

## PHOTON UPCONVERSION

## Nanocrystals feel the heat

Phosphors often suffer luminescence quenching at elevated temperatures. Now, thermal quenching can be combated with surface phonon-assisted energy transfer, enabling the luminescence of ultrasmall upconversion nanophosphors to be dramatically enhanced.

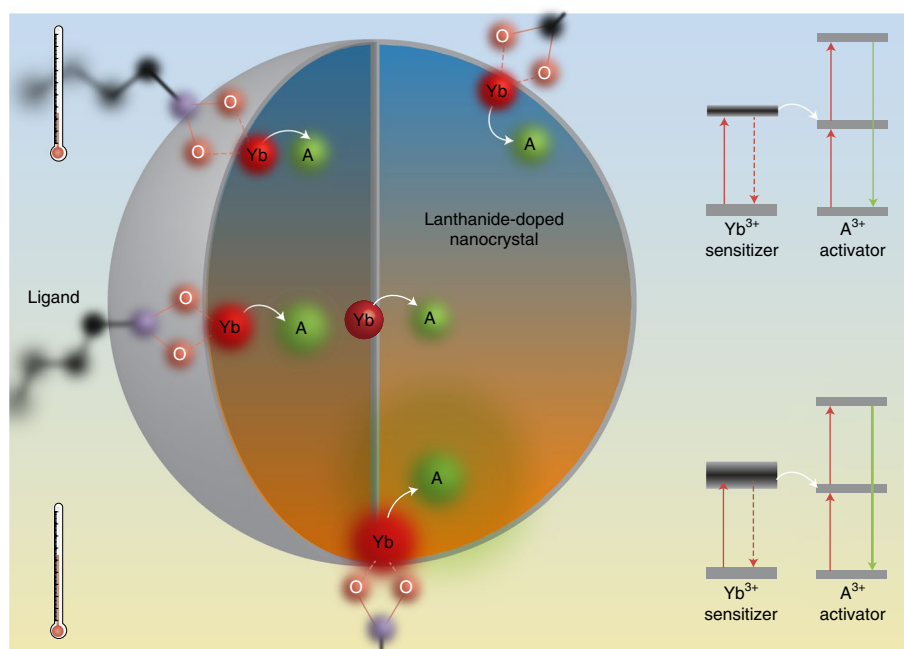
Liangliang Liang and Xiaogang Liu

The photoluminescence intensity of a phosphor usually diminishes with increasing temperature — an effect that leads to a longstanding technical problem best known as ‘thermal quenching’. This problem, which still plagues scientists, often impedes practical applications of luminescent materials in electronic devices and circuitry, where efficient thermal management of the heat build-up in and around the devices remains a complex task<sup>1</sup>.

At an elevated temperature, the lattice vibration of a phosphor tends to intensify. As a result of energy transport mediated by phonons, the non-radiative depopulation of excited states to the ground state could also be aggravated, thus resulting in substantial reduction in the emission luminance of the phosphor. As it happens, this problem provides a strong motivation for preparing thermally stable phosphors, for example, by selecting host materials with good structural rigidity or by coating the phosphors with an extra layer of ceramics<sup>2,3</sup>. However, except in special cases, the issue of thermal quenching has never been solved.

Now, writing in *Nature Photonics*, Zhou et al.<sup>4</sup> from the University of Technology Sydney report that with the help of surface phonons, the amount of excess heat, once detrimental, can be harnessed by coupling lanthanide-doped upconversion nanocrystals with surface ligands to boost the photoluminescence by up to three orders of magnitude.

Lanthanide-doped upconversion nanocrystals enable anti-Stokes emission on near-infrared excitation. Their exceptional properties, such as large anti-Stokes shift, long excited-state lifetime and high photostability, have led to a broad range of applications spanning from bioimaging to security<sup>5</sup>. For an upconversion process to proceed, lanthanide ions such as  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  are typically selected as activators and a  $\text{Yb}^{3+}$  ion with a larger absorption cross-section is usually co-doped as the sensitizer. When illuminated with near-infrared light, incident low-energy photons can primarily be absorbed by the



**Fig. 1 | Schematic of surface phonon-assisted upconversion on heating.** At a higher temperature, surface phonons arising from the vibrations of surface-bound ligand molecules can help to broaden the energy band of the  $\text{Yb}^{3+}$  sensitizer and reduce the amount of energy required for upconversion processing (bottom right). This results in greater energy transfer to the activator (resulting in the thicker green arrow).

$\text{Yb}^{3+}$  sensitizer and then the energy can be transferred to adjacent activators that are homogeneously confined in the crystal lattice for sequential population at higher excited states. Consequently, the activators release high-energy photons that can be clearly distinguished from background noise.

It should be noted that the energy transfer efficiency from lanthanide sensitizer to activator ions dictates the ultimate photoluminescence intensity of upconversion nanocrystals<sup>6,7</sup>. For commonly used activators ( $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$ ), the minimum energy for activation supplied through the  $\text{Yb}^{3+}$  sensitizer is typically in the range of 200 to 2,000  $\text{cm}^{-1}$ . Although the energy transfer from the sensitizer to activator always occurs in a phonon-assisted manner, a large mismatch in energy levels between the two and the parity-forbidden nature of

