Global Journal of Researches in Engineering: C
Chemical Engineering
Volume 19 Issue 1 Version 1.0 Year 2019
Type: Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4596 & Print ISSN: 0975-5861

The Exploration of Enhanced Photocurrent with Zn-Perylene Metal Organic Frameworks Thin Film and Bodipyvia Triplet Triplet Annihilation Upconversion

By Shargeel Ahmad, Jinxuan Liu & Licheng Sun

Dalian University of Technology

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.

GJRE-C Classification: *FOR Code: 090499*

THEEXPLORATIONOFENHANCEDPHOTOCURRENTWITHZN-PERYLENEMETALORGANICFRAMEWORKSTHINFILMANDBODIPYVIATRIPLETTRIPLETANNIHILATIONUPCONVERSION

Strictly as per the compliance and regulations of:

The Exploration of Enhanced Photocurrent with Zn-Perylene Metal Organic Frameworks Thin Film and Bodipyvia Triplet Triplet Annihilation Upconversion

Shargeel Ahmad α, Jinxuan Liu σ & Licheng Sun ρ

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.

I. Introduction

The exploration of highly efficient materials for dye sensitized solar cell technology is the 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 Bodipyas 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 fig. 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].

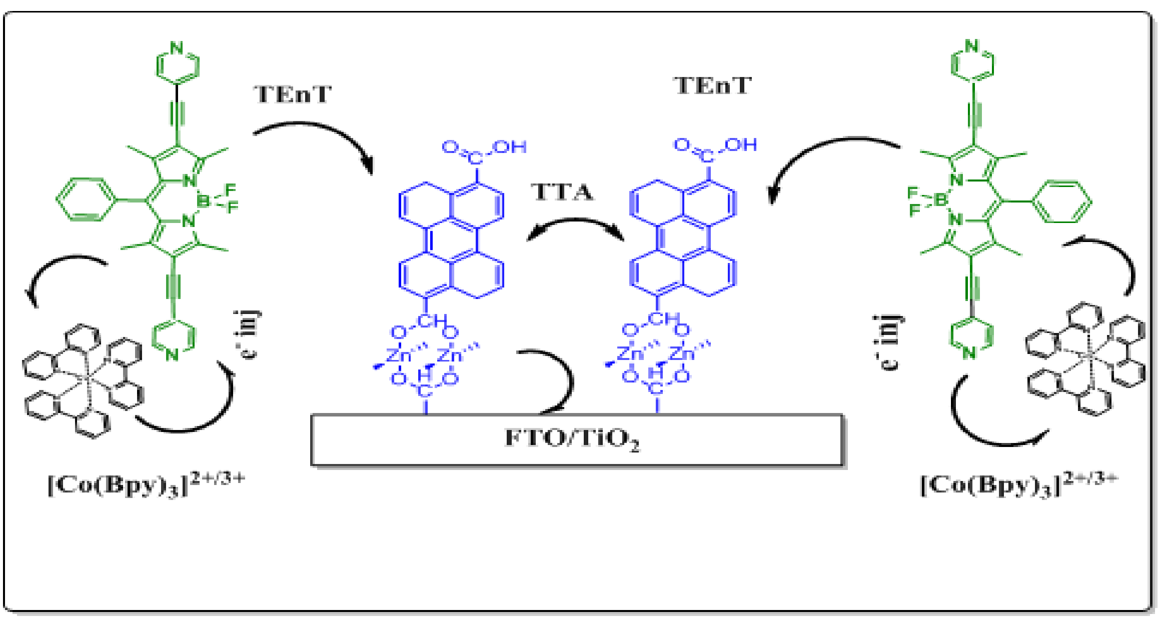

Fig. 1: Schematic Illustration of an Epitaxial Zn-Perylene SURMOFs Anchored on Mesoporous TiO_2 Substrate as Emitter, and PTOEP as Sensitizer in $[Co(Bpy)_3]^{2+/3+}$ Acetonitrile Solution for the Enhancement of Photocurrent via TTA UC.

