

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

Shargeel Ahmad*, Jinxuan Liu and Licheng Sun

State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Dalian University of Technology, China

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 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 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].

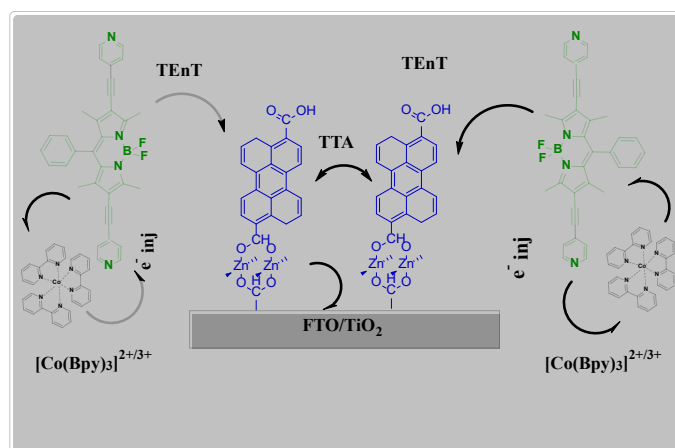


Figure 1. Schematic illustration of an epitaxial Zn-Perylene SURMOFs anchored on mesoporous TiO_2 substrate as emitter, and PTOEP as sensitizer in $[\text{Co}(\text{Bpy})_3]^{2+/3+}$ acetonitrile solution for the enhancement of photocurrent via TTA UC

Experimental

Materials

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

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.

Preparation of Zn-perylene SURMOF: Liquid phase epitaxy technique are used for the preparation of the Zn-Perylene SURMOFs on top of FTO/ TiO_2 substrates. We prepared a concentration zinc acetate ethanolic solution (1 mM) on top of FTO- TiO_2 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

*Correspondence to: Shargeel Ahmad, State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Dalian University of Technology, Dalian 116024, China, E-mail: shargeel@mail.dlut.edu.cn

Received: November 07, 2018; Accepted: November 16, 2018; Published: November 20, 2018

[1,2] observed with out-of-plane XRD pattern suggesting that the fabricated Zn-erylene SURMOF can be grown exclusively along with (100) direction on TiO₂ 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-erylenedicarboxylic acid and Zn paddle-wheel structure. It has been inferred that the Zn-erylene 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 erylene powder is being compared with the Zn-erylene MOF thin film. It has been inferred that the C=O stretching in free carboxylic groups was found at the 1686 cm⁻¹ for erylene dicarboxylic acid, whereas 1589 cm⁻¹ and 1552 cm⁻¹ for Zn-erylene SURMOF which are attributed to the asymmetric and symmetric stretching of COO- groups, respectively [10].

Scanning Electron Microscope (SEM): The morphology of the Zn-erylene SURMOF films prepared with LPE method on TiO₂ 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-erylene 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-erylene SURMOFs showed strong absorption at about 420 nm. The combined system for of Bodipy plus Zn-erylene 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 TiO₂-erylene 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 TiO₂-Zn-erylene+Bodipy or TiO₂-Zn-erylene, or TiO₂+Bodipy as working electrodes, Ag/AgNO₃ 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 TiO₂-Zn-erylene+bodipy system were irradiated with the 532 nm light, we found the transient photocurrent (~7.1 μA/cm²) with TiO₂-Zn-erylene/Bodipy was higher ~two times higher than TiO₂-Zn-erylene (~0.3 μA/cm²) and ~3.3 μA/cm² (TiO₂+Bodipy) respectively which is shown in Figure 4a. Comparative analysis of the transient photocurrent shows that the TiO₂-Zn-erylene-two times enhanced photocurrent is due to triplet triplet annihilation mechanism [2].



