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Rod-shaped $NaY(MoO_4)_2$:Sm^{3+}/Yb^{3+} nanoheaters for photothermal conversion: Influence of doping concentration and excitation power density

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ABSTRACT

Thermal effect of rare earth (RE) ions doped nanoparticles under near-infrared light irradiation has been underestimated, because main interest and efforts still fall into the distinctive up-converting luminescence property of these particles. In this work, we demonstrate an approach to convert 980 nm light energy to heat energy via a designed nanoheater which is Sm^{3+}/Yb^{3+} codoped $NaY(MoO_4)_2$ nanorods derived from a microwave-assisted hydrothermal reaction. To inspect the photothermal conversion effect of the nanoheaters, Er^{3+}/Yb^{3+} codoped $NaY(MoO_4)_2$ nanorods are prepared via the same synthesis route. A convenient strategy, in which $NaY(MoO_4)_2$:Er^{3+}/Yb^{3+} nanorods are used as nanothermometer, is proposed to monitor the laser-induced temperature change of the nanoheaters by mixing a small amount of nanothermometer with nanoheater. The influence of Sm^{3+}/Yb^{3+} concentrations and excitation power density on the final temperature of the nanoheaters is studied. It is found that when Yb^{3+} concentration is fixed to be 10 mol%, the influence of increasing Sm^{3+} concentration on the photothermal conversion effect is limited; but when Sm^{3+} is fixed to be 5 mol%, the photothermal conversion is enhanced greatly with the increase of Yb^{3+} concentration. In addition, the temperature for all the $NaY(MoO_4)_2$:Sm^{3+}/Yb^{3+} nanoheaters after laser irradiation is linearly dependent on the excitation power density. In order to examine the photothermal conversion effect of the nanoheater in liquid media, the PVP (polyvinyl pyrrolidone) solution is used for accommodating the nanoheaters, and effective photothermal conversion is observed.

1. Introduction

During the past few years, upconverting nanoparticles (UCNPs) doped with RE ions have been extensively studied due to their potential biological applications [1–3]. Unlike other traditional hazardous materials, such as fluorescent dyes and semiconductor quantum dots, UCNPs could be designed with low biotoxicity [4,5], and could be excited by near-infrared (NIR) light and then emit ultraviolet, visible and NIR lights. A necessity for UCNPs applications in the biological milieu is the coincidence between NIR wavelengths and tissue penetration window (700–1000 nm) [6,7]. Moreover, NIR light of certain wavelength can penetrate deeply into the biological tissue and will not induce fatal damage of cell and tissue, simultaneously, causes only limited autofluorescence background. Thus, UCNPs are qualified for various biological applications, including vivo bioimaging, biodetection and drug delivery, etc [8–11]. Typically, nanoparticles for upconversion are doped with activator (Er^{3+}, Ho^{3+} or Tm^{3+} in most cases) and sensitizer (Yb^{3+} for example). Yb^{3+} is widely employed as sensitizer because of its large absorption cross section at 980 nm ($^2F_{7/2} \rightarrow {}^2F_{5/2}$), and could efficiently transfer the excitation energy to activators. Much academic attention and research interest for the RE doped nanomaterials was focused on their luminescence properties for biological applications, but their photothermal conversion was normally ignored. In fact, the heat generation always accompanies the luminescence processes of RE doped nanomaterials, thus providing a possible route for designing and developing novel nanoheaters. It should be noticed that when the upconversion luminescence

