Journal of Luminescence 192 (2017) 675–683

Contents lists available at ScienceDirect

Journal of Luminescence

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

Colloidal PbS quantum dot-$AlPO_4$ nanoporous glass composites: Controllable emission and nonlinear absorption

Zhengyuan Bai[a,b], Jin He[c,d], Yan Wang[a,b], Kangpeng Wang[e], Rihong Li[a], Long Zhang[a,*]

[a] Key Laboratory of Materials for High Power Lasers, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
[b] University of Chinese Academy of Sciences, Beijing 100029, China
[c] Institute of Chemistry, the Hebrew University of Jerusalem, Jerusalem 9190401, Israel
[d] School of Materials, University of Manchester, Manchester M13 9PL, UK
[e] School of Physics, Trinity College Dublin, Dublin 2, Ireland

ARTICLE INFO

Keywords:
PbS
Nanoporous $AlPO_4$
Controllable near-infrared luminescence
Nonlinear absorption
Z-scan
Stability

ABSTRACT

In recent years, near-infrared (NIR) materials beyond the visible region (700–2500 nm) has emerged as a promising research field with applications toward telecommunications, photovoltaic, in-vivo imaging, etc. Such technologies will benefit greatly from the advantageous properties of NIR materials including broadband tunable emission, nonlinear optical properties, photostability, and simple chemical processing. Here, we report a facile approach to fabricate high stable and controllable luminescent NIR-emitting composites by confining PbS colloidal quantum dots (CQDs) in sol-gel nanoporous $AlPO_4$ glasses. The transmission electron microscopy images combined with X-ray photoelectron spectra in different depth of PbS-$AlPO_4$ composites (PACs) reveal the successful solidification of CQDs in nanoporous structure of glasses. The controllable luminescence of PACs is dependent on the size of PbS CQDs in solution and glass pore size. We show that the broadband (270 nm) and bimodal emission of PACs are tailored by designing different composited strategies on the incorporation of colloidal quantum dots in $AlPO_4$ nanoporous glasses. Ultrafast nonlinear optical properties of PACs were investigated using an open-aperture Z-scan technique with 515 nm 340 fs pulses. The PACs exhibited obvious reverse saturable absorption in our experiments, with a nonlinear absorption coefficient of 7.17×10^{-2} cm/GW. Furthermore, the stability of PACs is investigated by emission spectra from a few days to 180 days. The results imply PACs has a better stability than other regular PbS-solid materials such as PbS-Al_2O_3 films and close-packed PbS-filter paper systems.

1. Introduction

The rapidly growing interest on the development of near-infrared (NIR) materials is related to the increasing number of applications in this spectrum [1–3]. In optical communication, glass fiber systems rely on the low-loss propagation of infrared optical signals with the wavelength band spans 1200–1700 nm [4]. In NIR imaging application, deep-tissue imaging requires the use of infrared light within the biological window from 650 to 1350 nm which is separated from the major absorption peaks of hemoglobin and water [3]. Infrared photovoltaics are also receiving increasing attention for nearly 50% of the solar energy reaching the earth is in the form of NIR radiation [1]. The recent research in pursuit of novel NIR materials mainly focus on the nanoscale, e.g., semiconductor nanocrystals and transition-metal complexes [1,2]. However, these low-dimensional materials face severe challenges in stability and durability when they are directly exposed to ambient air, which becomes a major obstacle to application in practical devices. Hence solidification of low-dimensional materials in 3D solid matrices that possess stable and controllable NIR emitting properties are required. Traditional 3D NIR emitting solids which are rare earth-doped (Er^{3+}, Yb^{3+}, Pr^{3+}, Tm^{3+}, Nd^{3+}, etc.) glass and ceramics [5,6]. The fixed electronic energy levels of trivalent rare earth ions lead to the narrow gain bandwidth (< 100 nm) and low tunability. Although transition metal ions (Bi, Mn^{2+}, etc.) activated glasses show tunable NIR emission, their performance are usually limited by the low efficiency as a result of parity-forbidden d-d transitions [7,8]. Thus, it remains a challenge to fabricate 3D-solids NIR emitting systems with excellent tunability and stability.