Author α σ ρ: State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Dalian University of Technology, Dalian 116024, China. e-mail: shargeel@mail.dlut.edu.cn

II. Experimental

a) Materials

All chemical reagents were purchased were purchased from Sigma-Aldrich. The $TiO_2$18-NRT is purchased from Heptachroma Company.

b) Preparation of FTO-TiO_2 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 O_2 (0.3 mbar) for 3 min. After that, TiO_2 thin films were prepared with TiO_2 nanoparticles (mixture of TiO_2 and EtOH, 1 g: 4 g) by spin coating (2000 r/s, 30 s). Subsequently, the TiO_2 coated films were dried at 70 °C for one hour, and annealed at 500 °C for 12 hours.

c) Preparation of Zn-perylene SURMOF

Liquid phase epitaxy technique is used for the preparation of the Zn-Perylene SURMOFs on top of FTO/TiO_2 substrates. We prepared concentration zinc acetate ethanolic solution (1 mM) on top of FTO-TiO_2 which was sprayed for 15s. After 30s wait 3, 9 perylene dicarboxylic acid ethanolic solution was sprayed (40μM; spray time: 20s, waiting time: 30s). 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.

d) XRD Characterization of Zn-perylene SURMOF

The as-prepared Zn-perylene SURMOF thin film showed (100) and weak (200) peaks[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_2 surface, which is accordance with the simulated XRD diffractogram with preferred [100] orientation[9]. Moreover, the XRD pattern with $2\theta=5.8°$ corresponds to a *d* value of 1.5 nm which suggest the same length 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].

e) 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^{-1} for perylene dicarboxylic acid, whereas 1589 cm^{-1} and 1552 cm^{-1} for Zn-perylene SURMOF which are attributed to the asymmetric and symmetric stretching of COO^- groups, respectively.[10]

f) Scanning Electron Microscope (SEM)

The morphology of the Zn-perylene SURMOF films prepared with LPE method on TiO_2 substrate was characterized with scanning electron microscope (SEM) as displayed in Fig. 2. which exhibits a homogeneous and compact surface with a thickness of ~600 nm (60 LPE cycles).[11]

Fig. 2: Scanning Electron Microscope Showing the Thickness of Zn-perylene MOF thin film.

III. 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 fig. 3.

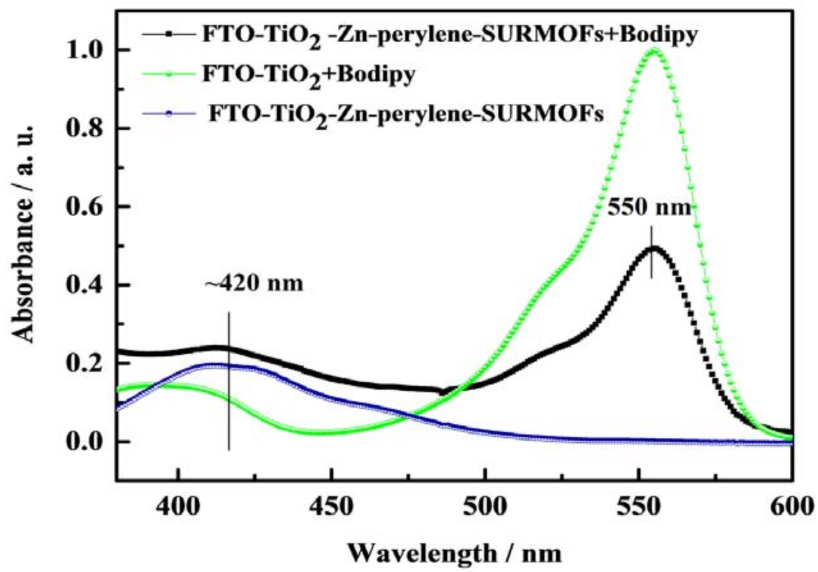

Fig. 3: UV-Vis of Zn-perylene SURMOFs (Blue), Zn-perylene SURMOFs/Bodipy (Black), and Bodipy (Green).

