Near-infrared-to-visible photon upconversion in solid state using PbS QD sensitized triplet-triplet annihilation system by 980-nm excitation

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Development of near infrared (NIR)-to-visible upconversion materials is extremely important for the efficient use of solar energy because it can boost the performances of existing photovoltaics by converting the unusable long wavelength to the usable short one. Triplet-triplet annihilation photon upconversion (TTA-UC) may allow to achieve it under the excitation intensities as low as sunlight. Though TTA-UC had been extensively investigated with molecular sensitizers, usage of quantum dots (QDs) of a narrow bandgap semiconductor (such as PbS) as sensitizer has advantageous for the conversion of long wavelength NIR light. However, upconversion performance of QD-sensitized hybrid system is affected by various factors, *i.e.*, capping ligand,[1] defect states etc. Changing the physical state of the system from solution to solid also give significant impact. Despite of extensive works, reports are very limited for the conversion from 800 nm or longer, which is an interesting region for photovoltaic devices such as perovskite solar cells. Moreover, solution processed solid upconversion films are preferrable for combining with solar device structure.

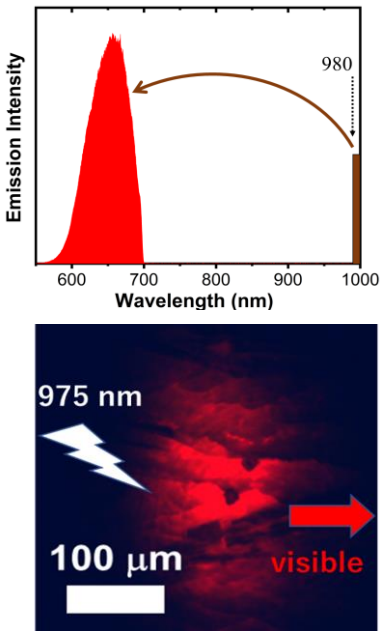

Figure 1. *(a) Upconverted emission spectra of PbS QD/TES-ADT solid films at 980-nm excitation. (b) Upconversion emission microscopic image.*

We developed a solid-state TTA-UC system using PbS QD as sensitizer and (5,11-bis(triethylsilylethynyl)anthradi-thiophene, TES-ADT) as visible emitter, which successfully converts 980-nm photons into a 660-nm visible photon (**Fig.1**). A narrow bandgap PbS QD with λ_{em} = 1100 nm, is suitable to absorb NIR photons and TES-ADT having ability to attach to QD, providing ~93% triplet energy transfer (TET) from QD to TES-ADT. With optimized concentrations and other experimental conditions, the best upconversion emission efficiency ($\eta_{UC,}$ at 100% scale) of 0.68% under the 980 nm excitation[2]. These solid UC films showed superior η_{UC}, compared to than that of the solution system previously reported [1]. This is due to the fact that intermolecular distance is reduced in solid form, therefore sensitizer-emitter interactions are enhanced. These results are further supported by time resolved spectroscopy, which suggested much faster TET time constant for the solid films than that for the solutions. These results revealed that possibly TES-ADT acts as transmitter of triplet energy due to close association to the PbS QD core, thus minimizing the triplet energy dissipation through any other channels and higher η_{UC} is achieved.

References

1. N. Tripathi et al., *ACS Appl. Nano Mater.* **2021**, 4, 9680.

2. N. Tripathi et al., *J. Mater. Chem. C* **2022**, 10, 4563.