2-6-2. Photon Upconversion Materials

Overview

Upconversion (UC) generally is the process of obtaining the luminescence with a shorter wavelength than the incident light. It includes multi-step excitation and energy transfer in rare earths, and in a broad sense, two-photon-induced fluorescence. Here, we focus on triplet-triplet annihilation (TTA)-based upconversion (TTA-UC). TTA-UC is a complex process involving spin conversion, consisting of triplet sensitization and TTA-type (pyrene (P)-type) delayed fluorescence (Fig. 1). The sensitizer molecule absorbs the excitation light and undergoes ISC and TET. This generates the emitter (or annihilator) triplet state ($^3A^*$). TTA-type delayed fluorescence occurs between $^3A^*$ molecules and generates a photon with higher energy than the incident light.

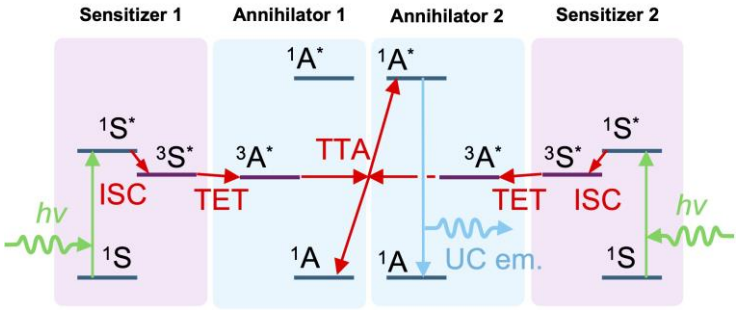

Figure 1. Mechanism of TTA-UC. S: sensitizer, A: annihilator, ISC: intersystem crossing, TET: triplet-triplet energy transfer, TTA: triplet-triplet annihilation.

Current Status and Frontiers

As seen in the discovery of TTA-UC by Packer and Hatchard in 1962 and in the research on the TTA mechanism by Tanaka and Tanaka et al. the following year, TTA-UC had been known since the 1960s as a subject of basic research. In 2005, Castellano et al. demonstrated that the UC emission, which is observable with the naked eye, can be induced by a laser pointer. This sparked explosive worldwide growth in UC material research in the 2010s, targeting the efficient utilization of solar energy through wavelength conversion. In Japan, multiple groups have conducted pioneering research on TTA-UC, beginning with the Tanaka and Chujo et al.'s work on the hybridization with caged silsesquioxanes (POSS) in 2010.

Early TTA-UC studies focused primarily on the green-to-blue conversion using a solution system that contained Pt-octaethylporphyrin (PtOEP) as the sensitizer and 9,10-diphenylanthracene (DPA) as the emitter. The rate-determining step is the process in which a sensitization-generated $^3A^*$ encounters another $^3A^*$ through molecular diffusion within their lifetime, causing TTA. Therefore, to overcome the limitations of molecular diffusion of emitter molecules in solution, research was focused on utilizing exciton diffusion in a condensed emitter system. Yanai and Kimizuka et al. synthesized DPA derivatives that are in liquid phase at room temperature, by introducing a branched alkyl chain. This enables them to achieve TTA-UC in liquid phase without using a solvent. The molecular modification of the emitter evolved into the efficient UC materials through the dimensional control of triplet exciton migration via the self-organization of the emitter (60% in UC efficiency against a full scale of 100%) and into MOFs consisting of emitter

as the backbone. Meanwhile, Kamada et al. fabricated an emitter solid by optimizing solution-cast conditions to prevent sensitizer aggregation. They discovered that 20% UC efficiency in a crystalline solid was possible by using the DPA derivative with loop-like alkyl-chain substituents. Murakami et al. overcame flammability and volatility issues by using an ionic liquid and its gel as medium. They also developed a solid solution of emitter crystal and demonstrated that high UC efficiency of over 60% and the threshold excitation intensity as low as 1/10 of sunlight. Matsui and Ikeda et al. accelerated the TTA process by doping the dimer into a DPA matrix. Furthermore, Kawai et al. have studied the environmental effects on TTA-UC by using the intercalating the emitter molecule into a DNA strand and hybridization with vesicles.

Extending the conversion wavelength is also an important issue and mainly depends on the sensitizer. In the early green-to-blue and red-to-greenish blue conversion systems, Pt or Pd complex of porphyrin and phthalocyanine were used. Since extending to the near-infrared (NIR) wavelength range is important for efficiently using solar spectrum resource, π-conjugation extended porphyrin (Kamada and Yamada et al.), usage of Os complex (Yanai and Kimizuka et al.) have been extensively studied. Moreover, semiconductor quantum dots (Yanai and Kimizuka et al., Kamada et al.) were also used, and conversion from a wavelength longer than 1000 nm to the visible wavelength was demonstrated although the efficiency remains low. In a new direction, instead of the triplet sensitization, generation of triplets through photoinduced charge separation and subsequent recombination at the interface of a solid system was used for to achieve efficient TTA-UC from 850 nm NIR region (Izawa et al.). Furthermore, significant progress has been shown in use of Au cluster as sensitizer (Mitsui et al.). From an application viewpoint, conversion from the visible to ultraviolet (UV) is important for polymerization curing and photocatalysis. Research in this area has become more active (Yanai and Kimizuka et al.).

References

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Future Perspectives and Directions

Issues to be solved and realized within the next 10 years: Achieving adequate efficiencies for visible-excited photocatalysts and NIR-excited photovoltaic devices. On-site UV generation by harmless visible light excitation. Developing a wavelength conversion sheet that enables NIR imaging by using cost-effective Si-based imaging devices.

(Author: Kenji Kamada)