The exploration of enhanced photocurrent with Zn-perylene metal organic frameworks thin film and bodipy via triplet triplet annihilation upconversion

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Abstract
Highly crystalline surface supported metal organic framework thin film has been used to generate enhanced photocurrent in the photoelectrochemical cells. The combination of Zn-perylene SURMOF and pyridine functionalized Bodipy has ~ two times higher photocurrent due to triplet triplet annihilation upconversion than its own parts. This experimentally determined data shows that MOF thin film material is well suited for overcoming the energy loss due to Shockley-Queisser limit for dye sensitized solar cell technology.

Introduction
The exploration of highly efficient materials for dye sensitized solar cell technology is one of the challenges of this century. The highly oriented and crystalline Zn-perylene SURMOFs as acceptor/emitter [1] and pyridine functionalized Bodipy photosensitizer [2] has recently been used to generate the enhanced photocurrent. There are cost and performance reasons to use the Bodipy as photosensitizer inside the photoelectrochemical cell.

It has been reported that due to large molar absorption coefficients, relatively long excited-state lifetimes, excellent photo-stability, facile preparation, strong visible light absorption, and most importantly low cost, it is believed that the Bodipy [3,4] is suitable for reducing the cost and improved performance which follows TTA UC mechanism shown in Figure 1. Moreover, the triplet triplet annihilation upconversion is the wavelength shift methodology where the photons having the high wavelength is upconverted into the photons of lower wavelength [2,4-8].

Experimental
Materials
All chemical reagents were purchased were purchased from Sigma-Aldrich. The TiO218-NRT is purchased from Heptachroma Company.

Preparation of FTO-TiO2 substrate: All the FTO glasses were cleaned with acetone, isopropyl alcohol, ethanol and deionized water for half hour, respectively. Then, the FTO glasses were treated with plasma (Diener FEMTO SR CE, 70 W) under O2 (0.3 mbar) for 3 min. After that, TiO2 thin films were prepared with TiO2 nanoparticles (mixture of TiO2 and EtOH, 1 g: 4 g) by spin coating (2000 r/s, 30 s). Subsequently, the TiO2 coated films were dried at 70°C for one hour and annealed at 500°C for 12 hours.

Preparation of Zn-perylene SURMOF: Liquid phase epitaxy technique are used for the preparation of the Zn-Perylene SURMOFs on top of FTO/TiO2 substrates. We prepared a concentration zinc acetate ethanolic solution (1 mM) on top of FTO-TiO2 which was sprayed for 15 s. After 30 s wait 3,9 perylene dicarboxylic acid ethanolic solution was sprayed (40 µM; spray time: 20 s, waiting time: 30 s). This alternate spray process of Zn-acetate as metal linker and 3,9 perylene dicarboxylic acid as organic linker supported the formation of highly crystalline metal organic framework thin film which can be found somewhere in the literature [2]. The pure ethanol was used for rinsing to get rid of the unreacted zinc acetates and perylene molecules from the surface.

XRD characterization of Zn-perylene SURMOF: The as-prepared Zn-perylene SURMOF thin film showed (100) and weak (200) peaks

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[1,2] observed with out-of-plane XRD pattern suggesting that the fabricated Zn-perylene SURMOF can be grown exclusively along with (100) direction on TiO\textsubscript{2} surface, which is accordance with the simulated XRD diffractogram with preferred (100) orientation [9]. Moreover, the XRD pattern with 2θ=5.8° corresponds to a d value of 1.5 nm which suggest the same length of of 3,9-perylenedicarboxylic acid and Zn paddle-wheel structure. It has been inferred that the Zn-perylene SURMOF shows a similar structure similar to SURMOF 2 analogues [9] having the perpendicular layers to the substrates which is comprising 1D channels with a diameter of ~1.5 nm, and a layer distance of ~0.58 nm [1].

The infrared characterizations: The infrared spectra of perylene powder is being compared with the Zn-perylene MOF thin film. It has been inferred that the C=O stretching in free carboxylic groups was found at the 1686 cm\textsuperscript{-1} for perylene dicarboxylic acid, whereas 1589 cm\textsuperscript{-1} and 1552 cm\textsuperscript{-1} for Zn-perylene SURMOF which are attributed to the asymmetric and symmetric stretching of COO- groups, respectively [10].

Scanning Electron Microscope (SEM): The morphology of the Zn-perylene SURMOF films prepared with LPE method on TiO\textsubscript{2} substrate was characterized with scanning electron microscope (SEM) as displayed in Figure 2. which exhibits a homogeneous and compact surface with a thickness of ~600 nm (60 LPE cycles) [11].

Results and discussions

The UV visible is measured by dipping the Zn-perylene MOF thin film into the acetonitrile Bodipy solution. It demonstrates that the strong absorption at ~550 nm is the signature absorption of the Bodipy chromophore whereas the Zn-perylene SURMOFs showed strong absorption at about 420 nm. The combined system for of Bodipy plus Zn-perylene SURMOFs showed both of these characteristics shown in Figure 3.

The process of triplet triplet annihilation upconversion is absorption of low energy and upconvert it into high energy using the sensitizer acceptor pair [3,5,6,12-14]. On the basis of UV-vis profile it is idealized that TiO\textsubscript{2}-perylene SURMOF+Bodipy [2] can be an effective architecture to facilitate the triplet energy transfer and the enhancement of energy via triplet-triplet within a photoelectrochemical cell. Moreover,

Photoelectrochemical experiments

The chronoamperometric experiments were performed in a standard electrochemical cell using TiO\textsubscript{2}-Zn-perylene+Bodipy or TiO\textsubscript{2}-Zn-perylene, or TiO\textsubscript{2}+Bodipy as working electrodes, Ag/AgNO\textsubscript{3} as reference electrode, and platinum wire as counter electrode with an external potential (0.2 V). During this process, the electrochemical cell was irradiated by using simulated solar light (AM1.5 solar) passing through a 532 nm long pass filter coupled with an automatic shutter control the light irradiation i.e. light on and light off.

The triplet triplet annihilation upconversion (TTA UC) system consisting of TiO\textsubscript{2}-Zn-perylene+Bodipy system were irradiated with the 532 nm light, we found the transient photocurrent (~7.1 µA/cm\textsuperscript{2}) with TiO\textsubscript{2}-Zn-perylene/Bodipy was higher ~two times higher than TiO\textsubscript{2}-Zn-perylene (~0.3 µA/cm\textsuperscript{2}) and ~3.3 µA/cm\textsuperscript{2} (TiO\textsubscript{2}+Bodipy) respectively which is shown in Figure 4a. Comparative analysis of the transient photocurrent shows that the TiO\textsubscript{2}-Zn-perylene-two times enhanced photocurrent is due to triplet triplet annihilation mechanism [2].

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Figure 2. Scanning electron microscope showing the thickness of Zn-perylene MOF thin film

Figure 3. UV-Vis of Zn-perylene SURMOFs (Blue), Zn-perylene SURMOFs/Bodipy (Black), and Bodipy (Green)

Figure 4. Upon 532 nm excitation photocurrent enhancement of TiO\textsubscript{2}-Zn-perylene SURMOFs/Bodipy than rest of its parts TiO\textsubscript{2}-Zn-perylene SURMOFs and TiO\textsubscript{2}-bodipy (b) Upon 430 nm excitation photocurrent enhancement of TiO\textsubscript{2}-Zn-perylene SURMOFs/ Bodipy than rest of its parts TiO\textsubscript{2}-Zn-perylene SURMOFs and TiO\textsubscript{2}-bodipy
Therefore, this initial and important experimental approach can be considered for our future research.

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