ABSTRACT

The cost effective polymer/metal-oxide hybrid bulk heterojunction solar cells that combines the merits of both polymer and metal-oxide, have attracted global attention due to their promising characteristics. The creative ability exhibited by these cells is the flexibility available to control the morphology and interface by varying the composition of the materials. These hybrid thin film solar cells also exhibit better electrical properties due to the direct interfacial interaction of polymer with inorganic metal-oxide where the polymer acts as donor and inorganic metal-oxide acts as acceptor.

Among the conducting polymers, polyaniline (PANI) finds wide application due to its environmental stability, ease of preparation, conductivity control and low cost. Similarly the inorganic material, TiO$_2$ is non-toxic, biocompatible and has suitable charge transport properties. For the preparation of PANI based hybrid materials, TiO$_2$ is highly preferred because, the conduction band of TiO$_2$ matches well with the lowest unoccupied molecular orbital (LUMO) of PANI and this improves the electronic transport properties. PANI-TiO$_2$ is used as super-capacitor electrodes, corrosion protection coatings, photo catalysts and gas sensors. However, PANI-TiO$_2$ hybrid, as a photoactive material, has been rarely studied. Thus in the present study an attempt has been made to fabricate solar cells based on PANI/TiO$_2$ hybrid bulk heterojunction thin film.

HCl-doped PANI (PANI-HCl) thin films were prepared by in-situ chemical oxidative polymerization, at three different temperatures (4°C, 13°C and 31°C) of reaction medium with two different dopant concentrations (1M, 2M). The thickness of the films determined using profilometer was found to
be around 100 nm. The FTIR study shows the presence of Cl⁻ ion in the prepared PANI polymer. X-ray diffraction studies reveal that the films are amorphous in nature. The scanning electron microscope images show that the films have a rough surface due to nanofiber formation along with high dense inter-fiber fusion. Hall-effect analysis showed that the films are p-type semiconductors. Increase in HCl-dopant concentration (2M) and decrease in film preparation temperature (4°C), has been found to increase the film conductivity. UV-visible light absorption by the films is observed to increase with increase in dopant concentration invariably for all the films prepared at different temperatures. But such absorption is highly enhanced for films prepared at very low temperature (4°C). The photoluminescence (PL) spectra shows that the improved PL quantum yield can be achieved only by the combination of low temperature film preparation (4°C) along with 2M-HCl dopant concentration.

CSA-doped PANI (PANI-CSA) thin films were prepared by spin coating technique with three different PANI:CSA weight ratio (1:0.5, 1:1 and 1:2). Thickness of the films was found to be in the range of 54 - 88 nm. The degree of polymerization was observed to increase with CSA ratio. X-ray diffraction studies reveal that the films are of amorphous nature. SEM images show that the films exhibit a smooth surface morphology without the presence of any cracks. Hall-effect study shows that the films are p-type semiconductors. Moreover, the electrical conductivity, optical absorption and photoluminescence intensity was observed to increase with increase in dopant ratio. Analysis of the films prepared using the dopants (HCl and CSA) shows that PANI thin film with CSA dopant is stable with better conductivity and exhibits good sticking efficiency to glass/ITO substrates. Titanium-di-oxide (TiO₂) nanoparticles have been prepared by simple sol-gel solution technique followed by annealing at 500 °C. The particles exhibited rutile tetragonal structure and the crystallite size was found to be about 32 nm. TiO₂
nanoparticles exhibited maximum absorption in the UV region due to its wide 
band gap of 3.45 eV.

CSA-doped PANI/TiO$_2$ hybrid thin films with different 
PANI:CSA:TiO$_2$ weight ratio of (1:4:0.5), (1:4:1) and (1:4:2) have been 
prepared by powder blend technique. The hybrid thin films were also heat-
treated at a temperature of 100 °C for 12 h in oven. Thickness of the films was 
found to lie in the range of 67 – 88 nm. The FTIR study shows the presence 
of TiO$_2$ and CSA within the PANI polymer. X-ray diffraction studies of the 
hybrid thin films show the presence of crystalline phase and this may be due 
to the inclusion of TiO$_2$ nanoparticles and the crystallinity was observed to 
improve with heat-treatment. The SEM studies of the hybrid films show the 
presence of rough surface and this may be due to coalescing and 
agglomeration of hybrid particles and this roughness was found to increase 
with both increase in TiO$_2$ ratio and heat-treatment. PANI-CSA with 
PANI:CSA weight ratio of (1:4) was observed to exhibit high absorption in 
the UV region and had a band gap of 3.67 eV. This absorption in UV region 
and PL emission in UV and visible region were observed to increase with 
addition of TiO$_2$ nanoparticles and with heat-treatment.

Hybrid films were also prepared by solution blend technique with 
PANI:CSA:TiO$_2$ weight ratio as (1:8:2), (1:8:3) and (1:8:5). Thickness of the 
films was found to lie in the range of 98 – 125 nm. The X-ray diffraction 
studies revealed that the films are polycrystalline in nature and the 
crystallinity may be due to the presence of higher percentage of CSA. SEM 
image of polymer thin film shows the presence of root like structure spread 
throughout the film, which is made of large number of horizontally grown, 
short micro-wires assembled in series. With addition of TiO$_2$ and with 
increase in TiO$_2$ ratio, the length of the micro-wires increased and the 
uniformity in their alignment has been observed to have got improved. TEM
image of hybrid film with lower TiO\textsubscript{2} ratio shows uniform distribution of nanoparticles in the polymer. Absorption spectra of PANI with high CSA ratio show highly intense and broad absorption in the wavelength range from UV to visible region and in IR region. Hybrid thin films are found to have higher absorbance and PL emission than the PANI-CSA thin films, due to the interaction of TiO\textsubscript{2} nanoparticles with the CSA-doped PANI at the interface of PANI and TiO\textsubscript{2} nanoparticles. PL quenching in CSA-doped PANI hybrid films has been observed and this occurs due to the blending of TiO\textsubscript{2} nanoparticles with PANI-CSA forming hybrid thin film. This indicates the successful dissociation of excitons at the PANI/TiO\textsubscript{2} interface and this hybrid structure can be used as a photoactive material for solar cells. Based on these studies, CSA-doped PANI/TiO\textsubscript{2} hybrid thin films prepared by solution blend technique have been used to fabricate hybrid bulk heterojunction solar cells of structure ITO/PEDOT:PSS/PANI:CSA:TiO\textsubscript{2}/Al and their current-voltage characteristics have been studied.

Hybrid BHJ solar cell devices with structure ITO/PEDOT:PSS/PANI:CSA:TiO\textsubscript{2}/Al, were fabricated using the films with three different PANI:CSA:TiO\textsubscript{2} weight ratio of (1:8:2), (1:8:3) and (1:8:5). The device with lower TiO\textsubscript{2} weight ratio (1:8:2) exhibited a short circuit current density of 1.62 mA/cm\textsuperscript{2} and photo conversion efficiency of 0.21%.