Sustainable Organic Polymer Solar Cells Using TiO_2 Derived From Automobile Paint Sludge

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***Abstract*— We demonstrate green synthesis of TiO_2 nanoparticles (Nps) derived from automobile paint sludge (APG) and its application in the development of sustainable and solution processable polymer solar cells (PSCs). The APG contains TiO_2 > 35% of its weight with several surfactants, organic polymers and ~ 2 to 10 % inorganic matter depending on the type of paints used. The TiO_2 is generally present as micro sized particles in the APG which on hydrothermal treatment transform into nano sized particles. These organic matter is thermally extracted by a specially designed reaction vessel, where as the inorganic impurities are removed by repeated washing with dilute acids and bases. The TiO_2 Nps are characterized by SEM imaging, EDX analysis, powder XRD, TG/DTA and FTIR, spectroscopy techniques. The TiO_2 Nps are re-suspended in methanol for application in PSCs as an efficient electron transport layer. The TiO_2 layer was spin coated on bulk hetero junction active layer of low band gap donor polymers P3HT with PCBM as electron acceptor. The performance of the TiO_2 Nps is analyzed by fabricating devices in ITO/PEDOT:PSS/active layer/TiO_2/Al configuration. The present work has implication for ultra low cost and sustainable PSCs with advantage of recycling of a highly hazardous industrial waste.**

***Index Terms* — : TiO_2 nanoparticles, Paint Sludge, Solar cell; Hydrothermal; P3HT; Green chemistry.**

I. INTRODUCTION

TiO_2 is a high value industrial material, its large quantities are used in making premium quality paints. The automobile industries use several thousand tons of these paints to protect the vehicles from corrosion and giving a base for top colour coating. About 25% of the paint used is wasted while doing the paint job, this creates huge piles of paint sludge. These piles are generally used as landfill. Some processes are reported to reformulate it into poor quality primers for low quality paint jobs and its use as ceramic composite. [1-4] We developed a novel process to extract TiO_2 nanoparticles by a zero emission process from the paint sludge. These nanoparticles are used in organic polymer solar cells as electron transport layer (ETL).

Organic photovoltaic devices are the promising candidate for future cost effective, efficient, stable and flexible source of electricity generation. [5-12] Recently, significant efforts have been dedicated to the interface engineering of polymer solar cells to increase its efficiency. [10] Interface properties are critical to the device performance and can be tuned by incorporating a functional interfacial layer between active layer and metal electrode. Many interfacial materials, such as metal oxides, self assembled monolayers and conjugated polyelectrolytes (CPEs), have successfully enhanced power conversion efficiencies (PCEs) of solar cells fabricated through solution processing.[10] In present this work we used the TiO_2 nanoparticles extracted from the paint sludge to understand the effect TiO_2 interface layer and its solvent treatment on the device physics of polymer solar cells. Methanol is chosen as solvent for TiO_2 because it is recently known to improve device performance of PSCs. [10] The positive effect of TiO_2 nanoparticles and the methanol are both observed in the open circuit voltage and short circuit current which in turn enhances the efficiency of a PSC.

II. EXPERIMENTAL DETAILS

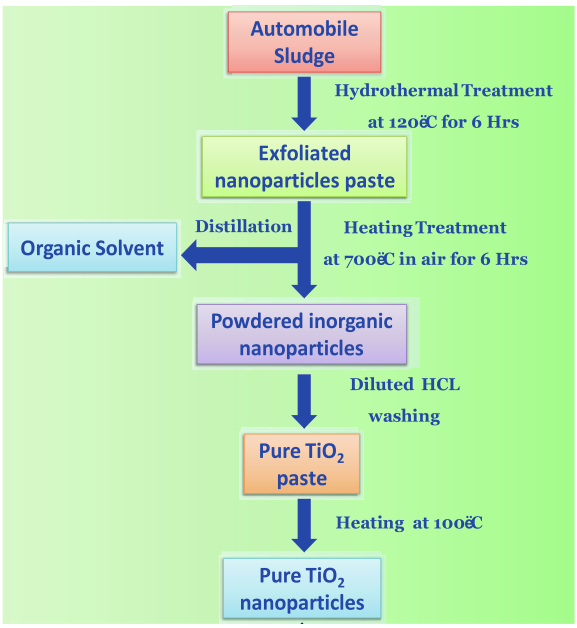

FIG1: Flow diagram of the process of TiO_2 nanoparticles synthesis from paint sludge of automobile industries

The experimental procedure is illustrated in the following flow diagram (fig1). The paint sludge is provided from J & S Research and Innovations, New Delhi. The hydrothermal bomb is in-house custom made. Scanning electron microscope (SEM) images of powered samples were

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recorded on Oxford . Powder XRD was recorded on Bruker D-8 Advance X-ray diffractometer. FTIR of samples were recorded using KBr pallet samples on Perkin Elmer spectrum 2. TG/DTG curves of powder samples were simultaneously recorded on PerkinElmer Model TGA-7, USA, in static air at heating rate of 10°C/min from 50-900°C. Solutions were centrifuged using Eppendorf, Germany centrifuge 5804 R.

