

## Plasma Polymerized Aniline/TiO<sub>2</sub> Assembly for p-n Heterojunction Fabrication

Sadia Ameen, Kyeongseop Lee, Im Yu-Bin, Minwu Song, Young Soon Kim,  
Hyung- Shik Shin\*

Thin Film Technology Laboratory, School of Chemical Engineering,  
Chonbuk National University

(hsshin@chonbuk.ac.kr\*)

### Introduction:-

As a typical conducting polymer, polyaniline (PANI) has unique electrical, optical and photoelectric properties and most importantly cheaper than other conducting polymers. Polyaniline (PANI) presents some structural variants according to the degree in which its molecules are oxidized, resulting in a diversified electric conductivity [1-6]. PANI has been synthesized by several techniques, one of which is carried out by means of plasmas, allowing the direct formation of the polymer from the vapor phase onto surfaces where thin films of the polymer are developed [7-9]. The importance of plasma polymerization over several other techniques is the formation of smooth polyaniline film, without using other reagents such as the oxidant or the solvent in the liquid phase, thus, giving a product without major contamination. The plasma-polymerized polyaniline films are of improved physical properties compared with those formed by electrochemical polymerizations or chemical syntheses followed by spin coating, solvent casting or melt extrusion. Plasma technique shows a superb environmental stability towards high temperature, intensive light, and strong electric fields. Solar cells based on conjugated polymers have attracted much attention because of their potential advantages, including low cost of fabrication. Photo current generation in the polymer solar cells involves four steps: (1) absorption of light by the active layer, resulting in creation of excitons, (2) dissociation of excitons at the interface of electron donor/acceptor and formation of free charges, (3) transport of the charges under an electric field, and (4) charge collection by the electrodes.

In the present paper, we have reported a simple method for the polymerization of aniline through pulsed plasma deposition. In this article, a p-n heterojunction solar cells is created with nanocrystalline TiO<sub>2</sub> (n-type) and polyaniline as the hole conductor. Results indicate that the introduction of PANI to TiO<sub>2</sub> nanoparticles could enhance the photo catalytic efficiency of TiO<sub>2</sub> under visible light irradiation.

### Experimental:-

Plasma polymerization was carried out in an experimental setup, shown in Fig-(1). It consist of four parts-(1) a reactor chamber quartz tube (2cm), (2) Cu coil (4inch), (3) plasma system (R.F. generator: 0-600W, matching network frequency of 13.56MHz) and (4)-mechanical vacuum pump (speed 600 1/min). The glow discharges were introduced through RF amplifier with a resistive coupling mechanism at 13.5MHz and power of

120W. These discharges were set without carrier gas or any other additional chemical elements to prevent the contamination. Substrates, containing deposited thin  $\text{TiO}_2$  layer, were placed just below the RF coil, placed inside the quartz tube. Initially, the chamber was evacuated to a base pressure of  $10^{-3}$  Torr through a rotatory vacuum pump. After attaining the base pressure, aniline (monomer) was injected, using a hypodermic syringe (5mL), fixed at the opposite end of the exhaust. The injector was open for the duration of 15min. The reaction was promoted by the collisions of the monomer molecules with the ions/particles, present in the plasma. Aniline (monomer) flowed into the reactor was pumped by the vacuum system, using pressure gradient between the reactor and the container.

#### Fabrication of p-n heterojunction:-

First, the  $\text{TiO}_2$  layer was deposited on the surface of the fluorine-doped conducting tin oxide (FTO) glass substrate by doctor blade method. The nanoporous  $\text{TiO}_2$  film was prepared according to the following procedure. Titania (P25 powder) nanoparticles (500mg) were added to a 4% PEG (polyethylene glycol) solution into a mortar and ground to form slurry. The slurry was then spread using doctor blade procedure by preparing an active area of  $0.25\text{cm}^2$  and finally was allowed to dry. Then the substrate was sintered at  $450^\circ\text{C}$  for 10 min. This  $\text{TiO}_2$  deposited substrates were later subjected to plasma polymerization for the fabrication of p-n heterojunction.

