NONLINEAR PHOTONICS

Triplet state brightens upconversion

Efficient photon upconversion is desired for applications ranging from molecular sensing to solar-energy harvesting. Now, the population of hidden triplet state electrons, created on dye antennas and rare-earth-doped nanoparticles, has been amplified to brighten upconversion by five orders of magnitude.

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Upconversion nanoparticles (UCNPs), capable of converting near-infrared (NIR) light to visible, have enabled a broad range of emerging applications, including molecular sensing, super-resolution microscopy, multimodal imaging, nanomedicine therapy, display technology, security inks and NIR photovoltaics. In a typical upconversion system, ytterbium ions and erbium (or holmium or thulium) ions are co-doped as NIR sensitizers and visible emission activators, respectively. The small absorption cross-section area of ytterbium ions typically requires intense excitation from a coherent laser[1]. The management of efficiencies of both photon sensitization and energy-transfer processes becomes equally important for the development of brighter UCNPs. The key focus of intense global research is to develop more efficient and brighter material systems for performing upconversion[2].

Now, writing in *Nature Photonics*, David Garfield, Nicholas Borys and co-workers report the first experimental observation of a covert triplet state that forms when dyes are attached to the heavy atoms contained in UCNPs, enabling a 33,000-fold increase in emission intensity over bare UCNPs[3]. The long-lived triplet state centred at 981 nm, which perfectly matches the 976-nm absorption band of the ytterbium transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$, serves as a built-in energy bridge to connect the dye singlet state and the ytterbium excited state. The compelling discovery in this system relies on the presence of the triplet enhancer Gd^{3+}, which determines the sensitization effect of the dye triplets. The optimized amount of 30% Gd^{3+} leads to the striking emission intensity enhancement of five orders of magnitude over bare UCNPs, with a high upconversion quantum yield of 5.3 ± 0.4% (excitation wavelength 808 nm at 5 W cm^{-2}).

In 2012, a study on dye-sensitized UCNPs reported a 3,300-fold enhancement in emission by coupling a NIR dye, IR806, to the surface of UCNPs[4]. This result attracted the attention of researchers across a broad range of research areas. The key concern was the mismatch of the emission spectrum of IR806 and the narrow absorption spectrum of ytterbium ions, which should have hardly formed an efficient non-radiative resonance energy-transfer process. Following this work, Nd^{3+} ions were used as the intermediate bridge ions to overcome the large energy mismatch and a new record of upconversion quantum efficiency of 19% was achieved[5]. Here, non-coherent light was used to excite the hybrid UCNPs. To further improve this system, NIR dyes with various NIR excitation bands were coupled to the surface of ligand-free UCNPs, yielding a family of dye-sensitized UCNPs[6]. Because the efficiency of NIR dyes emitting above 900 nm drops significantly, the strategy of directly transferring the singlet state of dye-sensitized NIR photon energies to UCNPs has reached its limit.

To provide more evidence of the heavy-atom effect that induces the intermediate triplet state, Garfield and co-workers attached the IR806 dyes to the dopant-free $NaGdF_4$ nanoparticle, and successfully captured the phosphorescence spectrum of IR806 at 80 K. Moreover, they employed density functional theory and found that the calculated energy of the triplet state for the dye was in a good agreement with the spectral result. Furthermore, the authors performed the control experiment by using triplet quenchers, and observed a significantly decreased upconversion quantum yield from the IR806-$NaYF_4$:Yb^{3+}, Er^{3+}, Gd^{3+} UCNPs. This further confirmed the important role of the triplet state in dye-sensitized energy-transfer upconversion systems.

When the dye is in close proximity to the Gd^{3+} nuclei, the increased heavy-atom effect positively amplifies the triplet population, and enhances intersystem crossing (ISC) within the dye from its singlet to triplet excited states (Fig. 1). Following this model, Garfield and co-workers attempted to increase the triplet-state population by using a high concentration of Gd^{3+} ions[3]. Although the higher concentration of Gd^{3+} ions should lead to higher upconversion quantum yield, they encountered luminescence quenching when an extremely high amount of Gd^{3+} was used. The authors attributed this quenching to the optical interaction with Yb^{3+}, Er^{3+}, or surface traps, and future studies are necessary to avoid such a quenching effect.

Coating the inert shell has been a common strategy to improve the brightness of UCNPs, but because the shell separates dyes from the active core of UCNPs there is a trade-off between competing mechanisms (as described below) affecting brightness in dye-sensitized hybrid systems. If the dye–ytterbium energy-transfer mechanism is considered to be Förster resonance energy transfer (FRET), which has an effective range of less than ~1.5 nm, growing a thin 1.2 nm inert shell should both increase the emission of the UCNP core and maintain the effectiveness of the dye sensitization. However, the authors reported that the performance of their design of coating the thin inert shell was not as good as when direct dye coupling is employed. Garfield and co-workers' experiment indicated that both long-range FRET and other short-range (for example, Dexter-like) pathways co-contribute to the efficient energy transfer from dye to ytterbium ions.

