Superlattices and Microstructures 102 (2017) 512–516

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

Near-infrared-emitting colloidal Ag_2S quantum dots exhibiting upconversion luminescence

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ARTICLE INFO

Article history:
Received 8 November 2016
Received in revised form 27 November 2016
Accepted 27 November 2016
Available online 28 November 2016

Keywords:
Quantum dots
Upconversion
Near-infraed emission
Surface
Two photon absorption

ABSTRACT

Ag_2S quantum dots (QDs) coated with thioglycolic acid (Ag_2S QDs-TGA) have been synthesized in an organic solvent via a stepwise addition of reagents. When excited by a 980 nm laser, the near-infrared-emitting colloidal Ag_2S QDs-TGA exhibit upconversion luminescence (UCL). The observed photoluminescence (PL) was attributed to the presence of ligand-modified Ag_2S on the QD surfaces. Hence, upon dilution of the solution, the PL intensity initially increased before subsequently decreasing, accompanied by a blue shift in the PL spectra. The PL phenomena can be attributed to the increase in the amount of ligand-modified Ag_2S on the QD surfaces upon dilution, which in turn affected the fluorescence resonance energy transfer (FRET) and re-emission of the surface energy level. The relations between the emission intensity of Ag_2S QDs-TGA and the excitation power are investigated, and the results confirm that the UCL in Ag_2S QDs-TGA can be ascribed to a two-photon-assisted absorption process via a real energy state.

1. Introduction

Near-infrared (NIR) colloidal semiconductor quantum dots (QDs) have attracted considerable attention from researchers over recent decades due to their unique properties, such as tenability over a wide spectral range by varying their size and shape, wide range of excitation wavelengths, and narrow and symmetric emission peaks [1,2]. Moreover, the fluorescence they emit can penetrate deep into the body and is only slightly absorbed by living tissues. Therefore, considerable research efforts have been dedicated to NIR photoluminescence (PL) applications of QDs for bio-imaging and bio-probing [3,4].

UCL refers to luminescence in which the emission wavelength has a higher energy than the excitation wavelength. Its process was first proposed by Bloembergen [5] and demonstrated by Porter [6]. QDs that exhibit UCL offer many advantages for biological applications. According to previous reports, auto-fluorescence and background fluorescence from biological species can be diminished in UCL [7], thus making higher sensitivity and resolution possible for imaging and probing.

Studies on UCL in QDs have been increasingly reported in recent years. Mark J. Fernée discovered the UCL phenomenon in PbS QDs [8], and Wei Chen found that colloidal CdS and ZnCdS semiconductor QDs emit at around 400 nm when they are excited at 660 nm [9]. Zhang's group reported the $CuInS_2$/ZnS QDs emitting green light upon excitation with an 800 nm laser [10]; Tae Seok Seo synthesized graphene oxide QDs emitting green light excited by an 800 nm laser that have been used as an

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http://dx.doi.org/10.1016/j.spmi.2016.11.060
0749-6036/

optical biosensor [11]. However, while the UCL of QDs emitting visible light has been widely studied, the UCL of QDs with NIR emission has very rarely been reported.

2. Experiments

The typical experimental procedure was as follows (as shown in Scheme 1): Solutions of TGA (0.80 M) and $AgNO_3$ (0.04 M) were prepared separately in 10 ml of n-butanol, and the TGA solution was then added dropwise to the $AgNO_3$ solution in a 50 ml beaker. The resulting mixture was heated to 90 °C until it turned yellow. The color change indicated the formation of the Ag^+-TGA complex [12]. The temperature was then maintained until the solution developed into a dark brown color, which indicated the formation of colloidal Ag_2S QDs. Nitrogen gas bubbled through the solution to prevent the oxidation of sulfur.

