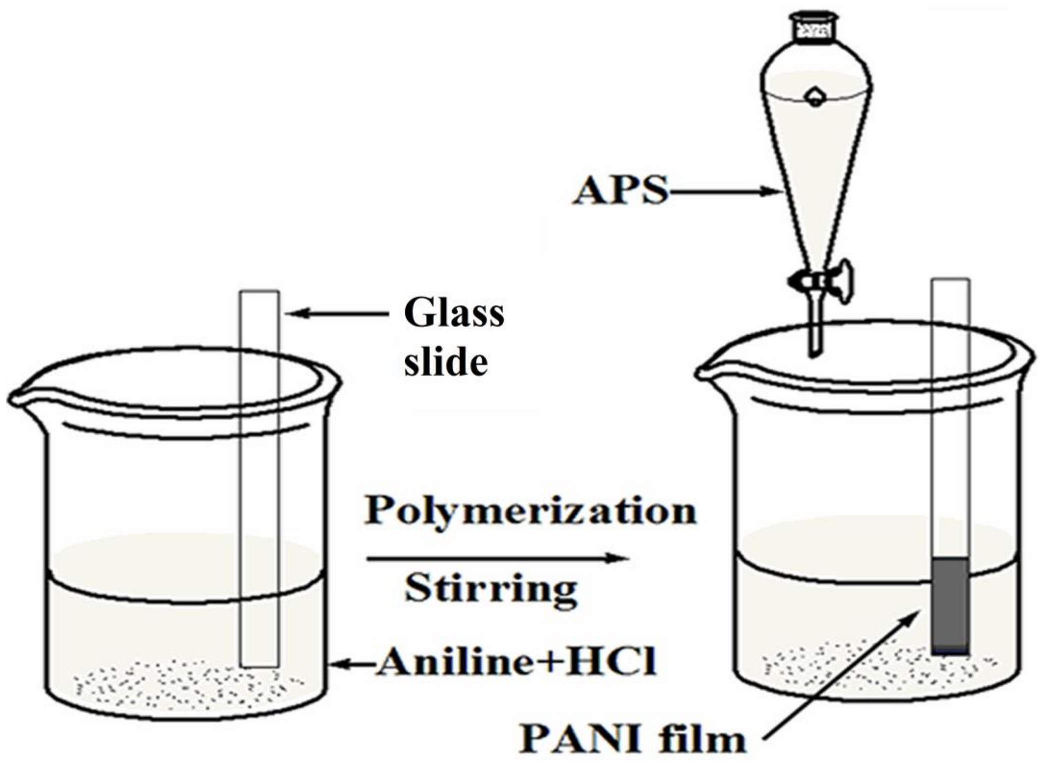

Figure 1: Scheme of in-situ polymerization in the presence of a glass substrate.

Structural properties by scanning electron microscopy (SEM)

PANI film on glass substrate, after 20 minutes of reaction time is shown in Fig. 2 a. Some nanofibrious structures can be observed over the granular morphology of the film. Same film, when washed with water, exhibit a clear granular morphology, strongly adherent to glass substrate. The heterogeneous (primary nucleation, globular) on the glass substrate gives rise to nanofibrous morphology, which is a consequence of anisotropic growth. These nanofibers are not strongly adherent to the substrate, hence there removal is necessary to get a smooth and adherent PANI film.

