A Comparative Study of Plasma Enhanced Polymerization of Aniline on Single and Bilayered TiO$_2$ Thin Film Electrode for Heterostructure Diode

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Introduction

Conducting polymers are consisted of π-conjugated system and offer unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. PANI is a known conducting polymer due to its unique electrical, optical and the photoelectric properties. Importantly, PANI is cheaper than other conducting polymers [1] and affirms good thermal and environmental stability as compared to other organic semiconductors. Recent developments on the interpenetrating electron donor–acceptor heterostructures offer enhanced electron mobility and the improved performance for photovoltaic applications [2-3]. TiO$_2$ is a promising electron accepting material in organic/inorganic heterostructure devices and for hybrid photovoltaic applications. In this work, the organic/inorganic thin film is obtained using plasma polymerized p-type PANI and n-type TiO$_2$ for the fabrication of p-n heterostructure. The obtained p-n heterostructures with top Pt thin layer contact displays non-linear I-V curves which confirm the formation of Schottky contact.

Experimental

2.1 Synthesis of ZnO nanoparticles

The plasma deposition was carried out by introducing glow discharges through RF amplifier with a resistive coupling mechanism at 13.5 MHz and power of 120 W. Before the deposition, the single and bilayered TiO$_2$ thin films were deposited separately on the fluorinated tin oxide glass substrates and were placed just below the RF coil, situated inside the quartz tube. Afterward, 1 ml aniline (monomer) was injected using a hypodermic syringe fixed at the opposite end of the exhaust. The injector was open for 15 min for the uniform deposition of PANI.

2.2 Fabrication of p-n heterostructure

The nanocrystalline TiO$_2$ slurry was obtained by using 0.5 g synthesized TiO$_2$ nanoparticles powder (particles size 20-25 nm) with the incremental addition of 2 ml polyethylene glycol (4 wt% PEG, Fluka, average MW of 20,000) solution. Each time, the aqueous PEG solution (0.1 ml) was continuously added to TiO$_2$ naoparticles for achieving uniform lump free slurry. The TiO$_2$ nanoparticulate thin film with an active area ~ 0.25 cm^2 was attained by simple doctor blade technique on FTO substrate and dried at 40°C under nitrogen. The bilayered TiO$_2$ was prepared by dip coating of single layered TiO$_2$ thin film electrode into TiCl$_4$ solution and again calcined at 350°C for 20 min.

Results and Discussion

The TiO_2 single layered thin film, as shown in Figure 1(a) exhibits less porous morphology. Figure 1 (b) shows non uniform and less penetration of PANI molecules by plasma enhanced polymerization into the pores of TiO_2 thin film electrode. The thickness of single layer TiO_2 electrode is ~10 μm. However, the bilayered improves the microstructure of the TiO_2 layer (Figure 1 (c)) and increases the thickness by ~14 μm, shown in Figure 1 (d). The extent of PANI deposition has been drastically enhanced by the additional layer of TiO_2 on the single layered electrode.
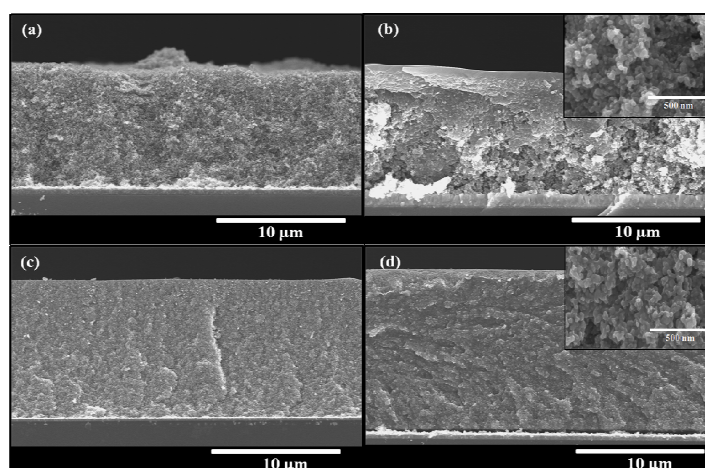

Figure 1. Cross-section FESEM images of (a) TiO_2 single layered thin film (b) PANI/TiO_2 single layered thin film (c) TiO_2 bilayered thin film and (d) PANI/TiO_2 bilayered thin film electrodes.

