

## Iodine Doped Polyaniline Thin Film Heterostructure Devices

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### Abstract

The deposition of undoped and iodine (I<sub>2</sub>)-doped polyaniline (PANI) on TiO<sub>2</sub> thin film was carried out using plasma-enhanced chemical vapor deposition (PECVD) under different power inputs for the fabrication of p-polyaniline/n-TiO<sub>2</sub> heterostructure devices. The significant changes in the structural and optical properties confirmed the I<sub>2</sub> doping of PANI with strong bonding to the TiO<sub>2</sub> nanomaterials. A device fabricated by PANI/TiO<sub>2</sub> or I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film with a top platinum (Pt) layer exhibited nonlinear behavior of current (I)-voltage (V) curve, i.e., moderate diode behavior. Compared to Pt/PANI/TiO<sub>2</sub> heterostructure device, the Pt/I<sub>2</sub>-PANI/TiO<sub>2</sub> heterostructure device showed improved I-V properties with a considerably higher current of 0.050 mA, which might be attributed to the I<sub>2</sub> doping-induced generation of large numbers of polarons in the PANI band gap.

### Introduction

Polyaniline (PANI) is a p-type conducting polymer which stands out due to low cost, simple polymerization, high chemical and environmental stability [1, 2]. Interest in PANI is vastly triggered due to its variable conductivity which could be tuned from the doping/de-doping procedure [3]. In this article, the undoped and I<sub>2</sub> doped PANI thin films are polymerized by PECVD on TiO<sub>2</sub> thin film for the fabrication of heterostructure devices. The power inputs are varied to obtain highly uniform and good penetration of PANI on the surface of TiO<sub>2</sub> thin films. The prepared PANI/TiO<sub>2</sub> and I<sub>2</sub>-PANI/TiO<sub>2</sub> thin films are extensively characterized and discussed in terms of their electrical, morphological, structural, optical, surface and device behavior. The employed method offers a scalable and easy route for the fabrication of heterostructure devices.

### Experimental

#### *Preparation of TiO<sub>2</sub> Thin Film*

TiO<sub>2</sub> (P25, approximately 70% anatase and 30% rutile, Degussa) nanoparticles slurry was prepared by the addition of aqueous polyethylene glycol solution (Fluka, average MW=20,000) to 0.5 g of TiO<sub>2</sub> powder under vigorous grinding using mortar and pestle. The obtained uniform TiO<sub>2</sub> paste was coated on cleaned fluorine doped tin oxide glass (FTO glass, Hartford Glass Co., 8 Ω/sq, 80% transmittance in visible spectrum) by achieving an active area of 0.25 cm<sup>2</sup> using a doctor blade technique. After natural drying at room temperature, the TiO<sub>2</sub> thin film electrodes were calcined in a static air at 450 °C.

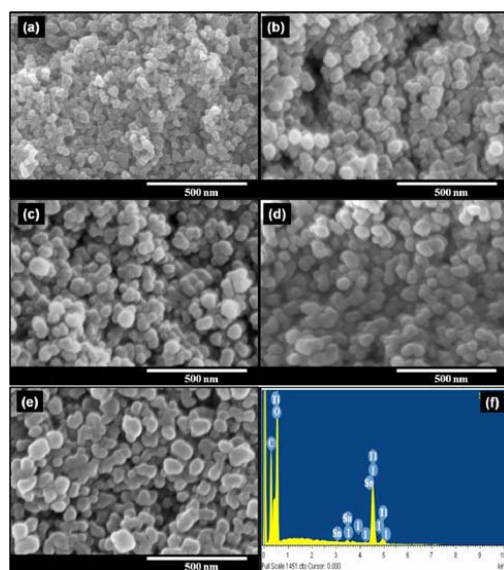
#### *Preparation of PANI/TiO<sub>2</sub> and I<sub>2</sub>-PANI/TiO<sub>2</sub> Thin Film*

The experimental setup for plasma polymerization was consisted of four parts: i) a reactor chamber quartz tube (2 cm), ii) Cu coil (4 inch), iii) plasma system (R.F. generator: 0-600 W, matching network frequency of 13.56 MHz), and iv) mechanical vacuum pump (speed 600 L/min). The chamber was initially evacuated to a base pressure of 10<sup>-3</sup> Torr through a rotator vacuum pump and the glow discharges were introduced through RF amplifier with a resistive

coupling mechanism at 13.5 MHz. Different power inputs in the range of 100-200 W were applied for igniting the glow discharges for the optimum duration of 10 min using 1 ml aniline monomer. For PANI/TiO<sub>2</sub> thin film, the prepared TiO<sub>2</sub> coated FTO glass substrates were subjected for the plasma polymerization of PANI under different power inputs (100-200 W). The I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film were prepared by the injection of the optimum ethanolic I<sub>2</sub> (0.02 M) solution through a syringe into the quartz tube containing the prepared PECVD PANI/TiO<sub>2</sub> thin film substrates. The I<sub>2</sub> doping was conducted at a specific power input of 200 W for 10 min. These PANI/TiO<sub>2</sub> and I<sub>2</sub>-PANI/TiO<sub>2</sub> thin films substrates were used for the fabrication of heterostructure devices.