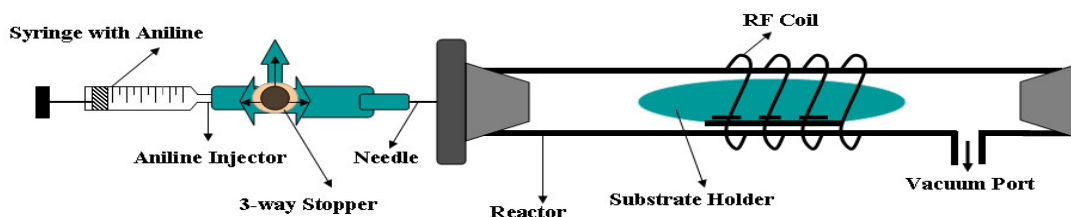


Fig 1:- Reactor setup for plasma polymerization of Aniline

#### Results and Discussion:-

FTIR of the plasma polymerized polyaniline, shown in Fig (2), shows the peaks at  $1496$  and  $1626\text{cm}^{-1}$  and are attributed to  $\text{C}=\text{C}$  interactions of benzenoid and quinoid rings respectively. The relatively high power input is required in the present investigation for an effective plasma polymerization at the low excitation frequencies that offers a wider range of discharge conditions under which the ring structure of aniline can possibly be preserved, as indicated by the presence of absorption bands at  $1496$  and  $1626\text{cm}^{-1}$ . The peak at  $3380\text{cm}^{-1}$  might due to  $\text{N-H}$  vibration. A peak belonging to the  $\text{C-H}$  aliphatic vibration is located at  $2353\text{cm}^{-1}$ . The  $\text{C-N}$  bond of the diphenyl amine group is observed in the IR spectrum at  $749\text{cm}^{-1}$ . Furthermore, as shown in [Fig 2 (a)], it is found that the intensity of the peak at  $3452\text{cm}^{-1}$  increases, which may probably due to the effect of plasma polymerization of aniline on  $\text{TiO}_2$ .

The XRD patterns are shown in Fig (3). In spite of the fact that PANI is a polymer capable of developing crystallinity, its amorphous part has covered the characteristic peaks of crystallinity in this kind of polymerization. It is possible that the energy of the plasma particles that confirm the polymer does not allow the formation of crystalline structures that are usual in other forms of synthesis. The plasma polymerized PANI [(Fig 3 (a))] on  $\text{TiO}_2$  presents a signal peak centered at  $2\theta \approx 23^\circ$ . The appearance of this peak suggests an amorphous nature of polyaniline. From [Fig 3 (b)], the anatase diffraction peaks at  $25.34^\circ$  and  $37.67^\circ$  are attributed to the 101, 004, reflections, respectively.

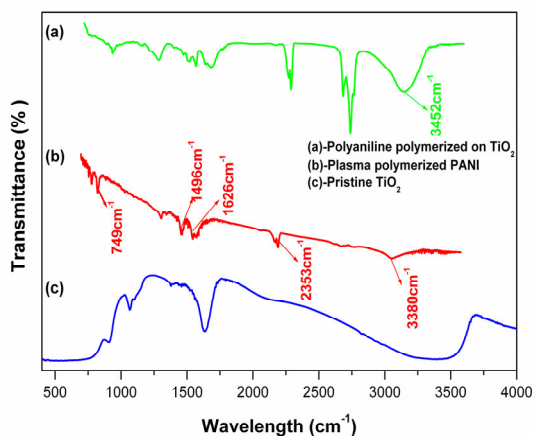


FIG (2):- (a) Typical FTIR spectrum of polyaniline polymerized on  $\text{TiO}_2$  (b) plasma polymerized PANI (c) Pristine  $\text{TiO}_2$

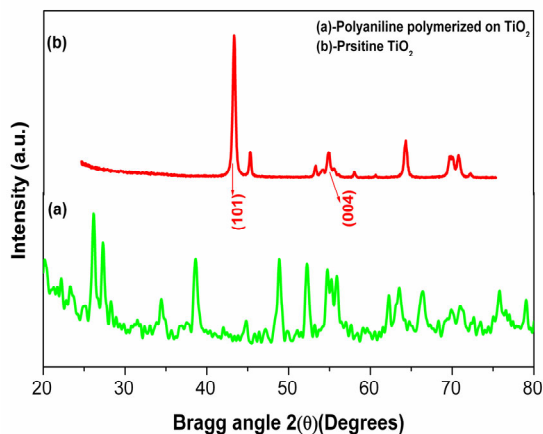
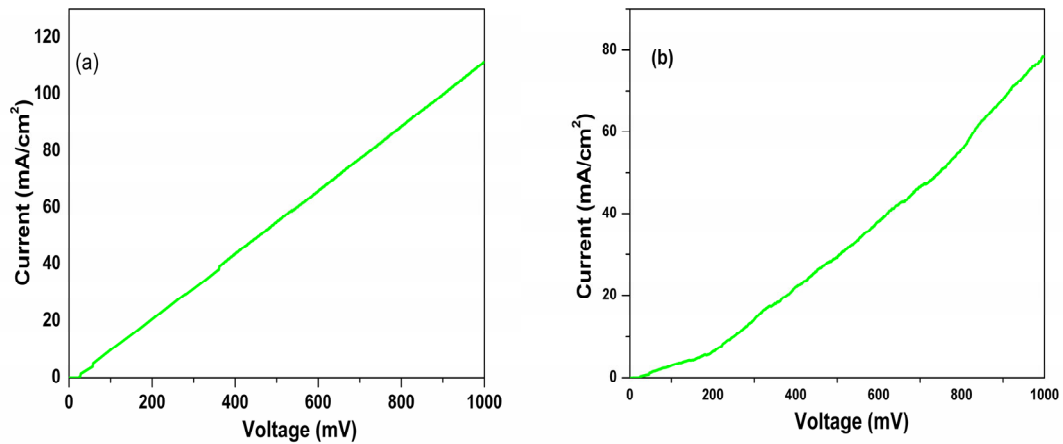


