Optical Materials 78 (2018) 102–106

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Q-switched Yb^{3+}:YAG laser using plasmonic $Cu_{2-x}Se$ quantum dots as saturable absorbers

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ARTICLE INFO

Article history:
Received 28 August 2017
Received in revised form
30 December 2017
Accepted 8 February 2018

Keywords:
Quantum dots
Ultrafast spectroscopy
Localized surface plasmons
Saturable absorbers
Q-switched lasers

ABSTRACT

$Cu_{2-x}Se$ quantum dots (QDs) were synthesized by organometallic synthesis methods. Due to heavy self-doping, the $Cu_{2-x}Se$ QDs exhibit particle plasmon resonance in the near-infrared. Transient absorption spectroscopic investigation revealed strong nonlinear optical absorption and bleaching performance of the QDs under femtosecond pulse excitation, which enabled the $Cu_{2-x}Se$ QDs to be excellent saturable absorbers and applied in Q-switched or mode-locked lasers. A passively Q-switched Yb^{3+}:YAG solid-state laser at 1.03 μm was achieved by coating $Cu_{2-x}Se$ QDs as saturable absorbers onto one of the output coupler of the V-shaped linear cavity.

1. Introduction

Surface plasmon resonance (SPR) or localized surface plasmon resonance (LSPR) has been observed in nanostructured metals, in particular in noble metals like gold and silver. SPR or LSPR is not a commonly observed photophysical performance in semiconductor nanostructures or quantum dots (QDs) [1–3]. However, based on the Mott phase transmission theory, semiconductors can also possess similar characteristics as noble metals, such as LSPR and fast electron-electron and electron-phonon interactions. Interestingly, plasmonic effects have been investigated in $Cu_{2-x}Se$ QDs [4–6], where metallic performances with a high free-carrier density have been achieved by controlling the chemical reaction parameters in the synthesizing process [7–10]. Generally, the concentration of electrons in noble metal is in the order of 10^{23} cm^{-3}, leading to LSPR in the UV–visible spectral range. However, the concentration of free charge carriers in the $Cu_{2-x}Se$ QDs can be adjusted by modifying the self-doping processes, which may reach 10^{19}~10^{22} cm^{-3}. Thus, the LSPR can be tuned to the near or mid infrared region [11]. According to previous studies, the band gap of $Cu_{2-x}Se$ nanocrystals is about 1.6 eV [12] and the LSPR wavelength can be tuned from 900 to 1700 nm through heavy self-doping [4].

The $Cu_{2-x}Se$ QDs exhibit multifold advantages over the metallic nanoparticles in nonlinear optical response based on plasmonic properties: (1) They possess an absorption cross-section 10 times larger than gold nanoparticles at the same optical frequency [3]. (2) They can be suspended in organic solvent with much better dispersity and stability than metallic nanoparticles, enabling much improved solution-processed techniques. (3) The plasmon resonance spectrum can be tuned in a broad spectral range from the red to near-infrared [4,13]. Therefore, this novel class of artificial plasmonic media based on heavily doped (self-doped) semiconductors opens a new route to nonlinear plasmonics [4].

Recently, colloidal PbS quantum dots were used as saturable absorbers in a passively Q-switched laser at 1.55 μm, producing 801-nJ pulses with a repetition rate of 24.2 kHz in a fiber laser [14]. Then, $Cu_{3-x}P$-quantum-dot saturable absorbers were used in a Q-switched laser that outputs 180-nJ pulses with a 30-kHz repetition rate [15]. Applications of CdTe/CdS QDs in Q-switched lasers have also been demonstrated [16]. In this work, we focus on the optical nonlinearities of the $Cu_{2-x}Se$ QDs and their applications in the Q-switched laser devices.

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https://doi.org/10.1016/j.optmat.2018.02.027
0925-3467/

2. Synthesis of the $Cu_{2-x}Se$ QDs

$Cu_{2-x}Se$ QDs were prepared using the method proposed by Deka et al. [10]. Anhydrous CuCl (0.099 g, 1 mmol) was added to a mixture of 5-mL oleylamine and 5-mL 1-octadecene (ODE) in a reaction flask. After evacuation for 1 h at 80 °C, the mixture was annealed at 300 °C in nitrogen. Meanwhile, a selenium (Se) precursor solution, which is a mixture of 0.039-g (0.5 mmol) selenium and 3-mL oleylamine, was prepared at a temperature of 100 °C before complete dissolution. Then, the precursor solution was transferred into a glass syringe and injected into the flask quickly. A reaction time of 15 min was required before the flask was rapidly cooled down to room temperature. In the last stage, 5-mL toluene was added into the reaction mixture solution, which was stored in glovebox for future used.

Fig. 1 shows the absorption spectrum of the $Cu_{2-x}Se$ QDs in toluene, where the solution with a concentration of 2.83 mg/mL and a thickness of 1 cm in a quartz cuvette was measured using an Agilent UV−vis spectrometer. The feature peaked at about 550 nm corresponds to the direct-band transition in bulk copper selenide [3,10]. The High-resolution transmission electron microscopic (HRTEM) image shown in the inset of Fig. 1, which was measured using a JEOL-2000 microscope with an accelerating voltage of 200 kV. From HRTEM image, we may determine a diameter of $Cu_{2-x}Se$ QDs. Using the average value of some typical sizes of the QDs, we determine a diameter of roughly 13.5 nm. The lattice constant was measured to be about 0.32 nm, as shown in the inset of Fig. 1. The thin film of $Cu_{2-x}Se$ QDs was obtained by spin-coating the diluted colloidal solution of the QDs in toluene with a concentration of 0.5 mg/mL at 1500 rpm for 30 s onto the output coupling mirror of the laser cavity, which has a rough thickness of 500 nm.