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_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,

a) Photoelectrochemical Experiments

The chronoamperometric experiments were performed in a standard electrochemical cell using TiO_2-Zn-perylene+Bodipy or TiO_2-Zn-perylene, or TiO_2+Bodipy as working electrodes, Ag / $AgNO_3$ 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 532nm 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_2-Zn-perylene+bodipy system were irradiated with the 532nm light, we found the transient photocurrent (~7.1µA/cm^2) with TiO_2-Zn-perylene / Bodipy was higher ~ two times higher than TiO_2-Zn-perylene (~0.3µA/cm^2) and ~3.3µA/cm^2 (TiO_2+Bodipy) respectively which is shown in fig. (4-a). Comparative analysis of the transient photocurrent shows that the TiO_2-Zn-perylene-two times enhanced photocurrent is due to triplet triplet annihilation mechanism[2].

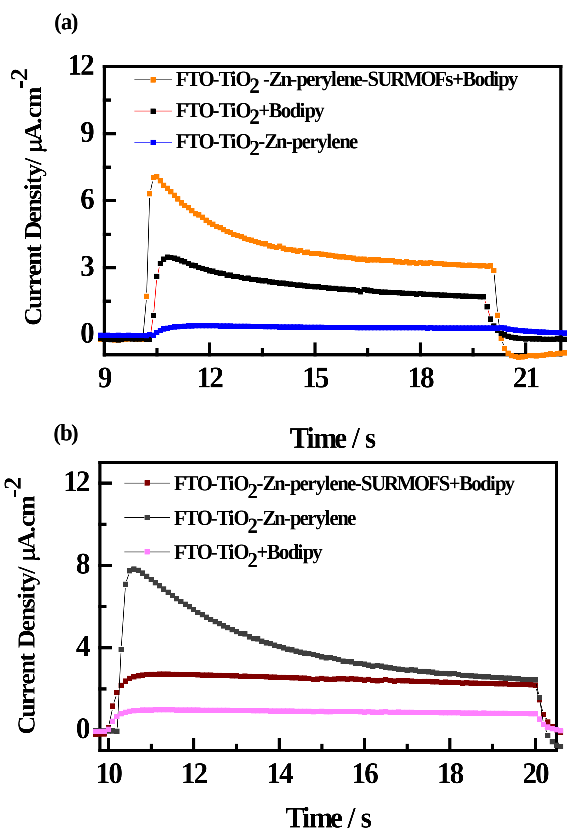

Fig. 4: (a) Upon 532nm Excitation Photocurrent Enhancement of TiO_2-Zn-perylene SURMOFs/Bodipy Than Rest of Its Parts TiO_2-Zn-perylene SURMOFs and TiO_2-Bodipy (b) Upon 430nm Excitation Photocurrent Enhancement of TiO_2-Zn-perylene SURMOFs/Bodipy than rest of its Parts TiO_2-Zn-perylene SURMOFs and TiO_2-Bodipy.

Similarly upon excitation with blue light at λ_{ex} = 420 nm, the TiO_2-Zn-perylene/Bodipy, Zn-perylene SURMOFs and TiO_2/Bodipy enhanced ~7.8μA/cm² photocurrent with TiO_2-Zn-perylene/Bodipy and also with TiO_2-perylene-SURMOFs (~2.9μA/cm²)and TiO_2/Bodipy (~0.9μA/cm²) shown in fig. (4-b).

The intensity dependent experiments are one of standard and basic experiments for the confirmation of TTA UC mechanisms. The important intensity dependent experiments were carried out with 532nm green light source to observe the phenomenon of TTA UC. Raising the light power from low energy to high energy displays the linear behavior from TiO_2-Zn-perylene / Bodipy which is consistent with the TTC UC[3] which is demonstrated in fig. 5.

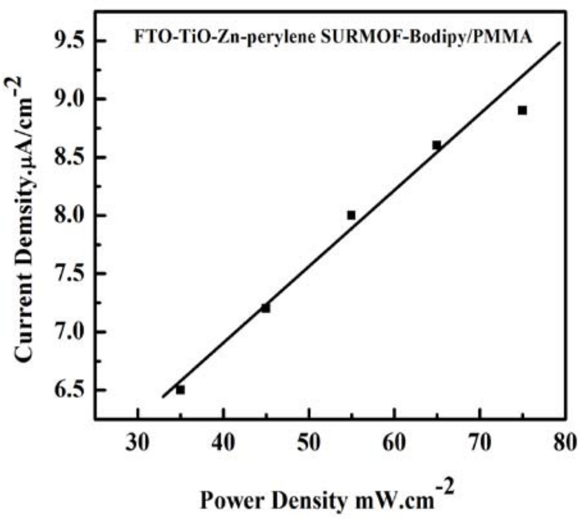

Fig. 5: Intensity Dependent Experiment of TiO_2-Zn-Perylene SURMOF/Bodipy Showing the Linear Behavior.

