High Order Multiphoton Upconversion Processes and Intense Ultraviolet Upconversion Luminescence under NIR Excitation

Since the advent of lasers, high order multiphoton upconversion processes (HOMUPs) have been widely investigated throughout the scientific community owing to their great fundamental significance and numerous applications in short wavelength light generation, optical imaging, and spectroscopy. Especially, upconversion pumping by means of intrinsic energy level matching of certain rare-earth (RE) ions plays a significant role in achieving short-wavelength light, due to ample availability of high power semiconductor diode lasers in the near-infrared (NIR) range. In the past decades, many efforts have been devoted to getting breakthroughs in HOMUPs, and achieving short wavelength (ultraviolet or vacuum ultraviolet) light by exploring HOMUPs in RE ions-doped materials by the researchers around the world. Before the starting of this project, only high efficient visible upconversion light had been realized in RE ions-doped materials when pumped by NIR light.

In this prize-winning project "High order multiphoton upconversion processes and intense ultraviolet upconversion luminescence under NIR excitation", Profs. QIN Weiping, SONG Hongwei, QIN Guanshi, ZHAO Dan, who are all from Jilin University, and LV Shaozhe with the CAS Changchun Institute of Optics, Fine Mechanics and Physics achieved remarkable advances in HOMUPs. They successfully extended the wavelength range of upconversion emissions from visible to ultraviolet (UV) region, and realized strong UV upconversion luminescence in RE ions-doped materials under weak NIR excitation for the first time in the world. The completion of this project has placed this group at the international research forefront in the field of shorter wavelength light generation. This work provided novel schemes for generating high efficient UV light, and paved the road for applying frequency upconversion technology in various fields including green energy, environmental conservation, medical treatment, military, etc. Major achievements by Prof. QIN and his cooperators can be summed up as the following.

First of all, Prof. QIN and his colleagues observed strong NIR-UV upconversion luminescence from flying particles generated in pulse laser ablation (PLA) (Figure 1). PLA, one of the key technologies for exploring metastable phase materials, was used to prepare RE-doped materials with strong NIR-UV upconversion light for the first time in the world. UV and blue upconversion stimulated emissions were observed from the powders prepared by PLA. Based on the experimental results, they built the relations between UV upconversion and the Judd-Ofelt parameters. This work initiated the following research on strong NIR-to-UV upconversion luminescence and HOMUPs in RE

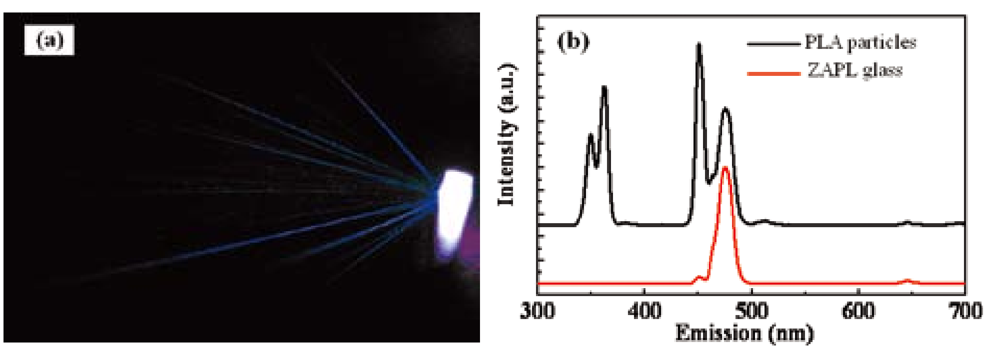

Figure 1: (a) Flying particles with blue and UV upconversion emissions in PLA procedure, (b) Upconversion emission spectra of Yb^{3+}, Tm^{3+} co-doped ZAPL glasses or particles under the excitation of a 980 nm laser diode.

