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Stabilizing NIR emission of Ag_2S quantum dots in water using SnS_2 Shell

Masoud Karimipour*, Alireza Keshavarz, Mehdi Molaei

Department of Physics, Vali-e-Asr University of Rafsanjan, 77139-36417 Rafsanjan, Iran

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ABSTRACT

In this study $Ag_2S@SnS_2$ core-shells were synthesized successfully for the first time. Pulsing microwave irradiation was quite an effective technique for the controlled growth of core-shells using a one pot technique. Different parameters were optimized in the synthesis of core-shells and they were verified structurally using X-ray diffraction (XRD), Energy dispersive x-ray spectroscopy (EDX), Transmission electron microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). Ultraviolet-Visible spectroscopy (UV–Vis) revealed a strong absorption at 805 nm. Photoluminescence spectroscopy (PL) showed that the samples had a considerable emission around 870 nm and it was stable for at least 30 days in water. EDX analysis confirmed the presence of Sn, Ag and S atoms in the samples and their atomic ratio was quite close to their nominal chemical values. XRD analysis showed the formation of Ag_2S monoclinic and SnS_2 hexagonal phases. TEM images showed clearly formation of core-shells with sizes below 10 nm. FTIR spectroscopy revealed that thioglycolic acid (TGA) is an effective and stable capping agent for the synthesis of $Ag_2S@SnS_2$ core-shells using this pulsing technique.

1. Introduction

The preparation of stabilized Ag_2S quantum dots (QDs) in water has been tremendously attracting many researches due to its nontoxicity and near IR emission [1–9]. In 2015, Wu et al. prepared the near-IR emitting Ag_2S quantum dots coated with L-cysteine, by one-pot aqueous synthesis at room temperature. The effects of gold nanoparticles on the fluorescence intensity of Ag_2S were investigated and it was found that gold nanoparticles could enhance or quench the fluorescence intensity of Ag_2S QDs [1]. Kozhevnikova et al. reported the low temperature one-pot route for obtaining highly stable aqueous colloid solutions of Ag_2S QDs, using NH_3 molecules as monodentate ligands. The Ag_2S QDs possessed monoclinic (acanthite) crystalline structure with an average size about 33 nm. Nearly monodisperse Ag_2S QDs exhibited NIR emission at 1280 nm under 808 nm excitation [2]. In 2016, Ouyang et al. reported NIR fluorescent Ag_2S QDs in wheat endosperm cells. Ag_2S QDs were synthesized in an aging process under the effect of endogenous glutathione in the cells and they possessed good NIR emission properties [3]. Ovchinnikov et al. analyzed the size dependences of the absorption and luminescence spectra of ensembles of hydrophilic colloidal Ag_2S QDs produced by the sol-gel method and dispersed in gelatin. The unsteady variation in the position of the luminescence band peak and the slight size dependence of the position are interpreted as resulting from the composite character of the observed bands and from the recombination of electrons localized at emission centers with free holes (Lambe–Klick's mechanism of recombination) [4]. In 2016, Kondratenko et al. revealed amplifying and quenching of IR luminescence of colloidal Ag_2S QDs to take place when they couple to organic dye molecules of 3,3′-di-(y-sulfopropyl)-9-ethyl-4,5,4′,5′-dibenzo-thiacarbocyanine betaine and erytrosine pyridinium salts respectively. Dyes can sensitize or desensitize IR luminescence of colloidal Ag_2S QDs [5]. Moreover, Jin et al. exploited a facile aqueous synthesis of TGA-stabilized Ag_2S QDs by using thiourea as a new sulfur precursor. The quenched NIR PL of Ag_2S QDs was recovered due to the separation of aptamer/5Fu complex from QDs surface. When excited at 625 nm, the NIR PL hybrids regularly increased with the increment of CA125 aptamer [6]. In 2015, Gui et al. considered various methods used to synthesize QDs, including organic phase synthesis at high temperature, aqueous phase synthesis using small or macromolecules as ligands, polar phase synthesis, biomimetic synthesis and cation -exchange synthesis and they discussed these methods in detail [7]. Gui et al. also reported the aqueous synthesis of Ag_2S QDs by using thiol-based multidentate polymers as capping reagents and with bright and tunable PL emission from red to NIR-II region [8]. Moreover, in 2014, Rijun Gui et al. reported a facile synthesis of NIR-II Ag_2S QDs on the basis of cation exchange between visible-emitting CdS QDs and Ag+ ions in aqueous solution. The experimental results testified to the cation exchange being quick and complete and that the resultant products were single Ag_2S without CdS QDs. The prepared Ag_2S QDs showed typical NIR-II emission, high PL stability, small diameter and QY up to 2/3% [9]. All the reports are mentioning the excellent performance of Ag_2S QDs as a bio-imaging tool but the main issue is the low quantum