### 3. Results and Discussion

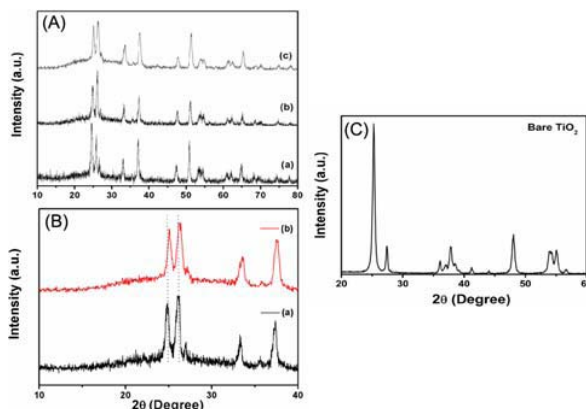
Fig. 1 shows the FESEM images of undoped and doped PANI/TiO<sub>2</sub> thin films. The sizes of bare TiO<sub>2</sub> nanoparticles are ~20-25 nm (Fig. 1(a)). After plasma polymerization, the agglomeration of TiO<sub>2</sub> nanoparticles causes the increment in the particle size to ~30-50 nm, as shown in Fig. 1 (b)-(d). Figure 1(e) shows the obtrusive increase in the size (~50 nm) of TiO<sub>2</sub> nanoparticles which might occur due to the incorporation of I<sub>2</sub> dopant into PANI/TiO<sub>2</sub> thin films. The spectra exhibit the peaks associated with C, O, Ti, and Sn along with the peak of iodine atom (0.14 wt%) which supports the I<sub>2</sub> doping in PANI/TiO<sub>2</sub> thin film.



**Fig. 1** Surface FESEM images of (a) Pristine TiO<sub>2</sub> and PANI/ TiO<sub>2</sub> thin film at power input of (b) 100, (c) 150, (d) 200 W, (e) I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film at 200 W, and (f) EDX analysis of I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film

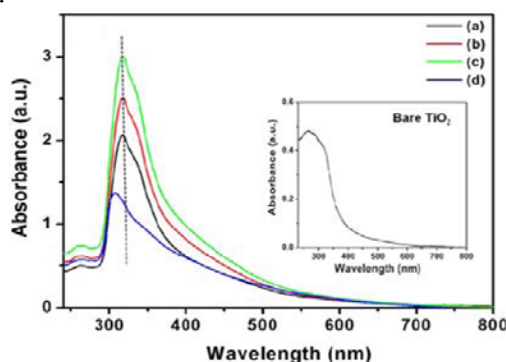
The XRD spectra of undoped and doped PANI/TiO<sub>2</sub> nanoparticulate thin film exhibit same pattern as shown in Fig. 2. The broader region between 10°-20° is ascribed to the periodicity parallel and perpendicular to PANI and the peaks at 26.1°, 27.1°, 37°, 48°, 54.4°, and 62.4° (JCPDS 21- 1276) confirm the existence of TiO<sub>2</sub> nanoparticles. The XRD patterns of PANI/TiO<sub>2</sub> thin film substrate also exhibit the peaks at 25°, 33.4°, 51.2°, 61.1°, and 65° correspond to the FTO layer of the conducting glass. The intensities of XRD peak changes with the change in power inputs during the PECVD of PANI, as shown in Fig. 2(A a)-(A c), suggests

that the crystalline phases of  $\text{TiO}_2$  have not changed by PECVD of PANI. However upon  $\text{I}_2$  doping (Fig. 2(Bb)), the visible peak shifts of the diffraction peaks from their original position indicates the effects of  $\text{I}_2$  doping on PANI/ $\text{TiO}_2$  thin film.



**Fig. 2** (A) XRD patterns of PANI/ $\text{TiO}_2$  thin film at power input of (a) 100, (b) 150, and (c) 200 W. (B) (a) PANI/ $\text{TiO}_2$  and (b)  $\text{I}_2$ -PANI/ $\text{TiO}_2$  thin film at power input of 200 W. (C) shows the XRD spectrum of bare  $\text{TiO}_2$ .

