Nanotechnology

Giant photon avalanches in tiny particles

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In some materials, the absorption of a single photon can trigger a chain reaction that produces a large burst of light. The discovery of these photon avalanches in nanostructures opens the way to imaging and sensing applications. **See p.230**

The rich energy-level structure of ions from the lanthanide series of elements allows them to be used for a process known as photon upconversion – in which two photons are combined to generate one higher-energy photon. Nanoparticles that emit upconverted photons can be used in imaging techniques to produce pictures that are free from background signals[1], thereby giving them an edge over other fluorescent probes used for imaging. Lee *et al.*[2] report on page 230 that a special type of upconversion called photon avalanching can occur in nanoparticles that contain lanthanide ions (known as lanthanide-doped nanoparticles). This phenomenon had previously been observed only in millimetre- to centimetre-scale crystals[3,4], and might enable a variety of laser applications.

Lanthanide-doped materials emit light with a narrow range of frequencies, which can be tuned from infrared to ultraviolet. This effect has underpinned most artificial light sources for decades, but research into these materials was given a further boost when lanthanides were incorporated into nanoparticles. Lanthanide-doped nanoparticles used for upconversion are being investigated particularly intensively because of their widespread applications[1] in, for example[5,6], bioimaging, nanothermometry and diagnostics for cancer and COVID-19.

The success of upconversion nanoparticles in biological and medical applications is based on their remarkable combination of properties: they absorb infrared light, to which tissue is transparent; they emit a narrow range of frequencies; and they are at least 1,000 times more efficient at upconversion than any naturally occurring material[7]. The discovery of photon-avalanche upconversion in nanoparticles adds a new dimension to this active field of research, potentially allowing the sensitivity of diagnostics and the resolution of imaging methods to be increased still further.

Photon-avalanche upconversion was first discovered[3] in lanthanum chloride crystals doped with ions of the lanthanide element praseodymium. The general process occurs as follows. First, the ions are promoted from their ground state to an intermediate excited state using laser light that is absorbed only weakly by this transition (Fig. 1); this step is known as ground-state absorption (GSA). Next, in the excited-state absorption (ESA) step, the excited ions absorb more of the light and thereby enter a higher-energy excited state. The light frequency is chosen to ensure that the light is strongly absorbed for this excitation.

Once in the higher-energy state, the lanthanide ions each interact with a neighbouring ion that is still in its ground state, distributing the excitation energy over the two ions – a process known as cross-relaxation (CR). This leaves both ions in the intermediate excited state. The combination of ESA and CR thus doubles the number of ions in that state. The two excited ions then re-enter the ESA–CR cycle, generating four excited ions, and so on. This continuous doubling of excited ions, triggered by an initial weak GSA, is termed an avalanche. The rapid increase of the number of ions in excited states leads to the emission of a burst of upconverted photons as the ions return from the higher-energy excited state back to the ground state.

The trick to achieving a photon avalanche is to carefully match a very weak GSA (to ensure that only a small fraction of the ions is excited) with a strong ESA that takes over and causes the avalanche. A second prerequisite is to have efficient CR to keep the avalanche going. This requires a high concentration of lanthanide ions to provide sufficient neighbours for CR. However, lanthanide concentrations that are too high can prevent avalanching (a problem known as concentration quenching). Previously reported efforts to produce photon avalanches in nanocrystals therefore used lanthanide concentrations of just 1–2 mole per cent (ref. 8). But these concentrations were too low to sustain a true photon avalanche.

Lee *et al.* have now obtained photon avalanching in nanocrystals that contain a higher fraction of lanthanide ions than in the previous studies. More specifically, the authors studied nanoparticles of sodium yttrium fluoride ($NaYF_4$, the workhorse material in this field) in which some of the yttrium has been replaced by thulium ions. These particles produce almost no emissions under weak illumination, but the authors realized that, under high-intensity laser excitation, concentration quenching could be overtaken by a photon avalanche.

