Lanthanide doping could help with new imaging techniques

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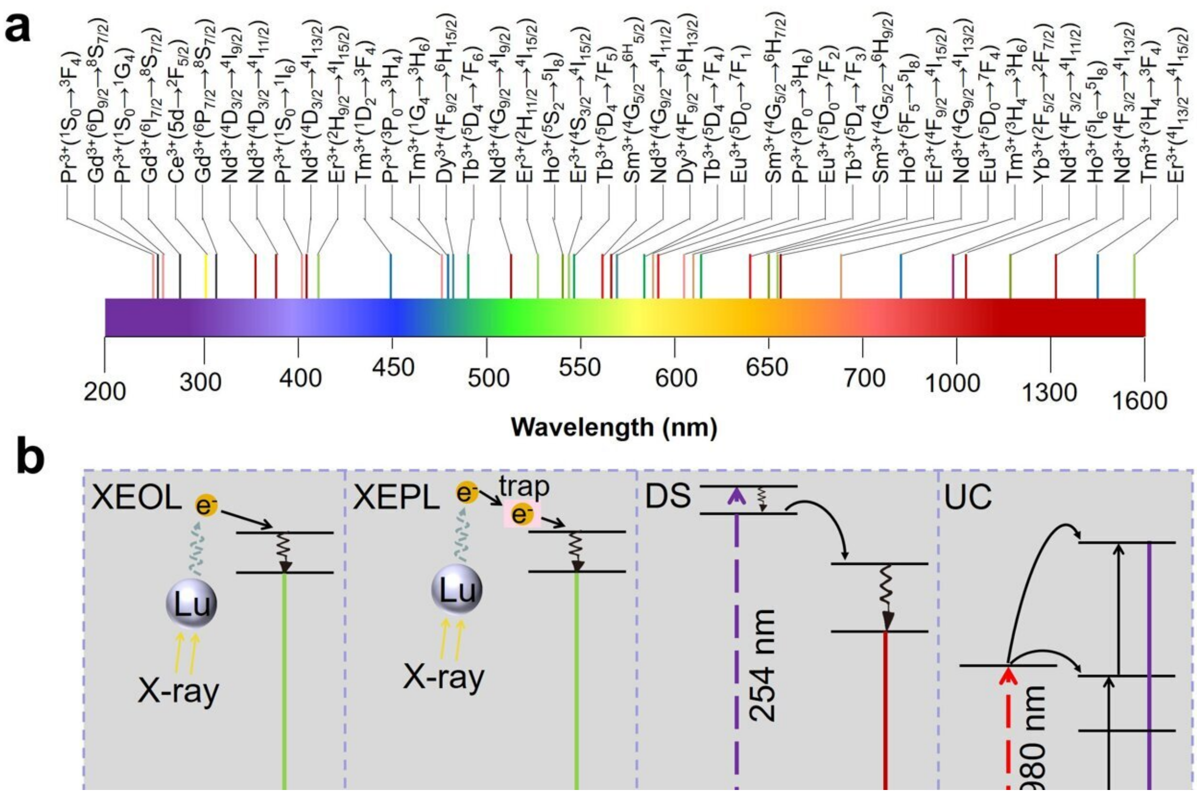

a) Main luminescent transitions of the lanthanide activators in the electromagnetic spectrum, spanning from UV to visible then extending to second near-infrared. b) XEOL, XEPL, DS and UC processes in lanthanide-doped fluoride NSs. c) Schematic illustration of the multimode color evolution based on fluoride core@shell@shell NSs. P represents excitation power. When different lanthanide activators generate diverse emission wavelengths of XEOL, UC and DS in a designed core@shell@shell NSs, plentiful multicolors can be modulated on demand by controlling the excitation wavelength and/or power.

Credit: Lei Lei, Yubin Wang, Andrey Kuzmin, Youjie Hua, Jingtao Zhao, Shiqing Xu and Prasad N. Paras

X-rays are electromagnetic waves with short wavelengths and strong penetrability in physical matter, including live organisms. Scintillators capable of converting X-rays into the ultraviolet (UV), visible or near-infrared (NIR) photons are widely employed to realize indirect X-ray detection and XEOL imaging in many fields. They include medical diagnosis, computed tomography (CT), space exploration, and non-destructive industrial material and security inspections.

Commercial bulk scintillators possess high light yield (LY) and superior energy resolution. However, they suffer from several drawbacks, such as complex fabrication procedures, expensive experimental equipment, non-tunable XEOL wavelength and poor device processability. They all produce emissions in the visible spectral range, but having XEOL in the NIR range may find more interesting applications in biomedicine. Thick crystals also generate light scattering followed by evident signal crosstalk in a photodiode array.