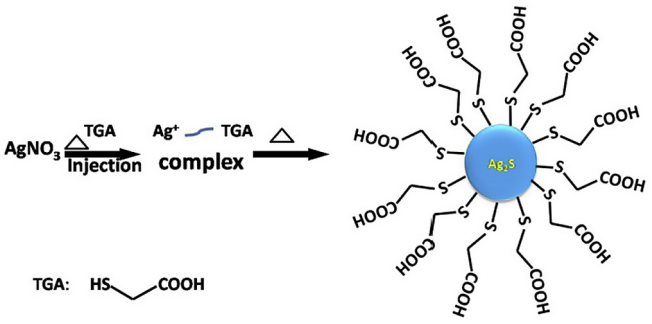
Different concentrations of Ag_2S QDs were prepared by diluting the as-prepared Ag_2S QDs with n-butanol for UCL measurements. The fluorescence spectra of the TGA-coated Ag_2S QDs were acquired using a Hitachi F-4600 fluorescence spectrophotometer equipped with a 980 nm laser. The UV–Vis absorbance spectra of the samples were measured on a UV-1100 UV–visible spectrophotometer. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL JEM-2100F TEM instrument. TEM and HRTEM samples were prepared by dip-coating a 400 mesh carbon-coated copper grid in a dilute sample solution and allowing the solvent to evaporate.

3. Results and discussion

Fig. 1a exhibits a typical transmission electron microscope (TEM) image of the Ag_2S QDs-TGA, in which the Ag_2S QDs were well dispersed on the copper grid, which indicates that the TGA completely encapsulates the QD surface. The inset in Fig. 1a shows a high resolution TEM (HR-TEM) image of Ag_2S QDs with well-developed lattice fringes, indicating good crystallinity of all the samples. Atomic planes with d-spacings of 0.231 nm are indexed to the (122) facet of monoclinic α-Ag_2S, suggesting the synthesis of Ag_2S QDs. To further characterize the composition of QDs, energy-dispersive X-ray spectroscopy (EDS) was carried out. The EDS (Fig. 1b) analysis confirmed the presence of Ag and S elements with an atomic ratio of 1.84:1 in the resultant QDs, which is close to the appropriate stoichiometry of bulk Ag_2S. The combined TEM and EDS results therefore demonstrate that the as-prepared products were indeed Ag_2S QDs.

The UV–vis absorption of the obtained Ag_2S QDs-TGA is shown in Fig. 2a. The absorption band between 500 and 600 nm (>2.0 eV) can be attributed to the band gap of the Ag_2S QDs, which was blue-shifted compared with that of bulk Ag_2S (0.9–1.1 eV) [13]. In addition, two distinct peaks located at 804 nm and 1040 nm are observed, which can be attributed to the trapped states, e.g., the surface energy level resulting from the surface sites of ligand-modified QDs, as suggested by previously reported studies [14,15]. Two new trapped states (EL1 corresponding to the peak of 804 nm; EL2 corresponding to the peak of 1040 nm) could deeply influence the luminescence properties of Ag_2S QDs-TGA.

Due to the presence of the EL2 of the Ag_2S QDs-TGA, a 980 nm laser was employed as the excitation light source. Remarkably, UCL was observed in the colloidal Ag_2S QDs-TGA (Fig. 2b). A facile dilution process was applied to further investigate the interesting UCL phenomena because dilution alters the surface structures of the QDs, which affects the optical phenomena, according to previous reports [16–18]. Fig. 2b shows the PL spectra obtained from different concentrations of colloidal Ag_2S QDs-TGA. Upon dilution of the QDs colloid, the PL intensity initially increased and then decreased, while wavelength of the signal blue-shifted, as clearly shown in Fig. 3, which shows the peak intensities and emission wavelengths from Fig. 2b as a function of the colloidal Ag_2S QDs-TGA concentration. Previous studies have reported that this blue shift can likely be attributed to many factors, e.g., surface effects and the agglomeration of QDs [19,20]. Meanwhile, many researchers have studied the impact of dilution on the surface structures of QDs, and they have proposed that dilution reduces the aggregation of QDs and increases the absorption of ligands on QD surfaces. We therefore propose a potential explanation for the discovered PL phenomena. The optical performance of the Ag_2S QDs is related to the surface energy level of the ligand-modified QDs. Thus, the degree of aggregation, which affects the amount and structure of ligand-modified Ag_2S on the QD



Scheme 1. Synthesis of Ag_2S QDs-TGA.