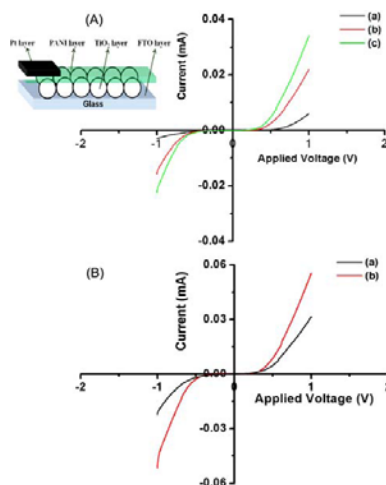
The UV-Vis spectra of undoped and doped PANI/ $\text{TiO}_2$  thin film are shown in Fig. 3. The PANI/ $\text{TiO}_2$  thin film exhibits the prominent peak at  $\sim 320$  nm, associated to  $\pi \rightarrow \pi^*$  transition in the benzene rings, as shown in Fig. 3(a-c). The bare  $\text{TiO}_2$  shows the typical absorption band at 300-400 nm, as shown in the inset of Fig. 3. It has been seen that the intensities of the absorbance peak increases as increasing the power inputs during PECVD of PANI. The highest absorption peak at 200 W (Fig. 3(c)), suggests the thicker deposition of PANI on  $\text{TiO}_2$  thin film. The considerable blue shift in the absorbance peak at  $\sim 308$  nm is observed in  $\text{I}_2$ -PANI/ $\text{TiO}_2$  thin film as shown Fig. 3(d), indicating the effects of  $\text{I}_2$  doping. This blue shift might originate from the “exciton” transition and causes the interband charge transfer from benzenoid to quinoid moieties of the protonated PANI.



**Fig. 3** UV-Vis spectra of PANI/ $\text{TiO}_2$  thin film at power inputs of (a) 100, (b) 150, (c) 200W, and (d)  $\text{I}_2$ -PANI/ $\text{TiO}_2$  thin film at 200 W. Inset shows the UV-Vis spectrum of bare  $\text{TiO}_2$ .

Fig. 4 shows the forward and reverse bias current ( $I$ )-voltage ( $V$ ) characteristics at room temperature (298 K) with an applied voltage ranging from -1V to +1 V. All fabricated devices exhibit non-linear behavior of the  $I$ - $V$  curves in which the current plot is approximately an exponential curve. It could be seen that Pt/PANI/ $\text{TiO}_2$  heterostructure devices display moderate rectifying behavior, indicating the formation of Schottky contact between the Pt layer and PANI/ $\text{TiO}_2$  thin film layer. The  $I$ - $V$  curve of the Pt/PANI/ $\text{TiO}_2$  heterostructure devices where PANI is polymerized under plasma at different power input is shown in Fig. 4(Aa)-(Ac). The

rectifying ratios of 1.7, 2.35, and 2.18 at 0.8 V are estimated for the devices fabricated with plasma polymerized PANI at 100, 150, and 200 W, respectively. Importantly, the maximum current obtained from the devices increases vastly as increasing the power inputs. The fabricated Pt/PANI/TiO<sub>2</sub> heterostructure diode with polymerized PANI at 200 W (Fig. 4(Ac)) shows relatively high current of ~0.031 mA current, whereas, the fabricated devices with the polymerization at 100 W (Fig.4(Aa)) and 150 W (Fig. 4(Ab)) exhibits comparatively low current of 0.022 and 0.006 mA, respectively. The superior I-V properties at high power input (200 W) might originate from the large deposition of PANI on the surface of TiO<sub>2</sub> thin film because the high power input increases the density of energetic ions or electrons during the plasma polymerization. Moreover, heterostructure device by I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film displays the considerable changes in the I-V properties as shown Fig. 4(Ba) and (Bb).



**Fig. 4** (A) I-V characteristic curves of PANI/TiO<sub>2</sub> thin film at power input of (a) 100, (b) 150, and (c) 200 W. (B) (a) PANI/TiO<sub>2</sub> and (b) I<sub>2</sub>-PANI/TiO<sub>2</sub> thin film at power input of 200 W. The inset shows the schematic of Pt/PANI/TiO<sub>2</sub>/FTO device

#### 4. Conclusions

The undoped and I<sub>2</sub> doped PANI are successfully deposited on TiO<sub>2</sub> thin film by PECVD under different power inputs for the fabrication of p-n heterostructure devices. The crystalline properties are altered upon I<sub>2</sub> doping, suggesting the subtractive interaction between PANI and I<sub>2</sub> moieties during PECVD. The structural and optical properties confirm the I<sub>2</sub> doping of PANI with the strong bonding to TiO<sub>2</sub> nanomaterials. Compared to Pt/PANI/TiO<sub>2</sub> heterostructure device, Pt/I<sub>2</sub>-PANI/TiO<sub>2</sub> heterostructure device shows improved I-V properties with considerably high current of 0.05 mA which might attribute to the generation of large number of polarons in the band gap of PANI by I<sub>2</sub> doping.

#### References

- [1] A. G. MacDiarmid, A. J. Epstein, W. R. Salaneck, D. T. Clark, E. J. Samuelson, in *Science and Application of Conducting Polymers*, IOP published, Bristol, 1991, p 117.
- [2] S. Ameen, V. Ali, M. Zulfeqar, M. M. Haq, M. Husain, *Curr. Appl. Phys.*, 9 (2009) 478.
- [3] W. S. Huang, B. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans.*, 82 (1986) 2385.