Recently, metal halide perovskites have been investigated for X-ray detection. Unfortunately, these materials also exhibited some intrinsic limitations, such as poor photo-/environmental- stability, heavy metal toxicity and low LY. Thus, the search for developing a new generation of scintillators is still a considerable focus of scientific research.

In a new paper published in *eLight*, a team of scientists, led by Professor Prasad N. Paras from the University of Buffalo, investigated the use of lanthanide-doped fluoride NSs. Their paper looked at design strategies and nanostructures that allow manipulation of excitation dynamics in a core-shell geometry.

Lanthanide-doped fluoride NSs avoid the limitations of bulk scintillators and metal halide perovskites. They also exhibit many useful properties. The core-shell structures of the lanthanide doped fluoride NSs can be tuned and designed on demand by employing a cheap and convenient wet-chemical method. The emission wavelengths can be tuned and extended to the second NIR window, benefiting from the abundant energy levels of lanthanide activators.

These NSs show superior photostability, low toxicity and convenient device processability. It makes them promising candidates for next-generation NSs and XEOL imaging. Moreover, they exhibit XEPL property, showing promising applications in biomedicine and optical information encoding. The combination of XEOL and XEPL makes them suitable for broadening the scope of their applications.

In recent years, significant advances have been made in NS development. The research team discussed design strategies and nanostructure that allow manipulation of excitation dynamics in a core-shell geometry. They also produce XEOL, XEPL, photon upconversion (UC) and downshifting (DS). It enables emission at multiple wavelengths and at varying time scales.

The fundamental working principle of XEOL imaging is to record the attenuation of X-rays after penetrating the subject with a scintillator and imaging with a camera. The scintillator screen is placed under the target to absorb the transmitted X-ray photons. A low dose of X-rays penetrating live organisms enables the application of computed tomography. Penetrating nonliving matter enables product quality and security inspection. The X-ray irradiation dose should be low enough to assure safety, while the high resolution and distinct contrast are important for image analysis.

X-ray, ionizing radiation with deep penetration depth in the human body, has been broadly studied for radiotherapy and bioimaging applications. The strong XEOL can activate the photosensitizers to generate reactive oxygen species. They directly slow or stop tumor growth by photodynamic therapy, causing inflammation and compromising microvasculature.

The XEPL in UVC range can be used for sterilization and in vivo killing of pathogens and cancer cells. Fluorides with large band-gap and facile creation of anionic defects are appropriate for generating UVC persistent luminescence. Experimental characterizations combined with first-principles calculations suggested that oxygen introduction-induced fluorine vacancies acted as electron traps.

Photodetectors have various applications in biomedical sensing, camera imaging, optical communications, and night vision. In commercial photodetectors, crystalline inorganic semiconductors are employed as photodiodes and phototransistors. They do not effectively respond to a broad scope of photon energy covering X-ray, ultraviolet-visible (UV-vis), and NIR light.

Under NIR excitation, the lanthanide-doped fluoride layer emits UV-vis light through energy-transfer UC processes. The subsequential radiation re-absorption process from lanthanide activators to the perovskite layer occurs. Visible emission from the perovskite layer is produced through recombining electrons in the CB and holes in the VB.

This nanotransducer exhibited a wide linear response to X-rays with various dose rates and UV and NIR photons at different power densities. As discussed in section 4.4, without integrating the perovskite layer, lanthanide-doped fluoride NSs can be used for the generation of XEOL, UC and DS as well, which might be possible for the realization of broadband detection in theory and need more study in the future.

Lanthanide-doped fluoride nanoparticles are suitable candidates for next-generation NSs owing to their low bio-toxicity, high photo-/environmental- stability, facile device processability, tunable XEOL and XEPL properties, and other useful features.

To promote the development of high-performance fluoride NSs and their practical applications, the team discussed the existing challenges and future multidisciplinary opportunities in this field below. Understanding the XEOL mechanism benefits the design and exploration of new fluoride NSs. At present, how the generated low kinetic energy charge carriers are transported to the luminescent centers or captured by defects and the corresponding influence factors are unclear.

The first populated nonradiative excited levels and the radiative levels of lanthanide activators are optimal when calculating or characterizing the energy differences among these charge carriers. These calculations will guide the design of energy transfer processes to match the energy differences followed by the enhanced light yield. High LY is a prerequisite for the realization of ultra-low dose rate applications.

More information: Lei Lei et al, Next generation lanthanide doped nanoscintillators and photon converters, *eLight* (2022). DOI: 10.1186/s43593-022-00024-0

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