Device Fabrication: Fabrications of these devices have been carried out on the blend of P3HT: PCBM with the ratio of 1:0.7 with the concentration of 1 wt% in chlorobenzene. Solar cells are fabricated on the ITO coated glass substrate prior to fabrication first of all patterned the ITO coated substrates to make the anode electrode and then cleaned the substrate carefully with soap solution, distilled water using ultrasonic bath after this, cleaned the substrates in acetone, trichloroethylene, isoproponol successively and then anneal the substrates at 150^{0}C in the vacuum oven for 15-20 min. Now, the dried substrates have been exposed to the UV ozone cleaning for 10-15 min. PEDOT: PSS (Sigma Aldrich, USA with 1.3% dispersion in water) were spin cast on the substrate with the 4000 rotation per min (rpm) for 60 sec. The substrate was dried at 120^{0}C for 30 min in the vacuum oven and then move into the glove box to develop the active layer on the substrate using spin cast method. This active layer is a solution containing a mixture of P3HT: PCBM in the chlorobenzene solvent with a concentration of 20 mg/ml. The pure dry TiO_2 nanoparticles are resuspended in methanol in dilute concentration (10µg/ml) and spin coated over the active layer of the PSC at 1500 rpm. The substrates, on which active layer spin cast, were cured at 140^{0}C for 20 min in the glove box. Finally, an aluminum electrode has been deposited with thickness 120 nm inside the thermal evaporator chamber with the vacuum 8x10^{-6} mbar through shadow mask. The active area of both the devices has been taken ~ 0.08 mm for all the pixels of the devices. The current density–voltage (J–V) characteristics of the device 1 and 2 were recorded using Keithley 2420 Source Meter unit interfaced with a computer. These characetrisirtics have been performed in the dark and under tungsten halogen lamp with illumination intensity 100mW/cm^2.

III. RESULTS & DISCUSSIONS

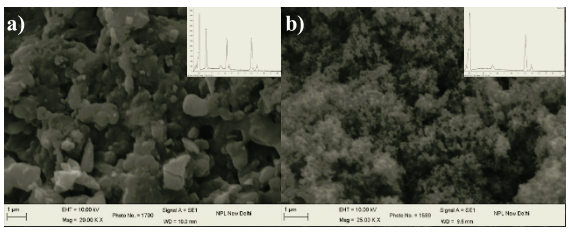

FIG 2: (a) SEM image of automobile paint sludge particles; b) SEM image of TiO_2 nanoparticles extracted from the automobile paint sludge. The selected section EDX of each sample is shown in the inset of the respective SEM image.

The SEM images of the automobile paint sludge and that of the TiO_2 nanoparticles derived from it clearly demonstrate the reduction in the particle size. The TiO_2 nanoparticles are seen as homogenous particles with size ~100 nm. The composition of the samples were observed by EDX attached with the SEM. It show the 2:1 atomic ratio of Ti:O which significantly highlights the purity of the TiO_2 of the nanoparticles prepared.

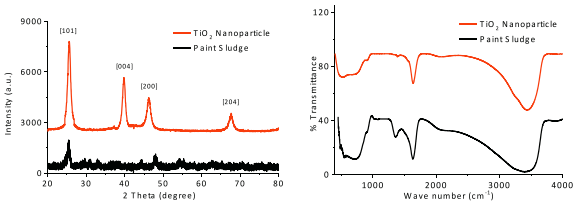

FIG 3: (a) XRD of paint sludge and TiO_2 nanoparticles synthesized from the paint sludge; b) FTIR of paint sludge and TiO_2 nanoparticles synthesized from the paint sludge. Red line shows TiO_2 nanoparticles whereas the black line represents the paint sludge.