$f-f$  transitions often lead to a less efficient upconversion process. For instance, although  $\text{Tm}^{3+}$  is an ideal activator for lighting up upconverted blue and ultraviolet emission,  $\text{Yb}^{3+}/\text{Tm}^{3+}$ -codoped nanoparticles typically give rise to rather weak luminescence, largely due to the existence of a considerable activation energy barrier ( $\sim 1,400 \text{ cm}^{-1}$ )<sup>8</sup>. It is possible to enhance luminescence emission intensity by lowering the local symmetry around the lanthanide ions, because the application of an asymmetric crystal field through crystal engineering can circumvent the problem of the parity-forbidden transition. There are also other means of enhancing upconversion emission, often involving doping of appropriate transition-metal ions (for example,  $\text{Zn}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Sc}^{3+}$ ) together with lanthanide activators in nanocrystals<sup>9</sup>. When compared with the

lanthanide ions, *d*-block transition metals, which have variable oxidation states available, can display a quite different set of parameters to control the upconversion dynamics. In particular, the larger radial extension of the *d* orbitals than that of the *f* orbitals does seem to lead to strengthened electron–phonon coupling and improved susceptibility to crystal-field and exchange perturbations. Nevertheless, the statistical and spatial distribution of doped transition-metal ions within an individual nanocrystal remains poorly understood.

Zhou et al.<sup>4</sup> propose that the vibrations of surface-bound molecules through Yb–O chelating can work as surface phonons to enable an efficient energy transfer from the Yb<sup>3+</sup> sensitizer to the activators. As illustrated in Fig. 1, the oxygen moiety can come from a ligand featuring a terminal carboxylic acid group. With surface phonons at work due to the Yb–O chelating interaction, the excited-state energy band of the Yb<sup>3+</sup> sensitizer becomes broadened and thus the energy mismatch between the sensitizer and activator ions is reduced. The broadband source also helps to facilitate the energy transfer from Yb<sup>3+</sup> to adjacent activators, thereby effectively mitigating the thermal quenching effect. This principle permits the photoluminescence of an upconversion process to be significantly amplified.

The concept of phonon-assisted upconversion enhancement at elevated temperatures for small-sized nanoparticles was first suggested by Li and colleagues<sup>10</sup>. Theoretical modelling of electron–phonon interaction has also been developed to explain the anomalous thermalization effect on luminescence dynamics in nanoparticles<sup>11</sup>. Focusing on the size effect on surface phonon population, Zhou et al.<sup>4</sup> find that a cut-off surface phonon frequency of 620 cm<sup>-1</sup> could be achieved from Yb<sup>3+</sup>-sensitized nanoparticles

with oleic acid as the chelating ligand. They further discover that the upconversion emission could be markedly boosted by varying the temperature from 300 to 450 K.

To determine whether the Yb–O chelating interaction has a mediating role, the authors examined a series of nanoparticles with different amounts of Yb<sup>3+</sup> content. As anticipated, larger enhancement factors were observed when the doping concentration of Yb<sup>3+</sup> was higher. Nonetheless, it is important to note that although the increase in temperature could intensify upconversion emission, the upconversion would still suffer emission loss at a temperature greater than 450 K. The possible reason is that the surface phonon-assisted energy transfer is not effective above a certain threshold temperature due to thermal quenching effects.

Complete understanding of surface phonon-assisted upconversion through Yb–O chelating is much more challenging. The distance between the surface ligand and the Yb<sup>3+</sup> sensitizer is critical. This was made evident in the temperature-dependent luminescence investigation of a collection of nanoparticles with a size range from 10 to 60 nm. The effect of emission enhancement is more pronounced for smaller nanoparticles as temperature rises. Notably, 10 nm nanoparticles doped with Tm<sup>3+</sup> show a large 2,000-fold enhancement in their blue emission. Indeed, the results of the experiment support the theory that a closer distance range between the surface ligand and the sensitizer ion could make surface phonons function better to combat thermal quenching.

Several aspects of this surface phonon-assisted energy transfer remain to be further investigated. For example, the range of ligand molecules that can be used should be broadened beyond oxygen-containing molecules. It also remains to be elucidated what other sets of phonon modes, if any,

these molecule-coupled nanoparticles have with increasing temperature. A major drawback of the datasets is the lack of information on the strength of molecular interactions in response to heating. Such information may be essential to understand the exact nature of energy transfer processes involving surface phonons. Nonetheless, the study of such molecule–particle systems is highly promising and will potentially be useful for the design and construction of nanothermometers in a physiological environment with high spatiotemporal resolution<sup>12</sup>. With this in mind, we can envision the next wave of exciting studies that will focus on hybrid inorganic–organic upconversion nanocrystals. □

Liangliang Liang<sup>1</sup> and Xiaogang Liu<sup>1,2\*</sup>

<sup>1</sup>Department of Chemistry, National University of Singapore, Singapore, Singapore. <sup>2</sup>Institute of Materials Research and Engineering, Singapore, Singapore.

\*e-mail: chmlx@nus.edu.sg

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## TERAHERTZ OPTICS

# Giant multiphoton absorption in silicon

With the availability of high-intensity terahertz free-electron lasers, surprisingly large multiphoton absorptions in a phosphorus atom doped in a silicon crystal have been obtained, providing the possibility of a hydrogen-like system in silicon photonics and quantum information devices.

Nobuhiko Yokoshi and Hajime Ishihara

**M**ultiphoton absorption is a typical nonlinear optical process where multiple photons are absorbed simultaneously by a substance. Since the theoretical work by Maria Goeppert-Mayer

in 1931<sup>1</sup>, this absorption process has been extensively studied for its significance in both fundamental science and technological applications. For instance, this process can be used for frequency conversion to realize

light at a frequency for which no available light source exists. Because the multi-harmonic frequency makes the beam spot highly localized, multiphoton absorptions enable the fabrication or microscopy