



Photon upconversion nanomaterials†

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Photon upconversion through the use of lanthanide-doped materials has been the focus of a growing body of research in the fields of materials chemistry and physics for more than 50 years.¹ The attraction of this field has been the ability to generate photons at shorter wavelengths than the excitation wavelength after laser stimulation. Despite its potential utility for a number of applications, photon upconversion has been primarily investigated in bulk glasses or crystalline materials.² That situation dramatically changed in the mid-2000s, with the widespread research in the development of upconversion

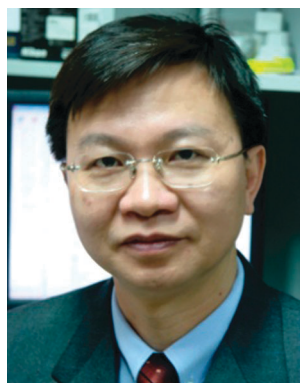
nanomaterials.³ As a unique class of optical materials, upconversion nanomaterials exhibit useful applications spanning from lighting to volumetric 3D displays to photovoltaics. Particularly, nanosized upconversion nanocrystals have proven valuable as luminescent labels for chemical and biological sensing with marked improvements in the sensitivity and versatility of the sensors. Recent advances in the field of upconversion nanomaterials have motivated us to initiate a thematic issue focusing on fundamental principles, synthetic strategies, materials characterization, broad applications, and



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major future opportunities and challenges for further development of the field. A common theme is the exquisite control of photon emissions afforded by lanthanide doping in a wide range of host lattices.

A key to the design of upconversion systems with precisely controlled emission profiles is the understanding of the electronic structure of the materials. In his contribution, Liu (DOI: 10.1039/c4cs00187g) uses theoretical models and methods to provide a critical analysis of nano-phenomena in upconversion. Using these approaches, it is possible to obtain accurate theoretical interpretations of the spectroscopic characteristics and luminescence dynamics of photon upconversion.

A photon upconversion process involving lanthanide-doped nanomaterials typically occurs in three steps; stepwise photon absorption, energy transfer and the emission of photons. Zhang and co-workers (DOI: 10.1039/c4cs00168k) survey examples of recent optical investigations on upconversion nanocrystals in order to reveal the impact of excitation energy migration dynamics on photon upconversion. Special attention is paid to the critical role of the spatial confinement of excitation energy in the enhancement of emission intensity. Meanwhile, Dong, Sun and Yan (DOI: 10.1039/c4cs00188e) provide a detailed overview of the fundamental mechanisms underlying energy

transfer over short- and long-range distances, and then highlight the principal guidelines for regulating emissions in lanthanide-activated nanocrystals.

A robust synthesis of deliberately designed high quality upconversion nanocrystals should lay the foundation for validating upconversion pathways. Chan (DOI: 10.1039/c4cs00205a) highlights the recently emerged combinatorial strategies for preparing upconversion nanocrystals and developing theoretical methods that allow the optical properties of the nanocrystals to be precisely modeled.

Spatially controllable assembly of different optical elements into a core-shell or composite upconversion nanocrystal opens the door to an efficient method for fabricating nanostructures with unprecedented flexibility in tuning the optical emission. Chen *et al.* (DOI: 10.1039/c4cs00151f) discuss the control of the core-shell interface within upconversion nanoparticles to achieve energy transfer processes with high efficiencies. As a parallel development, Chen, Prasad and co-workers (DOI: 10.1039/c4cs00170b) present a thorough assessment on photon upconversion arising from core-shell nanostructures. In their contribution, they describe the synthesis and characterization of the core-shell nanostructures, and then they comprehensively expound potential applications of these nanomaterials in bioimaging and light-triggered

drug release. Zhang and colleagues (DOI: 10.1039/c4cs00163j) have also focused on the production and emission tuning of upconversion nanocrystals, with routes to the construction of multifunctional counterparts.

For use in biological settings, the upconversion nanomaterial must have good water dispersibility. However, most luminescent upconversion nanocrystals are prepared with the coating of hydrophobic, long alkyl chain ligands. Sedlmeier and Gorris (DOI: 10.1039/c4cs00186a) review a number of methods for converting nanocrystals from hydrophobic to hydrophilic, a key criterion to consider when assessing the suitability of upconversion nanoparticles for biological applications. Chen and co-workers (DOI: 10.1039/c4cs00178h) also review the progress achieved in the design and synthesis of biocompatible upconversion nanocrystals for *in vitro* biodetection applications.

A number of instrumentation techniques have been utilized to probe the nature of upconversion nanocrystals and quantify structure-property relationships, as discussed by Liu *et al.* (DOI: 10.1039/C4CS00356J). In their contribution, they highlight the rational design and combination of a variety of instrumental tools for characterizing upconversion nanomaterials, from surface structures to intrinsic properties to ultimate challenges in nanocrystal analysis at single-particle levels.

Apart from the fascinating optical properties on display, upconversion nanomaterials can exhibit amazing magnetic and ferroelectric characteristics inherited from certain lanthanide dopants. These attributes are likely to provide an outlook on the generation of stimuli responsive upconversion emission. Tsang, Bai and Hao (DOI: 10.1039/c4cs00171k) review the efforts toward the elucidation of stimuli responsive properties displayed by upconversion nanomaterials, as well as potential applications of such nanostructures under different forms of stimulus control.

In view of the tremendous potential of upconversion nanocrystals as contrast agents for *in vivo* and *in vitro* imaging studies, the concerns on the biosafety of these nanocrystals must be evaluated. There are two balanced and carefully



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attention due to its potential applications in cell targeting, imaging, diagnostic medicine, photodynamic therapy, and drug delivery using photoswitching. He has held invited faculty fellowships at l'Universita di Trento, Italy, Université d'Angers, France, Universidad Autonoma de Madrid, Spain and l'Universita di Verona, Italy.

considered reviews devoted to this topic. Gnach *et al.* (DOI: 10.1039/c4cs00177j) report a summary of the main achievements in this area of research. Li and co-workers (DOI: 10.1039/c4cs00175c) discuss particle circulation-induced toxicity in organs and tissues of small animals after administration.

Easy structural modification and high levels of freedom in the functional multiplicity of upconversion nanocrystals are critical for their therapeutic applications. In their contribution, Zhang and co-workers (DOI: 10.1039/c4cs00158c) explore recent advances in the development of phototherapeutic agents activated by multifunctional upconversion nanocrystals. Li, Lin and co-workers (DOI: 10.1039/c4cs00155a) illustrate the aspects of

upconversion activation for drug delivery and exemplify the potential impact of this research area on biomedical science.

With features of high photostability and non-autofluorescence background factored in, upconversion nanomaterials are ideal for high-resolution bioimaging. Suh, Hyeon and co-workers (DOI: 10.1039/c4cs00173g) report on the use of upconversion nanocrystals as multimodal *in vivo* contrast agents, with particular emphasis on the feasibility of using such nanocrystals as a versatile platform for wide-field two-photon microscopy.

We wish to thank all of our contributing authors for their dedication and the reviewers for their constructive comments and suggestions. We owe a special debt of gratitude to the editorial staff of *Chemical*

Society Reviews for invaluable assistance in assembling this issue. It is hoped that this thematic issue provides an update on some of the best work and advances in the field of photon upconversion nanomaterials. At the very least, we hope that this special issue serves as a useful reference work that could appeal to members of the chemical as well as the biological and medical communities.

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