The discovery of the Gd^{3+}-enhanced triplet-state populations not only clarifies the underpinning mechanism in dye-sensitized UCNPs, but also suggests a direction to engineer brighter hybrid upconversion nanomaterials. While both the material interface and the existence of the triplet state in energy transfer certainly deserve more attention[7], the synergetic interactions between the surface molecules and the inorganic nanoparticles, particularly in certain environments and conditions, will contribute to the overall photophysical performance of the luminescent materials[8]. The atomic-scale heavy-atom effect (ISC $\propto Z_{eff}^4$, where Z_{eff}

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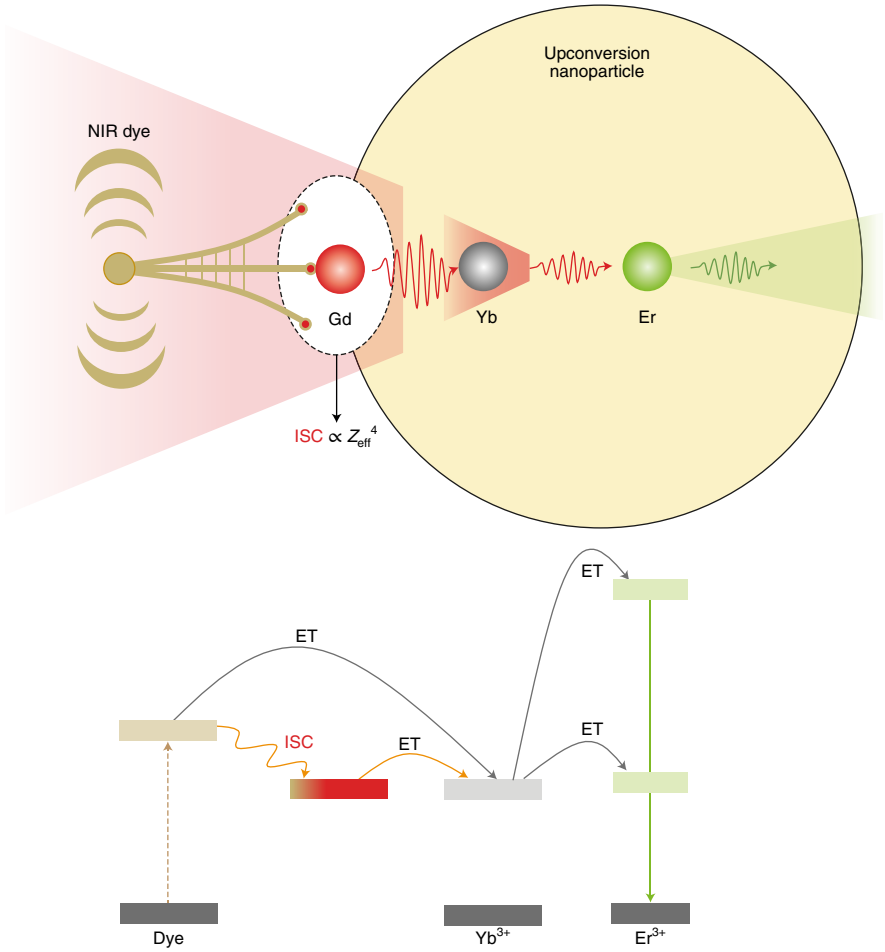

Fig. 1 | Schematic of a triplet-state-assisted dye-sensitized upconversion nanoparticle system. By attaching a near-infrared (NIR) dye in proximity to Gd^{3+} ions exposed on upconversion nanoparticles generates a large population of triplet states. This effect forms an intersystem crossing (ISC) that efficiently bridges the dye-sensitized NIR photons to ytterbium ions. The perfect matching of the as-discovered intermediate triplet state of dyes and the excited state of ytterbium ions removes the bottleneck in 'smoothing' the multistep upconversion energy-transfer (ET) process. The bottom panel shows the energy levels for the system depicted in the top panel.

is the atomic number) is bewildering, but Garfield and colleagues demonstrated its control and utilized it to enhance the energy-transfer process. Leveraging this mechanistic understanding may result in further enhanced performance of the dye-sensitized UCNPs, which will impact not only the upconversion community but also the broader field of photonics and photon energy management.

More systematic study is needed to optimize the triplet population, taking into account the concentration of the dye, species of heavy atom and morphology, as well as the dopant properties of UCNPs. The current protocol of simple mixing of the dye and UCNPs leads to the coexistence of dye and oleic acid/oleate surfactants on the surface. The surface ligands, introducing photons and quenchers, may hinder studies aimed at clarifying the roles of FRET and Dexter energy transfer. In Garfield and co-workers' experiment, the dyes remain well separated on the surface with an estimated intermolecular distance of ~3.4 nm, which suggests insufficient dye sensitizers compared with the large number of ytterbium ions within UCNPs. The low dye concentration on the surface is limited by the self-concentration quenching effect, which occurs when too many dye molecules are used. New strategies to overcome this limitation will allow more dye antennas to sensitize brighter upconversion. Moreover, other heavier lanthanide atoms, such as Lu^{3+} or Yb^{3+}, may induce a stronger heavy-atom effect to further promote the triplet population.

The authors reported that an excitation power density of less than 100 mW cm^{-2} can give a measurable signal, but more quantitative information should be considered, such as the concentration of UCNPs and the thickness of the sample used in the measurement. The push to generate brighter upconversion emissions by lower broadband excitation flux requires standardized measurements of quantum efficiency and brightness with a checklist of experimental details, such as laser beam quality, excitation density, the efficiency of detection optics and photon counts per unit time from a single nanoparticle when possible[1].

Another gap between this fundamental breakthrough and future adoption in a broad range of photonics applications is that the current demonstration of dye-sensitized UCNPs has been conducted in encapsulated films. Isolation of oxygen and water was the key to stabilize the films. The authors reported that the N_2 encapsulation strategy dramatically improved the stability of the films, showing no measurable photodegradation after continuous excitation for 30 minutes. Although encapsulation methods may address the drawback in stability from the point of view of NIR photovoltaic devices, exploiting the dye-sensitized UCNPs in biomedical and biophotonics applications (for example, as the fluorescence probes used in single-molecule detection, super-resolution microcopy, deep-tissue imaging and therapy) ultimately requires stability in the presence of oxygen and water. ❐

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