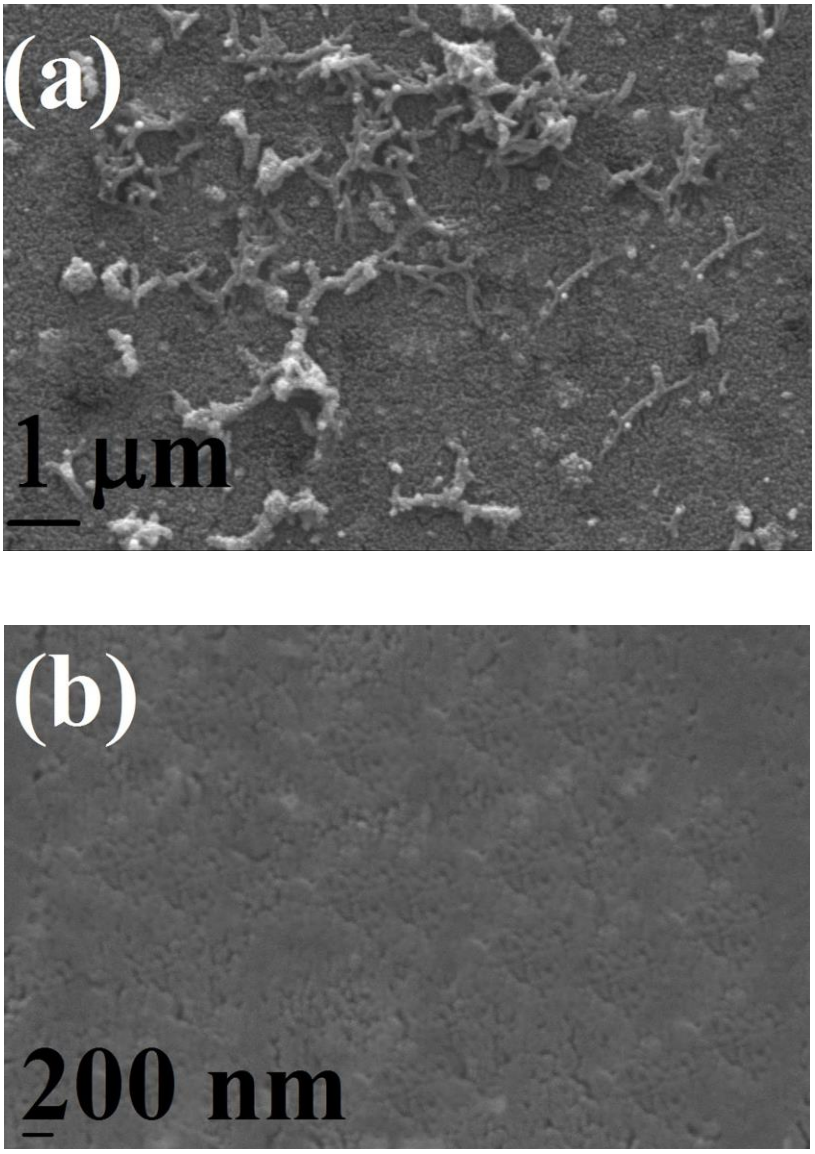

Figure 2: SEM images of polyaniline film grown on glass, for 20 minutes deposition time (a) unwashed, (b) completely washed.

UV Visible studies

For sensing, separate PANI films were utilized corresponding to each concentration of 2, 4-DNT. For all the virgin samples of PANI film, UV visible spectroscopy was done to assure, identical characteristics of the film. One can observe for all the PANI films, three peaks at nearly E_1 = 3.35 eV, E_2 = 2.84 eV and E_3 = 1.47 eV, respectively in the spectrum all the PANI films [10]. These three peaks are the characteristics peaks assigned to PANI thin films. The peak at E_1 is the first electronic transitions occurring from the upper defect band to the conduction band (π-π^* transitions). The peak centered at E_2 is direct optical transition from the second highest occupied molecular energy level in the valence band to the polaron band and the last peak at E_3 is direct optical transitions between the highest occupied energy levels of the valence band to the polaron band. Identical spectra was observed, on exposing the PANI film to ethanol, which is indicative of no effect of ethanol on PANI. However, it was observed, that on exposure to ethanolic solution of 2, 4-DNT, a systematic shift was observed in the E_3 peak, like for 10 mM concentration it got shifted to 1.53 eV . This can be attributed to competing nature nitrogen dioxide and methyl on one hand methyl increase in the electron density by releasing electrons, whereas nitrogen dioxide decreases the same due to electron withdrawing nature.