The characteristics peaks of pristine PANI at 1595 cm^{-1} and 1422 cm^{-1} are assigned to C=N and C=C stretching of the quinonoid and benzenoid units respectively, shown in Figure 2 A(b). The broader band at 3434 cm^{-1} corresponds to N–H stretching mode. The peak at 1103 cm^{-1} and 671 cm^{-1} are ascribed to the stretching peak of C=N and C-H bending out of the plane vibration of the benzene ring respectively. For PANI/TiO_2 thin film, shown in figure 2 A(a), the observed bands are slightly shifted with changed peak intensities. The peaks at 1422 cm^{-1} and 1595 cm^{-1} are negatively shifted to 1379 cm^{-1} and 1578 cm^{-1} after the deposition of PANI onto the TiO_2 thin film electrodes. Moreover, as compared with pristine PANI, the peak of N–H stretching has largely shifted from 3434 cm^{-1} to 3304 cm^{-1}. These results indicate that a hydrogen bonding has formed between NH group of the PANI and OH group of TiO_2.

The UV-Vis (Figure 2 B) shows the peaks at 324 nm corresponds to π–π* transitions centered on the benzenoid and quinoid units. The high intensity at 324 nm in PANI/bilayered TiO_2 thin film electrode indicates the enhanced deposition of PANI molecules on the surface of TiO_2. It could be attributed that highly porous surface of bilayered TiO_2 thin film absorbs large amount of PANI than the single layered TiO_2 thin film.
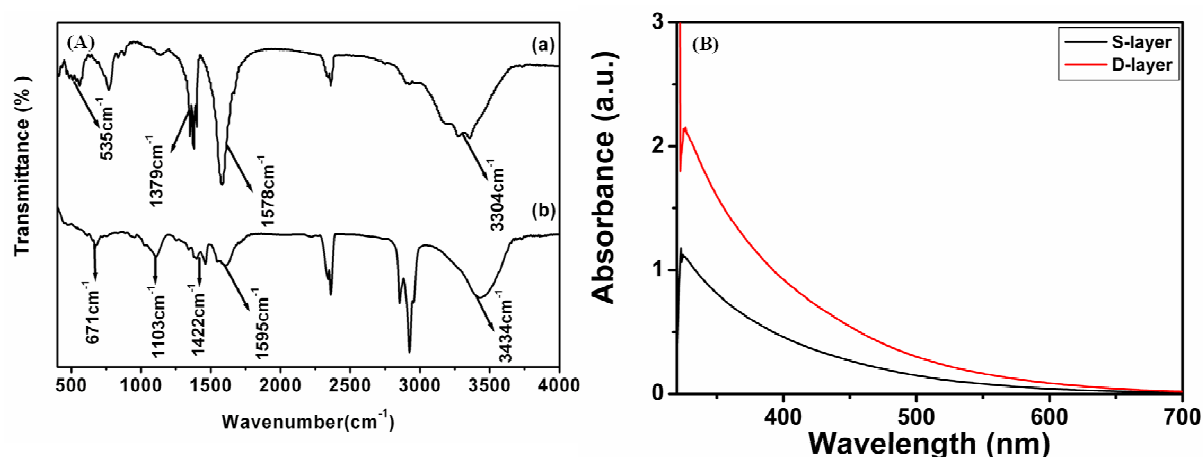
Figure 2. **(A)** FTIR of (a) PANI/TiO$_2$ thin film and (b) pristine PANI and **(B)** UV-Vis spectra of PANI/single layered and PANI/bilayered TiO$_2$ thin film electrode.
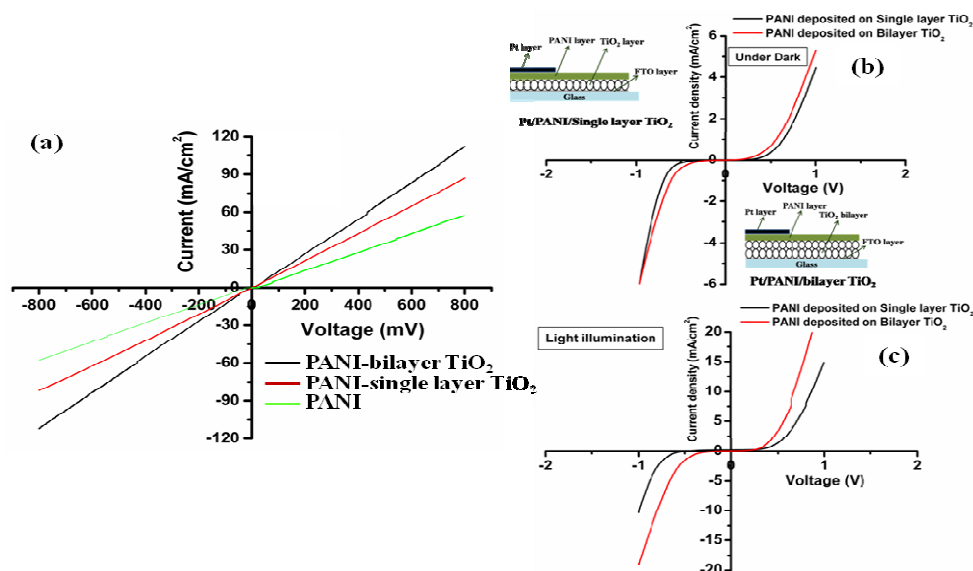

Figure 3. (a) I-V characteristics of PANI, PANI/single layered TiO$_2$ and PANI/bilayered TiO$_2$ heterostructures without Pt layer. I-V characteristics of Pt/PANI/single layered TiO$_2$ and Pt/PANI/bilayered TiO$_2$ heterostructure devices under dark **(b)** and light **(c)** conditions.