Infrared colloidal-quantum-dots (CQDs) such as PbS CQDs represent a novel class of NIR materials with several promising advantages, such as facile fabrication, broadband absorption, high quantum efficiency and size-tunable emission [1,3,9,10]. Emission of these CQDs could be

* Corresponding author.
E-mail addresses: jin.he@mail.huji.ac.il (J. He), lirihong@siom.ac.cn (R. Li), lzhang@siom.ac.cn (L. Zhang).

http://dx.doi.org/10.1016/j.jlumin.2017.07.043
Received 13 March 2017; Received in revised form 24 July 2017; Accepted 25 July 2017
Available online 26 July 2017
0022-2313/

easily tuned to the telecommunication wavelength band or the biological window by controlling the nanocrystal size. Moreover, the PbS CQDs provide variant nonlinear optical responses. In NIR, PbS CQDs exhibit saturable absorption, which can be exploited as Q-switcher or passive mode-locker for NIR lasers [11]. In visible, PbS presents strong nonlinear optical extinction and can be used as optical limiting for laser protections [12]. These nonlinear responses can also be tuned by controlling the nanocrystal size. Therefore, incorporating PbS CQDs into a solid matrix may be an ideal method to achieve tunable emitting and nonlinear optical bulk in NIR range. During colloidal-to-solid processing, while the ligands on the CQDs surface usually can be easily detached, resulting in the oxidation and aggregation which lead to luminescence quenching [9]. Much work has been focused on CQDs-solids system to prevent the degradation, including those based on polymers and porous films [13–16]. However, until now, most investigations in PbS CQDs-solids system were focused on the preparation and the micro-structure.

Here, we report a high stable and controllable NIR luminescent composites by confining PbS CQDs in sol-gel nanoporous $AlPO_4$ transparent glass. The structure of $AlPO_4$ glass is based on alternating AlO_4 and PO_4 tetrahedra, the chemical activity of which benefits the interaction between the guest species and porous network, leading to a suitable host for immobilizing a variety of luminescent species [17–21]. The controlled pore size distribution of nanoporous $AlPO_4$ glass is also remarkably suitable for CQDs of particle size within a few nanometers. We design different dipping processes and adjust the pore size of glasses to choose and load size matched PbS CQDs into the nanoporous structure. The tunability, broadband and bi-emission had been demonstrated in PACs. The PbS CQDs doped solid matrices also exhibited significant reverse saturable absorption (RSA) with a nonlinear absorption coefficient of 7.17×10^{-2} cm/GW and a third-order nonlinear figure of merit of 2.632×10^{-14} esu cm. The stability of PbS CQDs in $AlPO_4$ glass were investigated and compared with related works. A brief report for part of this work has been published in a previous paper, [22] here the various details are given together with further tunable luminescence and nonlinear properties. Our work indicates that such PbS-$AlPO_4$ composites (PACs) are promising candidate in NIR photoelectronic application.

2. Experimental

2.1. Materials

Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, 98%), A-monothioglycerol (TGL, 97%), 2,3-dimercapto-1-propanol (DTG, 98%), triethylamine (TEA, 99%) and aluminum L-lactate (98%) were purchased from Sigma-Aldrich. Phosphoric acid (H_3PO_4), ammonia, isopropanol and lead acetate (PbAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as purchased.

2.2. Preparation of PbS CQDs-$AlPO_4$ glass composites

Nanoporous $AlPO_4$ glasses were fabricated via a sol-gel method [23]. Aluminum L-lactate and H_3PO_4 were used as precursors and mixed in distilled water with molar ratio of Al/P focus to 1:1. After gelling at room temperature and annealing at 600 °C, transparent and colorless $AlPO_4$ glasses were obtained. The PbS CQDs was synthesized via an aqueous route similar to Bakueva's [24]. Typically, 15 mL of solution containing 0.25 mmol of PbAc, 1.5 mmol of TGL, and 0.5 mmol of DTG was adjusted to pH 11.2 by the addition of TEA with ice bath. A 0.1 M solution of Na_2S was added to the cooled mixture quickly under vigorous stirring (1200 rpm). The color of the solution changed from transparent to dark brown in a few minutes. The molar ratio of S/Pb varied from 0.2 to 0.8. PACs were prepared by designing different dipping methods. In a typical procedure, 100 mg of $AlPO_4$ glasses were immersed in 5 mL PbS CQDs dispersions for 15 min, followed by washing with absolute ethanol for several times to remove the organic solvent and ions on the surface of glass. The post-dipping glass were dried and subsequently stored in a desiccator. After dipping by PbS CQDs, the color of $AlPO_4$ glass changed from transparent to uniformly brown.