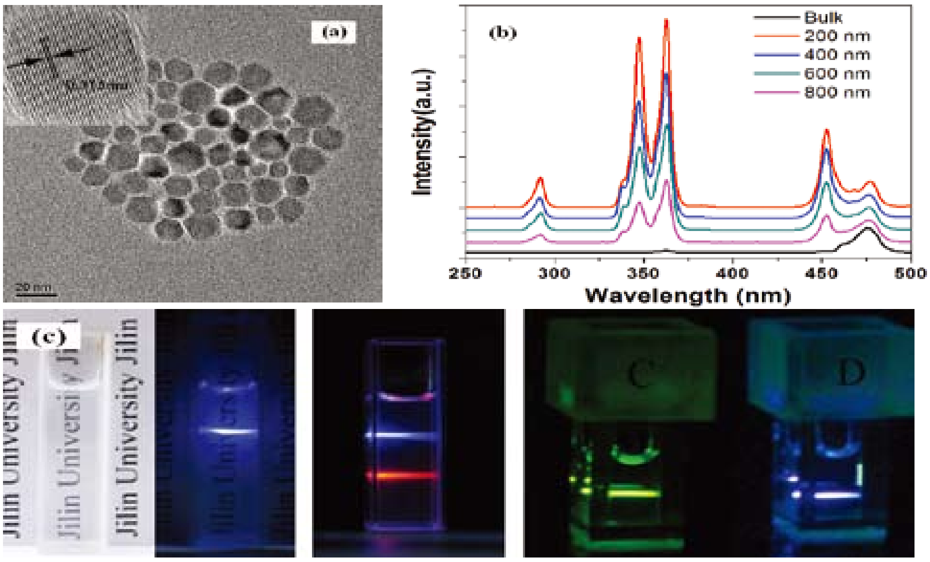

Figure 2: (a) TEM image of NaYF4: 20%Yb, 0.5%Tm nanocrystals. The Inset: a HRTEM image of a single nanocrystal. (b) Dependence of upconversion luminescence spectra on the size of nanocrystals. (c) Photographs of upconversion nanocrystals dispersed in deionized water.

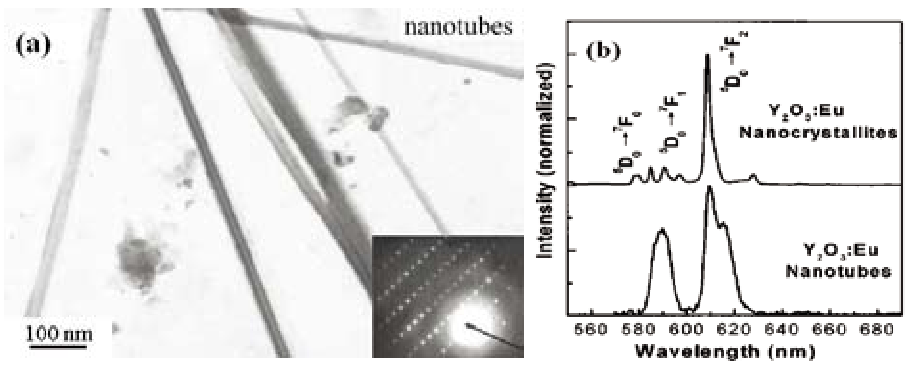

Figure 3: (a) TEM image of Y_2O_3: Eu nanotubes. The inset shows the electron diffraction pattern recorded perpendicular to the nanotube long axis. (b) Comparison of emission spectra between Y_2O_3: Eu nanotubes and Y_2O_3: Eu nanocrystallites.

ions-doped materials. Most importantly, this work paved the road for applying UV upconversion technology to various applications in their future works, and boosted the development of the related research fields.

Also, the researchers observed and discussed the size dependence of high order upconversion population process in RE ions doped nanocrystals (Figure 2). The results showed that it was easier to obtain high order multiphoton upconversion population process in RE ions-doped nanocrystals than that in RE ions-doped bulk materials. Furthermore, the enhancement mechanism for high order upconversion population process in RE ions-doped nanocrystals was clarified. This work provided novel schemes for generating high efficient HOMUPs.

At the same time, one-dimensional Y_2O_3 nanotubes were synthesized by the group for the first time worldwide (Figure 3). Different local symmetries between the inside and the surface of nanotube wall were found. The radiative transition rates and the luminescence quantum efficiency in one-dimension nanotubes were found to be much higher than those in the relative nanoparticles and bulk materials. The group also found that the refractive index near the boundary of nanomaterials had great influence on the spontaneous emission of the inside luminescence site. It was proved that the increase of refractive index of medium could enhance the spontaneous emission rate of the rare earth ions.

With more than two-hundred research papers published, among which many were frequently cited by various prestigious international journals, Prof. QIN and his colleagues were honored with this prize for their distinguished studies and innovative discoveries.