LSPR performance of $Cu_{2-x}Se$ QDs originates from the high density of holes in the valence band, which results from the excess holes due to the copper deficiencies with x larger than zero and is located in the near infrared [10,11]. Thus, different from the collective oscillation of free electrons in metallic nanostructures, the plasmonic charge carriers are holes in the $Cu_{2-x}Se$ QDs. The red-shift of the optical extinction spectrum in the near infrared with increasing the environmental refractive index is an important

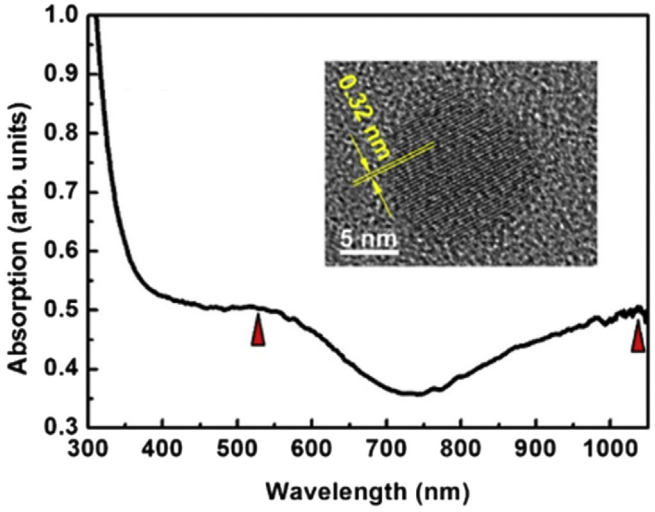

Fig. 1. Absorption spectrum of $Cu_{2-x}Se$ QDs dispersed in toluene. Inset: HRTEM image of $Cu_{2-x}Se$ QDs, showing a lattice constant of about 0.32 nm.

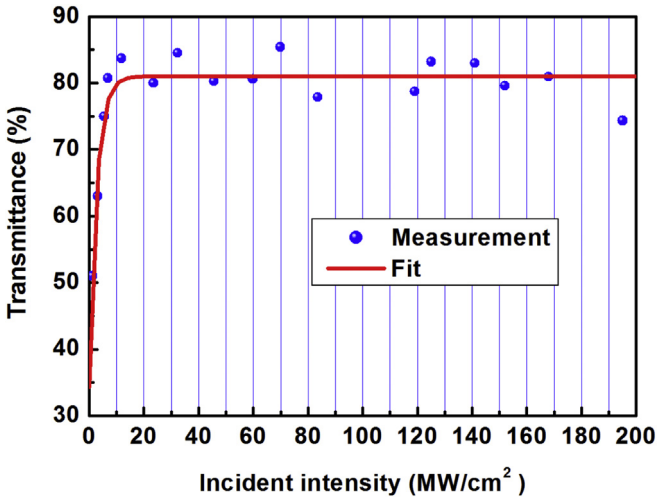

Fig. 2. Nonlinear optical absorption performance of the $Cu_{2-x}Se$ QDs in toluene with a concentration of 2.83 mg/mL.

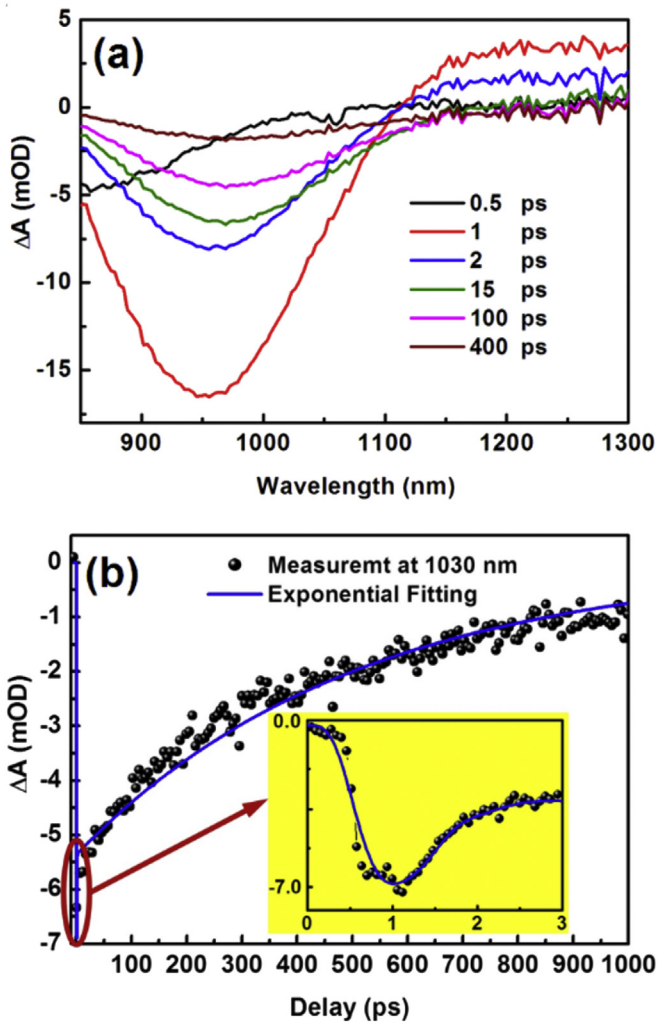

Fig. 3. (a) TA spectra at different delays. (b) TA dynamics at 1030 nm.