Fig 3:- (a) XRD patterns of plasma polymerized PANI on  $\text{TiO}_2$  (b) pristine  $\text{TiO}_2$

The sample of PANI/ $\text{TiO}_2$  semiconductor heterojunction is created by the film deposition of n-type  $\text{TiO}_2$  nanoparticles and p-type plasma polymerized polyaniline. Current-voltage measurements are done at  $25^\circ\text{C}$  or about 298K. The I-V characteristics, shown in Fig (4), indicate that no barrier is apparent at polyaniline/ $\text{TiO}_2$  heterojunction because their I-V characteristic curves are almost linear. Thus, we could conclude that a p-n hetero junction at nanostructured polyaniline/ $\text{TiO}_2$  interface has been created. When the cell is illuminated  $\text{TiO}_2$  absorb the photons at their interface and the efficient charge separation occurs at the interface leading to the generation of excitons. These excitons are swept to PANI layer polymerized under the influence of the plasma. Since, the conduction band of  $\text{TiO}_2$  and the LUMO level of the PANI are compatible for the charge transfer; the generated electrons can then be transferred to the conduction band of the  $\text{TiO}_2$ . The good conducting and mobility properties associated with PANI provides conducting pathway while reducing the degree of exciton recombination and thus, resulting in a more efficient charge separation. The greater order in the structure of the polymerized PANI improves the degree of contact with  $\text{TiO}_2$  and thus decreases the series resistance of the cell while increasing the current. Due to the internal electric field these charge carriers proceed toward their respective electrodes and transfer to the other side of the cell to generate electric current.



**FIG. (4) (a) The I-V characteristics in dark of of FTO/Polyaniline and (b) The I-V characteristics in dark of FTO/TiO<sub>2</sub>/Polyaniline heterojunction.**

#### **Conclusion:-**

We have prepared TiO<sub>2</sub>/polyaniline solar cells in a different way. The p-n hetero junction combines the plasma polymerized polyaniline and TiO<sub>2</sub>. The I-V characteristics showed that the photovoltaic phenomenon is present in an organic/inorganic hetero structure. The X-ray diffraction analysis showed that TiO<sub>2</sub>/PANI suffered structural modifications after the plasma polymerized deposition. Further, the structural verification of TiO<sub>2</sub>/PANI hetero junction is confirmed by IR analysis.

#### **References:-**

- [1] X. Zeng, T. Ko, J Polym Sci Polym Phys Ed, 35 (1997) 1993.
- [2] E. Virtanen, J. Laakso, H. Ruohonen, K. Va`kiparta, H. Jarviene, M. Jussila, P. Passiniemi, J.E. O. Sterholm, Synth Met, 84 (1997) 113.
- [3] J. Laska, K. Zak, A. Pron, Synth Met, 84 (1997) 117.
- [4] B. R. Mattes, H. L. Wang, D. Yang, Y. T. Zhu, W. R. Blumenthal, M. F. Hundley, Synth Met, 84 (1997) 45.
- [5] H. K. Chaudhari, D. S. Kelkar, Polym Int, 42 (1997) 380.
- [6] I. S. Rocha, L. H. Mattoso, L. F. Malmoge, R. J Gregorio, Polym Sci Polym Phys Ed, 37 (1999) 1219.
- [7] T. Suwa, M. Jikei, M. Kakimoto, Y. Imai, A. Takanaka, K Yoneda, Thin Solid Films, 273 (1996) 258.
- [8] G. J. Cruz, J. Morales, M. M. Castillo-Ortega, R. Olayo, Synth Met, 88 (1997) 213.
- [9] G. J. Cruz, J. Morales, R. Olayo, Thin Solid Films, 324 (1999) 119.