The I-V characteristics (Figure 3 (a)) of pristine PANI substrate and PANI/TiO$_2$ heterostructures with single and bilayered TiO$_2$ thin film electrodes exhibit almost symmetrical behavior in both the reverse and forward bias, in which the current increases linearly with the increase of the applied voltage. The increased current in PANI substrates at high voltage reveals the formation of the efficient charges carriers that results the generation of excitons within the plasma polymerized PANI interfacial layer. The linear I-V characteristics suggest the absence of barrier between PANI and TiO$_2$ layer of heterostructure devices. Moreover, the forward bias current increases with an increased applied voltage and have achieved almost the linear curve. It is seen that the PANI/bilayered TiO$_2$ heterostructure has attained the highest current of 115 mA as compared to pristine PANI substrate (58 mA) and PANI/single layered TiO$_2$ heterostructure

(97 mA). The proficient current in PANI/bilayered TiO$_2$ heterostructure is attributed to the advantageously additional penetration of PANI molecules into the pores of TiO$_2$ nanoparticles. Interestingly, the second layer of TiO$_2$ in PANI/bilayered TiO$_2$ provides a highly porous surface for high loading of PANI materials during the plasma enhanced polymerization. The high penetration of PANI molecules in PANI/bilayered TiO$_2$ electrode might lead the good conducting pathway and reduces the degree of excitons recombination and thus, delivers the linearly high current at high voltage. This result indicates that the efficient charge movement at the junction of PANI and TiO$_2$ interfaces has made the heterostructure which behaves as a typical ohmic system.

The I-V characteristics of both the devices, under dark and light conditions (Figure 3 (b, c)), are asymmetrical and non-linear, in which the current plot is approximately an exponential curve. Pt/PANI/TiO$_2$ single and bilayered heterostructure devices display moderate rectifying behavior which might be prevailed from the Schottky contact between the Pt layer and PANI/TiO$_2$ thin film layer. Additionally, this Schottky contact might create a barrier at the interfaces of PANI/TiO$_2$ thin film and Pt layer and thus, results to the non-linear curve of I-V characteristics. Upon light illumination, both the devices have generated the light-generated current. Generally, this current is produced by internal recombination of current source through shunt resistance and diode nature. This phenomena is absent in I-V characteristics under dark condition (figure 3 (b)), which means that the fabricated devices could absorb photons for the generation of current and having the photovoltaic behavior under light illumination. The improvement in I-V characteristics under light illumination (figure 3 (c)) is again attributed to the generation of high density minority charge carriers by PANI (p-type) to n-type TiO$_2$ thin film layer. Thus, the uniform and controlled thickness of PANI by plasma enhanced deposition onto TiO$_2$ nanoparticles thin film substrate provides the improved device performance of the p-n heterostructure devices under dark and light condition.

Conclusion

PANI molecules have been successfully deposited onto the n-type (single and bilayered) TiO$_2$ thin film by plasma enhanced polymerization technique for the p-n heterostructure devices. The morphological studies of PANI/TiO$_2$ thin film electrodes reveal that the bilayered TiO$_2$ thin film electrode exhibits the high extent of PANI molecule because of its highly porous surface. UV-Vis shows that the PANI/bilayered TiO$_2$ thin film electrode enhances the deposition of PANI molecules on the surface of TiO$_2$ as compared to single layered TiO$_2$ electrode. The proficient current in PANI/bilayered TiO$_2$ heterostructure is credited to the advantageous deposition of PANI molecules into the pores of TiO$_2$ layer due to the presence of additional second layer of TiO$_2$. The change of linear behavior of PANI/TiO$_2$ heterostructure to non linear behavior with top Pt contact layer confirms the formation of Schottky contact at the interfaces of Pt layer and PANI/TiO$_2$ layers.

References
[1] L. Xueyan, W. Desong, C. Guoxiang, L. Qingzhi, A. Jing and W. Yanhong, *Appl.Catal. B: Environ.* 81(2008) 267.
[2] K.M. Coakley and M.D. McGehee, *Appl. Phys. Lett.* 83 (2003) 3380.
[3] S. Gunes and N. S. Sariciftci, *Inorg. Chim. Acta* 361(2008) 581.