Using an optimum concentration of 8 mol% of thulium ions in high-quality nanocrystals, Lee *et al.* produced nanoparticles that exhibited three signatures of avalanching. First, they observed that a threshold laser intensity was needed to start the avalanche. Second, the process required a certain amount of irradiation time to begin, and then a further period (up to about 0.5 seconds at the threshold laser intensity) for the avalanche to grow to its full extent. And third, they found that the upconversion response was highly nonlinear. For the best-performing nanoparticles, the intensity

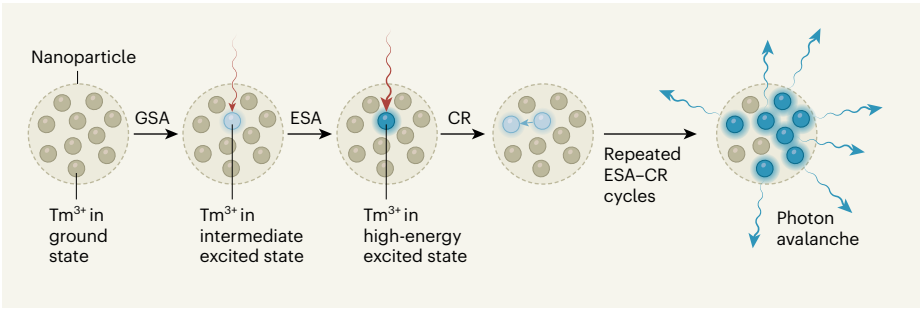

Figure 1 | The mechanism of photon avalanching. Lee *et al.*[2] report that a phenomenon known as photon avalanching can occur in nanocrystals that contain 8 mole per cent thulium ions (Tm^{3+}). The ions are initially in their ground states, but weakly absorb light (red arrow) from a laser. This ground-state absorption (GSA) promotes an ion to an intermediate excited state. The excited ion absorbs the laser light much more strongly than do the ground-state ions, and this excited-state absorption (ESA) produces an ion in a high-energy state. The highly excited ion shares its energy with a neighbouring ground-state ion, a process called cross-relaxation (CR), thereby producing two ions in the intermediate excited state. Further cycles of ESA and CR exponentially increase the number of intermediate excited ions, which undergo ESA to form ions in the high-energy state. These finally relax back to their ground state, emitting an avalanche of photons (blue arrows).

of the upconverted emission increased with the 26th power of the excitation intensity, which is a spectacular achievement.

The findings will trigger a search for other nanocrystals that enable photon avalanches. The ions of lanthanides such as praseodymium, neodymium, holmium and erbium also have promising energy-level structures for photon-avalanche paths[9]. Nanocrystals made of $NaYF_4$ or other materials that contain high concentrations of one these lanthanides might produce avalanche emissions at different frequencies from those observed by Lee *et al.*, potentially with an even greater nonlinear response.

The search might be facilitated by cutting-edge modelling studies. Lee *et al.* modelled the avalanche process using equations[4] that make some approximations to describe the average energy-transfer rates between neighbouring ions. More-modern computational approaches could be used to take into account the actual distance distributions between lanthanide neighbours and thereby provide a more accurate description of the energy-transfer dynamics — a key aspect of photon avalanches. Better insight into these dynamics might enable predictions of parameters such as the rise time (the period of time needed for the avalanche to begin and to reach its maximum) and the degree of nonlinearity of the response (that is, the power to which the excitation intensity is raised in the numerical equation that describes the avalanche response).

The extreme nonlinearity of the reported upconversion presents opportunities for applications. Lee and colleagues demonstrate that it can be used for super-resolution imaging — the nanoparticles could be imaged with approximately 70-nanometre resolution, well below the diffraction limit of the imaging system (the diffraction limit is a fundamental restriction associated with the wavelength of light that usually limits the resolution of optical imaging techniques). The authors' imaging set-up is simple compared with those of other super-resolution techniques[2,10], requiring only a single laser wavelength and less than one-tenth of the laser power. However, there are disadvantages: the long rise time of avalanche emission slows the recording process, which means that the technique is not yet suited for monitoring dynamic processes, such as those in biological systems.

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Other applications that depend on the nonlinearity of photo avalanching can also be envisaged. Photon avalanches are highly sensitive to competing processes that quench upconversion, or to changes that affect the absorption, emission or transfer of energy. Subtle environmental fluctuations that affect these processes will therefore cause strong variations in the avalanche emission. Single nanoparticles could thus be used to monitor the presence of quenching molecules, or local temperature or pressure changes, for example. The future of these new nanoparticles is bright.

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