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Review

Visible-to-ultraviolet Upconvertion: Energy transfer, material matrix, and synthesis strategies

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ABSTRACT

In recent years, Upconversion (UC) material has attracted much attention because of its fantastic energy transfer capability of converting the low-energy photons into high-energy photons via anti-Stokes process. Among UC materials, the visible-to-UV UC materials exhibit remarkable potential in laser conversion, photo-catalysis, the sterilization as well as antibiosis in biological areas because of their capability of converting the visible radiation into ultraviolet emission. Considering the interesting UC process and large potential application of the visible-to-UV UC materials, it is necessary to overview its intrinsic UC mechanism, material structure, as well as material synthesis techniques for the development of UC material. This work focus on the visible-to-UV UC materials and review its current research situation, the challenges in its research field, as well as analyzing and comparing recent investigations to provide valuable evaluation for such materials both from theoretical and commercial perspective. The most effective UC matrix and luminescent centers in recent works were summarized and the intrinsic mechanisms of visible-to-UV UC were introduced. The material design strategies and techniques for the synthesis of visible-to-UV UC phosphors were focused. The advantages and the limitations of visible-to-UV UC material are discussed in detail, and a reasonable expectation for the emerging trends of such potential material is provided.

Contents

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1. Introduction

In recent years, Upconversion (UC) material has attracted much attention because of its fantastic energy transfer capability of converting the low-energy photons into high-energy photons via anti-Stokes process [1–7]. During the anti-Stokes process, two or more photons were absorbed sequentially by a material to reach an excited state, which could then release one higher-energy photon. According to the wavelength range of energy transfer, current research of UC materials could be classified into three types: (1) the IR-to-visible UC materials which could transfer infrared (IR) light to visible light due to their NIR-triggered anti-Stokes emissions, (2) the visible-to-UV UC materials which could transfer visible light to ultraviolet (UV) light, and (3) the visible-to-visible UC materials which could transfer long-wavelength visible light to short-wavelength light [6]. Table 1 summarized the advantages and disadvantages of those UC materials in terms of their anti-Stokes shifts, chemical stability, UC conversion efficiency, toxicity, synthesis cost and mechanical stability. Application potential of the three materials not only depends on their UC capability, but is closely related to their chemical stability, toxicity, and synthesis cost.

Owing to their unique chemical and physical advantages (Table 1), the IR-to-visible UC materials exhibit wide potential in the fields of photocatalysis, optoelectronic devices, displays, solar cells, nonlinear optics, bio-imaging and molecular probes [8–14]. There are enormous progresses in the developments of IR-to-visible UC materials since the birth of the $NaYF_4$:Er^{3+},Yb^{3+} system in 1966 [10,11,13,14]. Current research situation not only focus on exploring appropriate luminescent centers and sensitizer, but construct high efficient material matrix for UC energy transfer. Various IR-to-visible UC materials have been invented, such as the Gd_2O_3:Yb^{3+}/Tm^{3+} nanoparticles, Er^{3+}/Tm^{3+}/Yb^{3+} tridoped ($NaY(WO_4)_2$/YF_3), and β-$NaYF_4$:Yb^{3+}/Er^{3+}. Those works indicate that hexagonal $NaYF_4$ is the most efficient matrix for IR-to-visible UC generation. Meanwhile, current research recognized that Yb^{3+} is the most effective sensitizer in IR-to-visible UC materials, owing to its simple 4f electronic structure and ability to enhance absorption and energy transfer without inducing quenching of excited activator ions [8,10,13,14]. A key challenge in IR-to-visible UC research fields is the UC efficiency are reduced due to large amounts of defects and dangling bonds on the surface of UC phosphors. This challenge triggered current boom of constructing core-shell and core-shell-shell sandwich structure research to down lower energy transfer loss and endow the IR-to-visible UC materials with novel optical/electronic properties.

Visible-to-UV UC materials facilitate the visible to UVC (220–280 nm) energy transfer via visible-light-triggered anti-Stokes emissions [18]. Research situation of visible-to-UV UC materials lags far behind that of IR-to-visible UC materials. The development of visible-to-UV UC materials mainly endure two challenges: one is lacking appropriate luminescent centers which have energy level to facilitate the visible-to-UV UC transition, the other is lacking of suitable material matrices which contain low phonon energy, high tolerance, and favorable chemical stability to provide the luminescent centers with an efficient energy transfer environment [15–18]. Nevertheless, considering that more than 50% of the solar spectrum is in the range of visible light, it could be expected that the visible-to-UV UC material will show remarkable potential in exploring solar energy to resolve present energy crisis and severe environmental problems of the world by taking advantage of stable semiconductor photocatalysts sensitive to UV light in water splitting to hydrogen. For instance, current research of visible-light-driven water splitting is highly limited due to absence of efficient and chemically stable photo-catalysts. TiO_2 and Ti based photocatalysts mainly respond to UV irradiation, so they could not make full use of the whole solar spectrum. Sulfide and Selenide based photo-catalysts could work under visible light irradiation, but their practical applications are highly restricted due to their poor photo-chemical stability (photocorrosion). The application of visible-to-UV UC material can effectively sensitize UV-responsive photocatalysts to promote visible-light driven water splitting. Besides, in biological research fields, visible-to-UV UC material also show huge potential that they exhibited amazing effects on sterilization and antibiosis even when the Visible-to-UV UC conversion efficiency is lower than 0.1%. Consequently, the Visible-to-UC UC materials could open a new window for making full use of sustainable solar energy.

Driven by great application potential of visible-to-UV UC material in energetic, environmental and biological research fields, it is necessary to summarize the mechanisms, matrix types, material design and synthesis techniques in detail for the development of such important material. In this review, it begins by summarizing the intrinsic mechanisms reported for visible-to-UV UC. Then, the most effective matrix types and luminescent centers in recent