Journal of Alloys and Compounds 735 (2018) 372–376

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Enhanced upconversion based on the ultrahigh local field enhancement in a multilayered UCNPs-metamaterial composite system

Shiping Zhan [a, *], Xiaofeng Wu [b, **], Chao Tan [b], Jian Xiong [c], Shigang Hu [b], Junshan Hu [a], Shaobing Wu [a], Yongyi Gao [a], Yunxin Liu [a, ***]

[a] College of Physics and Electronic Science, Hunan University of Science and Technology, Xiangtan, 411201, China
[b] College of Information and Electrical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, China
[c] Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, 541004, China

ARTICLE INFO

Article history:
Received 28 August 2017
Received in revised form
28 October 2017
Accepted 10 November 2017
Available online 13 November 2017

Keywords:
Surface plasmon
Upconversion nanoparticle
Emission enhancement
Perfect absorption
Metamaterial

ABSTRACT

In this paper, we reported a multilayer metamaterial system with ultrahigh absorption, consisting of silver nanoring, upconversion nanoparticles(UCNPs) and silver film, which can dramatically enhance the upconversion emission. A simplified theoretical expression of the upconversion enhancement factor(EF_{upc}) was derived, and the structure parameter and the local field-UCNPs coupling were considered for the EF_{upc} analysis. It was found that the bottom silver film was crucial for the tremendous upconversion enhancement since it gave rise to a pronounced absorption peak and resulted in a strong field confinement of the 980 nm excitation light. Comparing with the nanodisk, the nanoring performed better in enhancing the upconversion, and an enhancement factor of ~3.2×10^4 was achieved based on the numerical and theoretical analysis. This metamaterial system provided a novel approach in enhancing upconversion, and the research findings could be helpful to the design of biosensor and photovoltaic devices.

1. Introduction

Photon upconversion is an anti-stokes-type emission that possessing the ability to transform low-energy photons to higher ones, which played important roles in emitting, biosensor and photovoltaic(PV) devices [1–3]. In the past decade, the lanthanide doped upconversion nanoparticles(UCNPs) had attracted great attention due to their extraordinary advantages of long lifetime, narrow emission bandwidth, background free and deep tissue penetration [4–8]. However, some challenges also exist, one fundamental and key problem is their low upconversion efficiency [9]. Even the most efficient material such as fluoride, often possesses the fluorescence quantum yield(QY) below 1% [10–13]. To date, a high QY of ~7.6% was reported in the $LiLuF_4$ host material by Chen's group [14]. Even so, it was still far away to the theoretical limit. This problem seriously restricted their applications in bioimaging and PV devices. Recently, the combination of UCNPs and nanoplasmonic structure was found effective in enhancing the upconversion emission [15–20]. This enhancement can be attributed to the optical spectra match between the emission/absorption of UCNPs and the surface plasmon resonance (SPR) of nanoplasmonic structure [15], such as metal nanoparticle [16,17], nanograting [18,19] and core-shell configurations [20]. For example, S. Schietinger et al. reported an enhanced upconversion by using gold nanoparticles [16]. W. Park's group proposed a plasmonic silver grating, which can enhance the upconversion by ~40 folds, meanwhile leading to a more than half input energy loss by reflection [18]. It was found that for most plasmonic structures, the excitation energy loss caused by reflection or scattering were ubiquitous, which may reduce the absorption and restrict the further enhancement of the upconverison emission. Metamaterial is the material engineered to have extraordinary property, such as negative index [21], plasmon induced transparency [22] and perfect absorption [23]. The metamaterial with ultrahigh absorption can lead to strong local field

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: spzhan86@163.com (S. Zhan), xfwuvip@126.com (X. Wu), lyunxin@163.com (Y. Liu).

https://doi.org/10.1016/j.jallcom.2017.11.147
0925-8388/

enhancement, which is very promising in improving the upconverison efficiency of the lanthanide doped upconversion nanoparticles. However, rare attention was paid into the plasmon enhanced upconversion by metamaterial with perfect absorption and the related mechanism.

In this paper, we reported a silver nanoring-UCNPs-silver film multilayered metamaterial system, which can dramatically enhance the upconversion emission due to the perfect absorption of 980 nm excitation light and the high local field enhancement. The structure parameters and the coupling way were discussed detailly for analyzing the upconversion enhancement factor and the corresponding mechanism. This metamaterial system provided a novel approach in enhancing the upconversion efficiency, and the findings can be helpful in the design and application of biosensor and PV devices.