Summing up, the MOF thin film material is very efficient to upconvert the low energy into high energy due to its highly crystalline, porous and versatile nature. It has been analyzed that thetwo times higher performance of our observed system is due to triplet triplet annihilation upconversion (TTA UC). The studied demonstration canbe used for future dye sensitized solar cell technology. The limitation of the results can be overcome and optimized by using the more efficient electrocatalyst and conducting the detail investigations of mechanism. Therefore, this initial and important experimental approachcan be considered for our future research.

References Références Referencias

1. Ahmad S, Liu J, Gong C, et al. Photon Up-Conversion via Epitaxial Surface-Supported Metal–Organic Framework Thin Films with Enhanced Photocurrent [J]. ACS Applied Energy Materials, 2018, 1(2): 249-253.
2. Ahmad S, Liu J, Ji W, et al. Metal–Organic Framework Thin Film-Based Dye Sensitized Solar Cells with Enhanced Photocurrent [J]. Materials, 2018, 11(10): 1868.
3. Chen Y, Zhao J, Xie L, et al. Thienyl-substituted BODIPYs with strong visible light-absorption and long-lived triplet excited states as organic triplet sensitizers for triplet–triplet annihilation upconversion [J]. RSC Advances, 2012, 2(9): 3942-3953.
4. Ji S, Ge J, Escudero D, et al. Molecular structure–intersystem crossing relationship of heavy-atom-free BODIPY triplet photosensitizers [J]. The Journal of organic chemistry, 2015, 80(11): 5958-5963.
5. Schulze T F, Schmidt T W. Photochemical upconversion: present status and prospects for its application to solar energy conversion [J]. Energy & Environmental Science, 2015, 8(1): 103-125.
6. Monguzzi A, Tubino R, Hoseinkhani S, et al. Low power, non-coherent sensitized photon up-conversion: modelling and perspectives [J]. Physical Chemistry Chemical Physics, 2012, 14(13): 4322-4332.
7. Ji S, Wu W, Wu W, et al. Ruthenium (II) Polyimine Complexes with a Long‐Lived 3IL Excited State or a 3MLCT/3IL Equilibrium: Efficient Triplet Sensitizers for Low‐Power Upconversion [J]. Angewandte Chemie, 2011, 123(7): 1664-1667.
8. Singh-Rachford T N, Lott J, Weder C, et al. Influence of temperature on low-power upconversion in rubbery polymer blends [J]. Journal of the American Chemical Society, 2009, 131(33): 12007-12014.
9. !!! INVALID CITATION !!!,
10. Max J J, Chapados C. Infrared spectroscopy of aqueous carboxylic acids: Comparison between different acids and their salts [J]. Journal of Physical Chemistry A, 2004, 108(16): 3324-3337.
11. Arslan H K, Shekhah O, Wohlgemuth J, et al. High‐Throughput Fabrication of Uniform and Homogenous MOF Coatings [J]. Advanced Functional Materials, 2011, 21(22): 4228-4231.
12. Gray V, Dzebo D, Abrahamsson M, et al. Triplet-triplet annihilation photon-upconversion: towards solar energy applications [J]. Phys Chem Chem Phys, 2014, 16(22): 10345-10352.
13. Dilbeck T, Wang J C, Zhou Y, et al. Elucidating the Energy-and Electron-Transfer Dynamics of Photon Upconversion in Self-Assembled Bilayers [J]. The Journal of Physical Chemistry C, 2017, 121(36): 19690-19698.
14. Simon Y C, Weder C. Low-power photon upconversion through triplet–triplet annihilation in polymers [J]. Journal of Materials Chemistry, 2012, 22(39): 20817-20830.