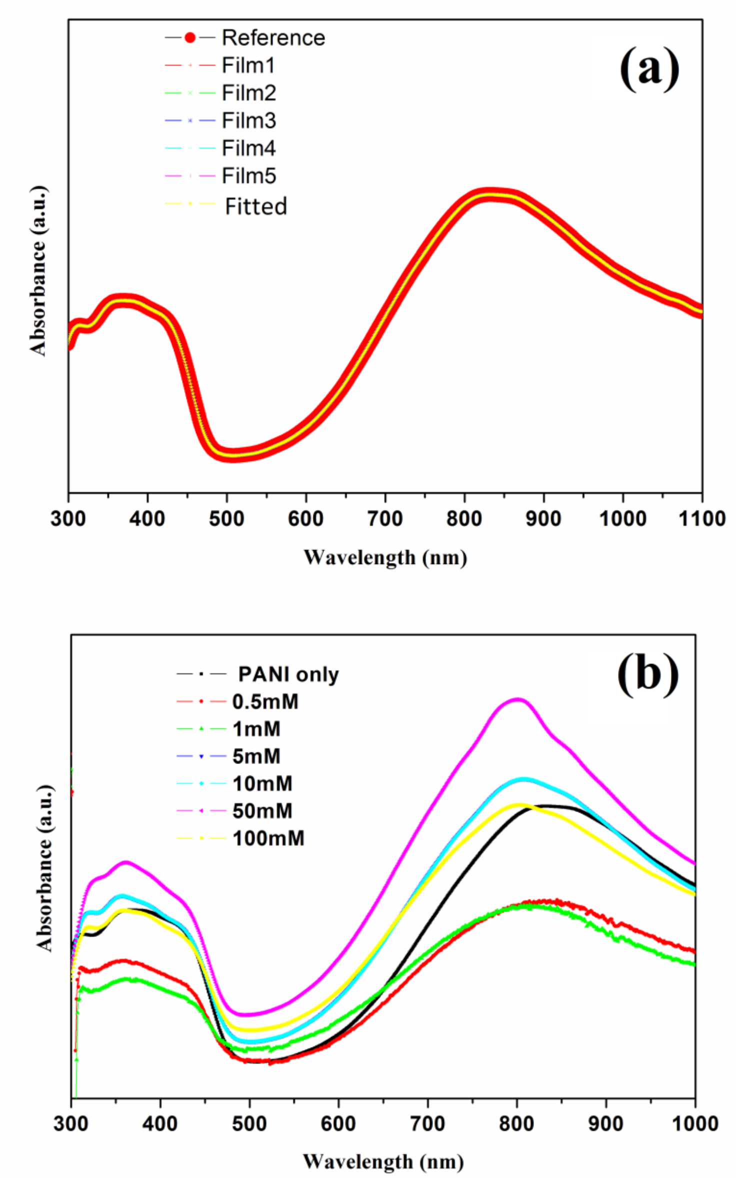

Figure 3**:** UV–Vis spectra of PANI films (a) only PANI films and fitted spectra, using Matlab software (b) On exposure to 2, 4-DNT, in the range 0.5 mM-100mM.

Molecular mechanics and semi empirical calculations were performed using the Hyper Chem 7 molecular visualization and simulation program for 2,4- DNT and PANI. This gives hydrogen bonding and π-π interaction, as shown in fig.4.

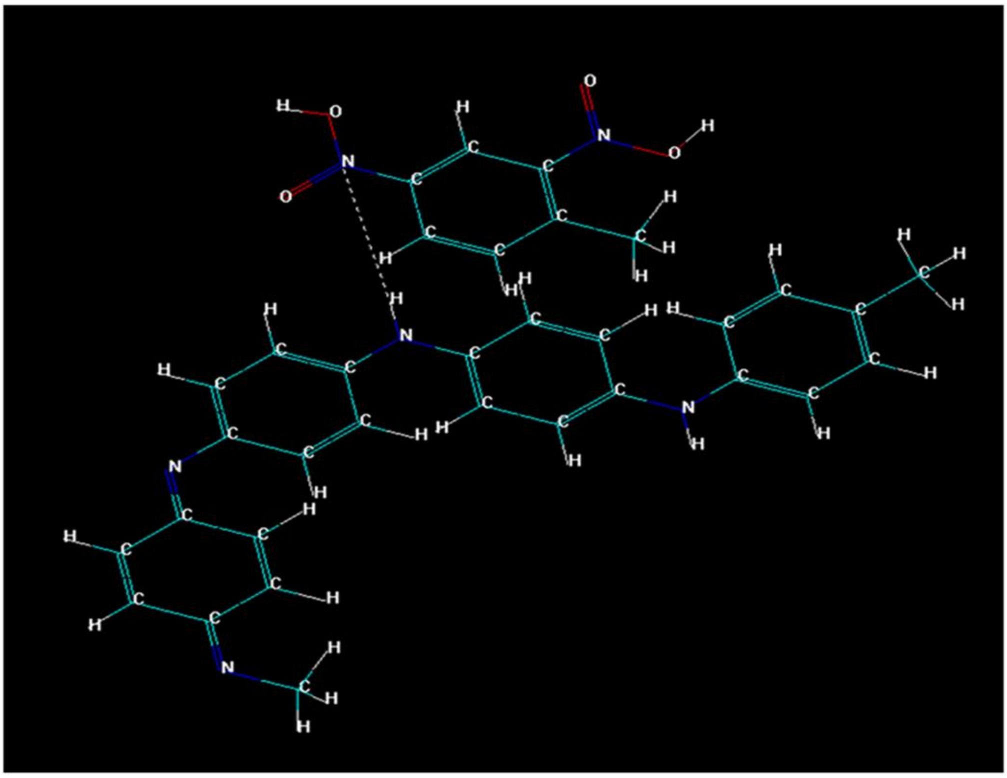

Figure 4: Schematic depiction of hydrogen bonding interactions between PANI and 2, 4- DNT molecules.

II. CONCLUSIONS

In summary, we demonstrated for the first time high sensitive and PANI based 2, 4-DNT sensor. This PANI sensor exhibits good magnitude of response, reproducibility and low detection limit to 2, 4-DNT at room temperature. Large sheets of PANI film can be synthesized using in-situ polymerization technique and then cut into smaller pieces, which can be directly used in the as produced state. The cost and complexity of sensor fabrication, maintenance and operation are therefore likely to be lower as compared to individually deposited PANI films. The simple, low-cost sensors described here could be deployed for a variety of applications, such as environmental monitoring, sensing in chemical processing plants, and gas detection for explosives.

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Conflict of interest: The authors declare that they have no conflict of interest.
Ethical statement: The authors declare that they have followed ethical responsibilities.

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