The powder XRD of the paint sludge shows presence of amorphous TiO_2 in it. After the treatment of sludge the synthesized nanoparticles are observed to show Anatase crystalline character. Also the FTIR spectra of the paint sludge and the TiO2 nanoparticles show the presence of TiO_2 in the paint sludge. Thus it may be inferred that the hydrothermal treatment induces crystalline character with a well defined particle size as seen in the SEM images. Further the curing at 600°C removes all the surfactants and other organic impurities from the sample. The powder XRD shows many small signals in the range of 2θ = 25°–65°. These signals may due to the presence of small quantity of inorganic impurities present in the paint sludge. These impurities are absent in the TiO_2 nanoparticles. The acid treatment after the curing readily washes the inorganic impurities.

Photovoltaic performance of polymer solar cell P3HT:PC_{61}BM with TiO_2 have been investigated by device configuration as indium tin oxide (ITO)/poly (3, 4-ethylendioxythiophene)-poly (styrene suffocate) (PEDOT: PSS)/P3HT:PCBM/Al and ITO/PEDOT: PSS/P3HT:PCBM/TiO_2/Al, respectively. These devices are representing as device 1 and device 2, respectively. The device configuration diagram and the schematic energy levels of various layers of the PSC is shown in FIG. 4 which shows that the TiO_2 act as an electron harvesting material and helps electron to move to the cathode.

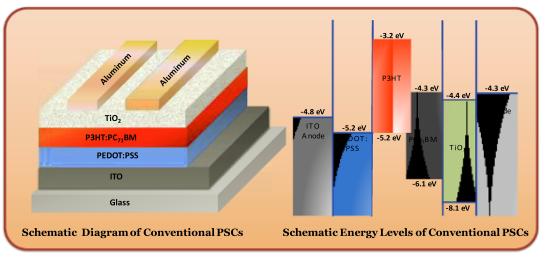

FIG 4: Schematic of the BHJ polymer solar cell, in which the TiO_2 is applied in between active layer and an Al anode. Schematic energy levels of the conventional device.

The device performance parameters are given in table 1. The *J-V* Characteristics under illumination are shown in Fig. 5. The increase in the Jsc from 6.84 to 7.54 mA/cm^2

may be attributed to the incorporation of the TiO_2 as electron transport layer. The energy level diagram (Fig. 4) shows that the LUMO of the TiO_2 is slightly lower than that of the PCBM due to which there is an increase in the potential of the PSCs. Also the solvent effect of methanol leads to decrease the series resistance, increase the mobility, accelerate and enlarge the charge carrier extraction and hence enhance in Voc. The overall effect of the TiO_2 and methanol is seen in the enhancement of the power conversion efficiency of the device from 1.30% to 1.63%. This 25% increment in efficiency is highly significant towards the development of high efficiency PSCs.

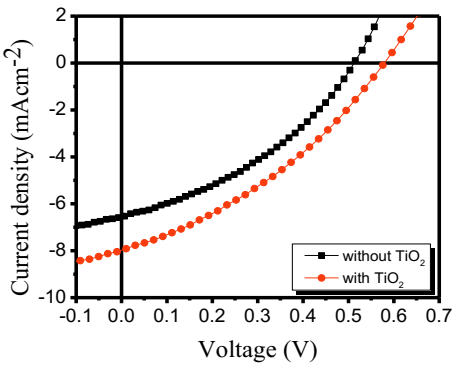

FIG 5: Experimental *J–V* characteristics for conventional device under illumination intensity of under 1,000 W/cm^2 AM 1.5G.

TABLE 1**.** Device parameters from P3HT:$PC_{61}BM$ polymer solar cells with conventional device structures, measured under illumination intensity of 1000 W/m^2.

	Device 1 Without TiO_2	Device 2 With TiO_2
$J_{sc}(mAcm^{-2})$	6.84	7.54
V_{oc} *(V)*	0.52	0.56
FF (%)	37.2	38.1
PCE (%)	1.30	1.63

IV. CONCLUSIONS

We successfully synthesized TiO_2 nanoparticles using highly hazardous industrial waste – automobile paint sludge. The zero emission process collects the organic volatile matter via distillation and inorganic impurities via acid washing. The pure anatase TiO_2 nanoparticles were achieved by curing the hydrothermally exfoliated matter at 600 °C. Also the value enhanced product i.e. TiO_2 nanoparticles are shown to enhance the power conversion efficiency by a factor of 25%. Enhancement of J_{sc} due to efficient electron transport layer derived from crystalline and optimized bandgap TiO_2. The solvent effect of methanol leads to decrease the series resistance, increase the mobility, accelerate and enlarge the charge carrier extraction.

V. ACKNOWLEDGEMENT

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