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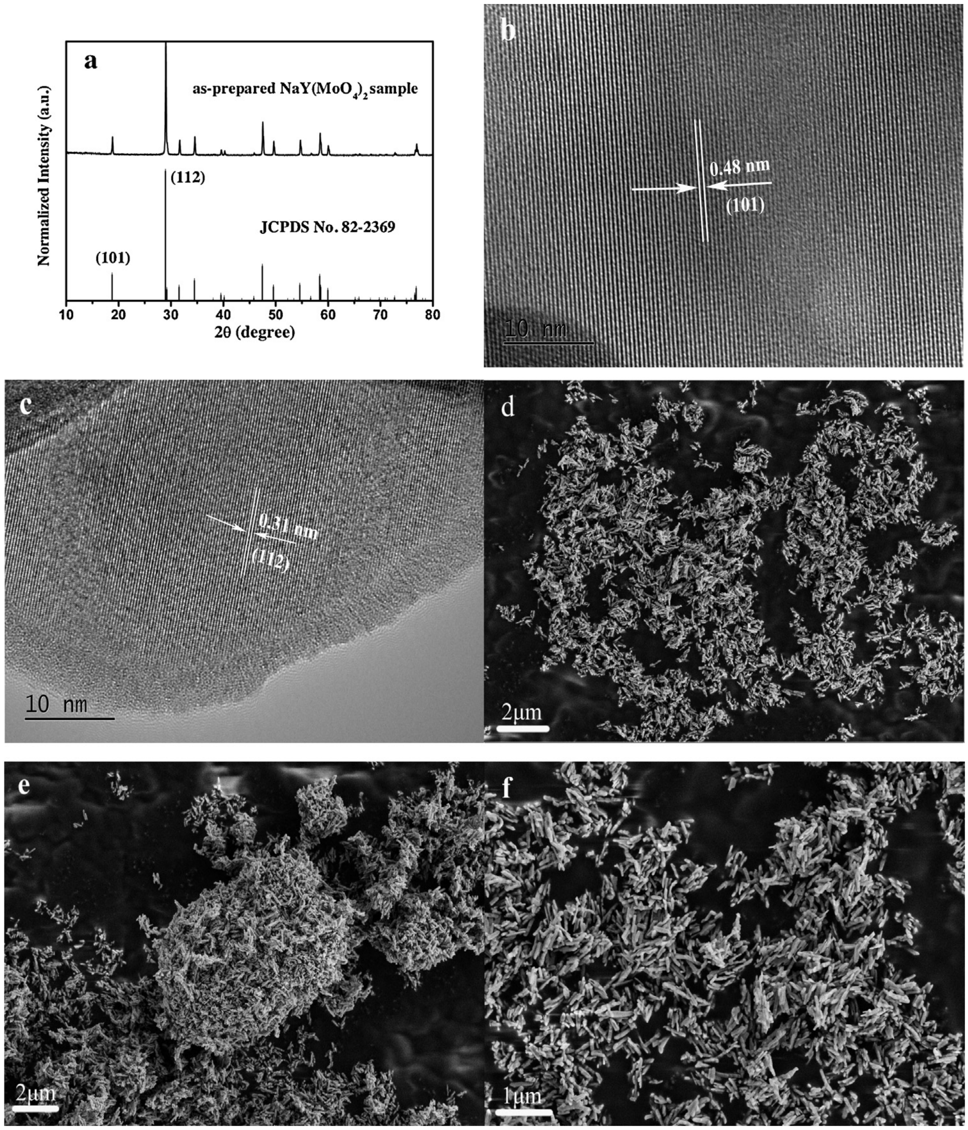

Fig 1. (a) XRD patterns of as- prepared $NaY(MoO_4)_2$ sample and PDF# 82-2369, (b) and (c) HRTEM images of as- prepared $NaY(MoO_4)_2$ sample, (d), (e) and (f) FESEM images of as- prepared $NaY(MoO_4)_2$ sample.

takes place, at the same time the excitation light energy would be partially converted to heat energy through cascade nonradiative transition channels [12–16]. While these two conversion processes of light-to-light and light-to-heat are competitive, between them one is efficient, the other must be inefficient. However, during the past years many efforts have been devoted to the highly efficient light-to-light conversion (upconversion), the light-to-heat conversion was rarely investigating.

Inspired by the light-to-heat conversion process, photothermal therapy (PTT) in cancer treatment could be another potential biological application of RE doped nanomaterials. PTT is the use of heating effect to cause targeted cancer cells' fatal injury at a temperature ranging from 40 to 45 °C, while the surrounding healthy cells survive in this treatment process [17]. The most investigated heaters in PTT are gold nanostructures, copper sulfide and carbon nanotubes, which could effectively convert the NIR light energy to heat [18–21]. However, these heaters for PTT exhibit some drawbacks such strict preparative conditions, weak biological compatibility and high biological toxicity. Moreover, to realize effective absorption of pump light with certain wavelength, the particle size and morphology of the gold nanoparticles are strictly restrained, and that the small gold nanoparticles prefer to be aggregated in bio-system and cause higher biotoxicity. The carbon nanostructures possess low biotoxicity and high photothermal conversion efficiency, but they could also quenching the upconversion fluorescence for temperature sensing [22]. Therefore, developing novel photothermal conversion heaters is imperative for the PTT. Thus, RE doped nanomaterials could be an alternative option for PTT [23]. Generally, the priority for application of RE doped nanomaterials in PTT is converting light to heat to an extreme, which could be subtly realized with specific RE doping strategy. First, in order to do so a rare earth ion (sensitizer) should be chosen to effectively absorb the excitation energy, then a quenching center should be introduced to accept the energy absorbed by the sensitizer and transforming the energy to heat via cascade nonradiative relaxation. Among all the rare earth ions, Yb^{3+} is known to have much larger absorption section at 980 nm which matches the output wavelength of commercialized laser diodes, thus it is selected as an absorber. Furthermore, to quench the radiative transition of Yb^{3+}, another quencher should be selected from rare earth ions. By inspecting the energy level diagram of trivalent ions, Sm^{3+} ion seems to be an ideal choice since its $^6F_{11/2}$ energy level matches well with $^2F_{5/2}$