2.3. Materials characterization

TEM images were obtained using a JEOL 2100 F microscope. Samples were prepared by dipping a TEM grid in a diluted CQDs and PACs suspension, which was prepared by grinding and dispersing PACs in absolute ethanol. XPS measurements were operated on K-Alpha (Thermo Fisher Scientific, USA) in ultrahigh vacuum (pressure $< 10^{-7}$ Pa) with spot size of 400 μm. XPS test of $AlPO_4$ glass and PACs were carried out on the middle of fracture surface of the glasses. BET (Brunauer-Emmett-Teller) surface area measurements were obtained from a Micromeritics ASAP 2010 volumetric adsorption analyzer with N_2 as an adsorbent at 77 K. Glasses were grounded into small pieces to fit the BET tube. Prior to analysis, samples weighing from 0.1 to 0.3 g were outgassed for at least 6 h under vacuum. Nanopore size distributions were obtained by the BJH (Barrett-Joyner-Halenda) method, assuming a cylindrical pore model. Absorption spectra of the PbS CQDs were measured on a PerkinElmer Lambda 750 UV–vis–NIR spectrometer. Fluorescence spectra were recorded using an FLsp920 spectrometer pumped by a semiconductor LD at 808 nm. All the spectroscopic measurements were performed at room temperature.

3. Results and discussion

3.1. PbS CQDs in $AlPO_4$ glass matrix

With large surface area (S_{BET}) as high as 508 $m^2\,g^{-1}$ and a nano-scaled pore diameter (D) about 2–10 nm, $AlPO_4$ glasses were characterized an excellent nanoporous structure for loading molecules and nano particles, and enable them to be separated in nano-scale by nanoporous network. As shown in Fig. 1(a) and (b), TEM images give the morphology of as-synthesized PbS CQDs and PACs. Highly crystalline PbS CQDs were synthesized and the size of these quasi-spherical CQDs is 3–5 nm [Fig. 1(a)]. After loaded with PbS CQDs, the color of $AlPO_4$ glass changed from transparent to uniform brown. As shown in Fig. 1(b), PbS CQDs were found embedding in the $AlPO_4$ glass matrix obviously.

To investigate the chemical components distribution and environment of PbS CQDs, $AlPO_4$ glass and PACs, the XPS spectra were employed and shown in Fig. 1(c). The pure $AlPO_4$ glass was characterized a single peak at 134.5 eV for P 2p. Whereas for both PbS CQDs and PACs, two characteristic peaks at binding energies of 137.1 and 142 eV ascribed to Pb 4f7/2 and Pb 4f5/2 core levels were displayed, and revealed the existence of Pb ions in PACs. The PbS contents were investigated by XPS spectra on the cross section of a typical piece of PACs from surface to center, which depicted in Fig. 1(c) as area a to area e (line a~e), corresponding to the detect spots from one surface region to the opposite surface region. As shown in Fig. 1(c), the signal from Pb ions were found at each area so that Pb ions fill all over the nanoporous $AlPO_4$ glass and the peak intensity of Pb 4f decreases from surface (1.2 at%) to center (0.32 at%) owning to the concentration gradient of Pb ions.

For further investigation of embedding effect, adsorption-desorption isotherms of the $AlPO_4$ glass was measured by BET analysis before and after dipping (Fig. 2). After doping with PbS CQDs, the pore volume of glass decreased from 0.67 $cm^3\,g^{-1}$ to 0.57 $cm^3\,g^{-1}$ accompanied with the decreased surface area from 403 $m^2\,g^{-1}$ to 260 $m^2\,g^{-1}$. Furthermore, as large as 15% of pore volume were decreased and supposed to filled with CQDs. The results strongly suggest that PbS CQDs were efficiently adsorbed by $AlPO_4$ glass.