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

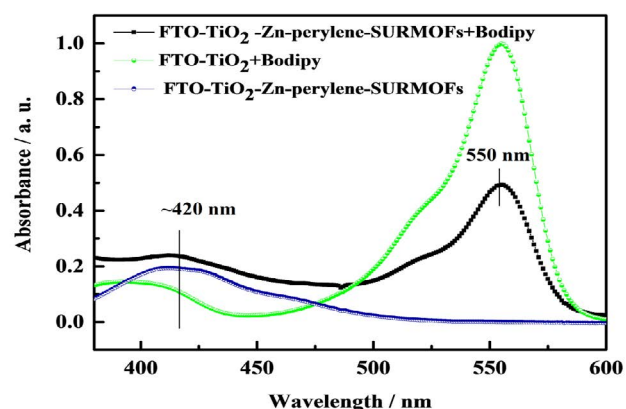


Figure 3. UV-Vis of Zn-erylene SURMOFs (Blue), Zn-erylene SURMOFs/Bodipy (Black), and Bodipy (Green)

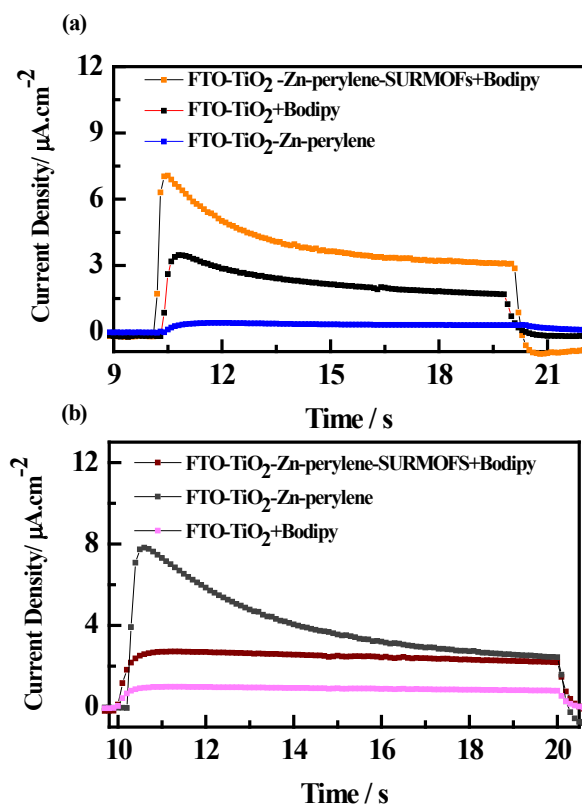


Figure 4. Upon 532 nm excitation photocurrent enhancement of TiO₂-Zn-erylene SURMOFs/Bodipy than rest of its parts TiO₂-Zn-erylene SURMOFs and TiO₂-bodipy (b) Upon 430 nm excitation photocurrent enhancement of TiO₂-Zn-erylene SURMOFs/Bodipy than rest of its parts TiO₂-Zn-erylene SURMOFs and TiO₂-bodipy

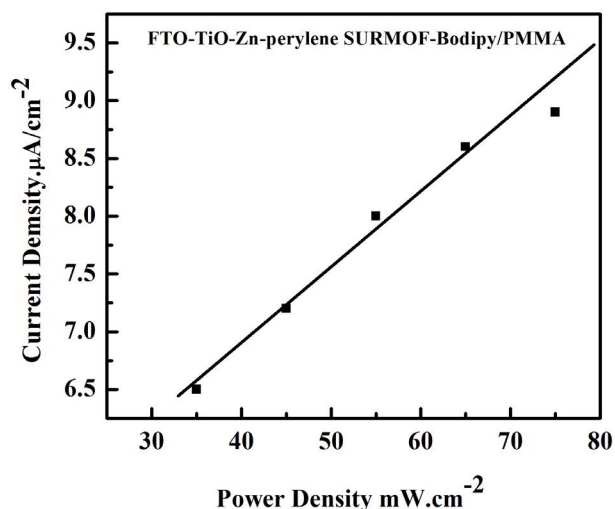


Figure 5. Intensity dependent experiment of TiO₂-Zn-Perylene SURMOF/Bodipy showing the linear behavior

Similarly, upon excitation with blue light at $\lambda_{ex}=420$ nm, the TiO₂-Zn-erylene/Bodipy, Zn-erylene SURMOFs and TiO₂/Bodipy enhanced ~ 7.8 $\mu\text{A}/\text{cm}^2$ photocurrent with TiO₂-Zn-erylene/Bodipy and also with TiO₂-erylene-SURMOFs (~ 2.9 $\mu\text{A}/\text{cm}^2$) and TiO₂/Bodipy (~ 0.9 $\mu\text{A}/\text{cm}^2$) shown in Figure 4b.