2. Structure and model

The schematic of the plasmonic metamaterial system is shown in Fig. 1(a). This periodic metamaterial is a triple layer structure, regarded as the metal-dielectric-metal structure(MDMS), from up to down are: silver nanoring array, the $NaGdF_4$:Yb^{3+}, Er^{3+} layer and the silver film, respectively. The excitation light was incident from the *z* axis. The numerical model of a unit cell for the composite system was shown in Fig. 1(b), where the inner radius, outer radius and the height of the ring are R_i, R_o and *h*, respectively. Here we proposed the metal-dielectric structure(MDS) and the MDMS, shown in Fig. 1(c). For the MDS, the bottom silver film was removed comparing with the MDMS. The thickness of the Ag film was denoted as *w*, which can remarkably reduce the transmission and leading to a nearly perfect SPR absorption of the input light [23]. Owing to the various incident light-metallic structure coupling efficiency in these systems, the SPR contribution differs from each other in enhancing the upconversion. Fig. 1(d) shows the TEM image of the $NaGdF_4$:Yb^{3+}, Er^{3+} nanoparticles which was synthesized by the method in our previous works [24–26] with an average diameter of $d = 30$ nm. Such a multilayered composite structure can be constructed layer by layer with the help of some nanostructure fabrication methods, and the physical vapor deposition(PVD) technique, the spin-coating and nano etching technologies such as the electron beam lithography(EBL) technology can be applied in the future experimental consideration. The numerical absorption, reflection, transmission and field distributions were calculated by the Finite-Diffinite Time-Domain method [27]with mesh step of $\Delta x = \Delta y = \Delta z = 2$ nm. The incident light was normally injected from the *z* direction, and the simulation domain was surrounded by a perfectly matched layer(PML) in the *z* direction while periodic boundaries in the *x* and *y* directions, period $P_x = P_y = 240$ nm for a unit cell. The metal silver was taken from Palik(0-2μm) [28], while the dielectric constant of the $NaGdF_4$:Yb^{3+}, Er^{3+} nanoparticle was set to be $\varepsilon_d = 1.4$. During the simulation, the monolayer UCNPs were assumed close contact.

3. Results and discussion

The transmission, reflection and absorption spectra of the MDS metamaterial with $R_i = 38$ nm, $R_o = 66$ nm, $d = 30$ nm and $h = 20$ nm was shown in Fig. 2(a). In our research, $R_o = 66$ nm, $h = 20$ nm, and $d = 30$ nm were fixed during the discussion. An apparent reflection(R) peak of 67% and transmission(T) dip of 9% around 825 nm were observed. Thus the absorption (A) to the incident light wave at 825 nm can be calculated by the relation [23]: $A = 1\text{-}T\text{-}R$, and reached to 24%. Due to the local field enhancement effect (inset in Fig. 2(a)), the $|E/E_0|^2{}_{z=d/2} = 7$ in the MDS was much higher than that in the referenced structure without metallic ring array. Here $|E/E_0|^2{}_{z=d/2}$ represented the effective excitation field intensity in the center position of the UCNPs layer(see the red dash line in Fig. 1(c)) due to the $|E/E_0|^2$ nonuniformity along the *z* axis. For the MDMS with $R_i = 0$ nm and $w = 50$ nm, the reflection spectrum changes from a resonance peak to a dip at 765 nm, shown in Fig. 2(b). Owing to the presence of the bottom silver mirror, the transmittance of the structure was nearly eliminated across the entire near-infrared wavelength regime. And most of the excitation light field was localized between the disk and the metal film which remarkably reduced the reflection to the free

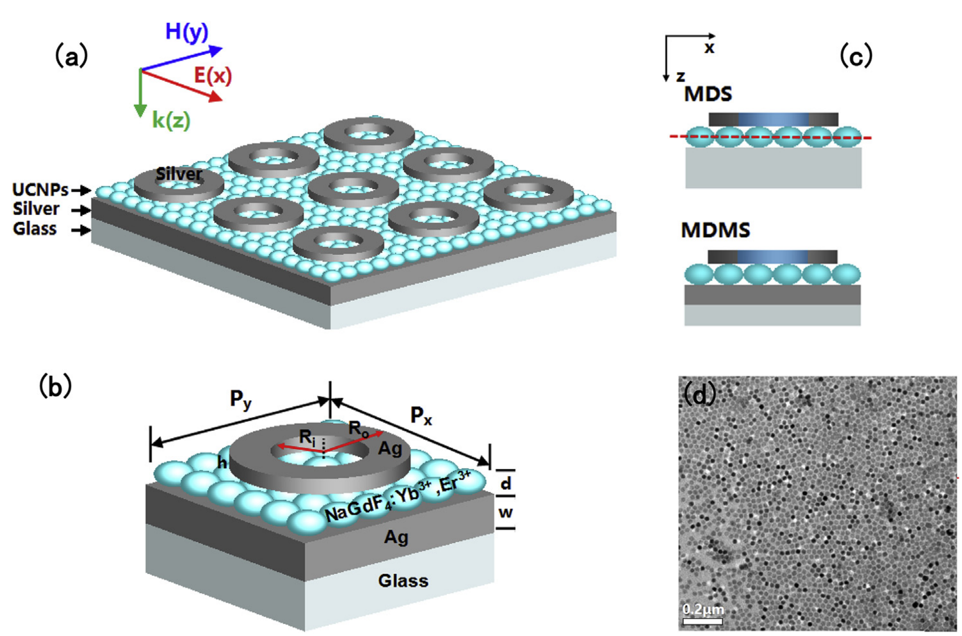

Fig. 1. (a) The schematic of plasmonic metamaterial-UCNP composite system. (b) The numerical model for a unit cell of the system. (c)The MDS and MDMS configuration of the plasmon enhanced upconversion system. (d)The TEM image of $NaGdF_4$:Yb^{3+}, Er^{3+} nanoparticles.