Colloidal PbS quantum dot sensitized NIR-to-visible photon upconversion via triplet-triplet annihilation

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Photon upconversion (UC) has recently been received growing attention due to potential application in various fields such as photocatalysis, photovoltaic and bio-imaging.^{1,2} More specifically, an upconversion system which absorbs NIR wavelengths (> 750 nm, 1.65 eV) is rather meaningful to utilize 46% of untended solar flux in this region. Triplet-triplet annihilation (TTA)-UC with inorganic quantum dot (QD) as sensitizer has recently shown an attractive possibility to utilize the NIR photons. The band gap tunability of QD of the narrow gap semiconductors such as PbS and PbSe makes it prime candidate for NIR sensitizer of TTA-UC by combining with the polyaromatic hydrocarbons that have low-lying triplet energy level (such as rubrene, $E_T=1.14 \text{ eV}$) as annihilator. Actually, as for TTA-UC system with NIR-QD, PbSe-rubrene³ and PbS-(TES-ADT)⁴ in dispersion solution and PbS-rubrene in solid film form^{5,6} have been investigated so far and the UC quantum yields (QY's) were reported. However, report on the dispersion solution of PbS-rubrene is seldom and limited for the relative comparison of UC-QY.⁷

Considering the profound features of PbS QD and rubrene as NIR TTA-UC system and the limited reports of them, it is important to investigate and accumulate the information on the energy transfer mechanism from the QD to organic chromophores and to develop new strategies for improving the QY in NIR (>900 nm)-to-visible regime. In this work we re-examined the QY of the NIR-to-visible UC using the combination of inorganic PbS QD and rubrene in dispersion solution. The upconversion samples were

prepared in colloidal form using various concentrations of PbS QD and rubrene. UC-QY was measured by comparison with reference dye solution excited at 785 nm and was scaled to 100% for full conversion. Some samples showed yellow upconverted emission by excitation of two NIR wavelengths (Fig. 1). The UC-QY of 0.12% at λ_{exc} 785 nm (12 W/cm²) and 0.02 % at λ_{exc} 975 nm (31 W/cm²) were achieved in the colloidal solution though they were obtained in the quadratic region of the excitation intensity dependence. Further, triplet energy transfer from colloidal PbS QDs to rubrene will be discussed.



Fig. 1. Upconversion emission spectra and measured QY of PbS/rubrene sample, excited at 785 nm and 975.

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