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 532 nm 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 TiO₂-Zn-erylene/Bodipy which is consistent with the TTC UC [3] which is demonstrated in Figure 5.

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 the two times higher performance of our observed system is due to triplet triplet annihilation upconversion (TTA UC). The studied demonstration can be 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 approach can be considered for our future research.

References

1. Ahmad S, Liu J, Gong C, Zhao J, Sun L, et al. (2018) Photon up-conversion via epitaxial surface-supported metal-organic framework thin films with enhanced photocurrent. *ACS Applied Energy Materials* 1: 249-253.
2. Ahmad S, Liu J, Ji W, Sun L (2018) Metal-organic framework thin film-based dye sensitized solar cells with enhanced photocurrent. *Materials (Basel)* 11: 1868. [Crossref]
3. Chen Y, Zhao J, Xie L, Guo H, Li Q (2012) Thienyl-substituted BODIPYs with strong visible light-absorption and long-lived triplet excited states as organic triplet sensitizers for triplet-triplet annihilation upconversion. *RSC Advances* 2: 3942-3953.
4. Ji S, Ge J, Escudero D, Wang Z, Zhao J, et al. (2015) Molecular structure-intersystem crossing relationship of heavy-atom-free BODIPY triplet photosensitizers. *J Org Chem* 80: 5958-5963.
5. Schulze TF, Schmidt TW (2015) Photochemical upconversion: present status and prospects for its application to solar energy conversion. *Energy & Environmental Science* 8: 103-125.
6. Monguzzi A, Tubino R, Hoseinkhani S, Campione M, Meinardi F (2012) Low power, non-coherent sensitized photon up-conversion: modelling and perspectives. *Physical Chemistry Chemical Physics* 14: 4322-4332.
7. Ji S, Wu W, Wu W, Guo H, Zhao J (2011) Ruthenium (II) Polyimine Complexes with a long-lived 3il excited state or a 3MLCT/3IL equilibrium: Efficient triplet sensitizers for low-power upconversion. *Angew Chem Int Ed Engl* 123: 1664-1667. [Crossref]
8. Singh-Rachford TN, Lott J, Weder C, Castellano FN (2009) Influence of temperature on low-power upconversion in rubbery polymer blends. *J Am Chem Soc* 131: 12007-12014. [Crossref]
9. !!! INVALID CITATION !!!,
10. Max JJ, Chapados C (2004) Infrared spectroscopy of aqueous carboxylic acids: Comparison between different acids and their salts. *J Phys Chem A* 108: 3324-3337.
11. Arslan HK, Shekhah O, Wohlgemuth J, Franzreb M, Fischer RA, et al. High-throughput fabrication of uniform and homogenous MOF coatings. *Advanced Functional Materials* 21: 4228-4231.
12. Gray V, Dzebo D, Abrahamsson M, Albinsson B, Moth-Poulsen K (2014) Triplet-triplet annihilation photon-upconversion: towards solar energy applications. *Phys Chem Chem Phys* 16: 10345-10352.
13. Dilbeck T, Wang JC, Zhou Y, Olsson A, Sykora M, et al. (2017) Elucidating the energy- and electron-transfer dynamics of photon upconversion in self-assembled bilayers. *J Phys Chem C* 121: 19690-19698.
14. Simon Y C, Weder C (2012) Low-power photon upconversion through triplet-triplet annihilation in polymers. *J Materials Chem* 22: 20817-20830.