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* Corresponding author.
E-mail address: masoud.karimipour@gmail.com (M. Karimipour).

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efficiency of its QDs and their stability.

Two general routs have been implemented to increase the quantum efficiency of Ag_2S QDs, one is to deactivate surface traps using ligand molecules [10] and the other is to use solid state crystals such as ZnS [10], ZnO [11] and CdS as shell. The most common shell yet has been investigated is ZnS due to its inertness, wide band gap (3.6 eV) and transparent window for NIR emission [10]. Khanchandani et al. [12] have prepared Ag_2S@ZnO core-shells for efficient clean energy based devices for Cd sensors. Many reports have been also dedicated for the formation of Ag_2S@CdS core-shells [13] using different methods such as ion-exchange crystal growth [14], hydrothermal treatment, etc. [15]. But CdS is quite toxic and is not favorable for environmental and biological applications [16]. Among metal sulfide materials, tin disulfide (SnS_2) is attracting attentions due to its visible light band gap (2.3 eV), inertness, non-toxicity and its chemical stability [17]. SnS_2 has a hexagonal structure in which Sn^{+4} cations are placed between two layers of S^{-2} anions. The neighboring layers are interacting via Van der Waals forces [18]. Its band gap is within the visible range of light making it a proper candidate for opto-electronic and solar cell applications and also as a visible light photo catalyst [19]. Thus its combination with Ag_2S as Ag_2S@SnS_2 core-shell can be a promising candidate for biological, photo catalyst and also solar cell applications. Some methods have been proposed for the preparation of SnS_2 nanostructures such as hydrothermal synthesis [20], solid state reaction [21], mechanochemical reactions [22], etc. which are mostly expensive and/or time consuming that has increased the demand for a simple, rapid and cheap method [19].

In this work, we present a one pot and rapid pulsed microwave method based our recent published paper [10] for the preparation of Ag_2S@SnS_2 core-shells for the first time that to the best of our knowledge there is no similar report on the synthesis of Ag_2S@SnS_2 core-shells. The whole synthesis procedure is less than 2 h which makes this method very favorable for the preparation of high quality, stable and water soluble Ag_2S@ SnS_2 QDs. The main idea of this research is to control the growth of both core and shell at the same time in a one pot approach which slows down the release of sulfur during microwave treatment at low power. With this idea and using TGA as an efficient capping agent, one could control the growth of Ag_2S as core and its coverage using SnS_2 as shell at the same time which is the main novelty of this study.

2. Experimental

2.1. Materials

All materials were purchased from Sigma-Aldrich. Tin chloride pentahydrate $SnCl_4·5H_2O$ was used as tin sulfide precursor. $Ag(NO_3)$ and $Na_2S_2O_3·5H_2O$ were used as silver and sulfur sources, respectively. Thioglycolic acid (TGA) was used as capping agent. NH_4OH was used as reducing agent and pH stabilizer.

2.2. Synthesis of Ag_2S@SnS_2 core-shells

The synthesis procedure is somewhat similar to our previous report [10]. Firstly, we have optimized the total volume of water. 0.1 g silver nitrate was dissolved in 100, 150, 200 and 250 ml deionized water and TGA (4000, 5000 and 6000 µlit of 1 M solution) was added to this solution while stirring and subsequently NH_4OH was added to it until the solution became clear and pH was adjusted between 7.5 and 8. Thereafter certain amount of $Na_2S_2O_3$ (0.08, 0.16 and 0.32 g) which had already been dissolved in 50 ml DI-water, was added to the first solution and stirred for 5 min. The resultant solution was exposed to microwave irradiation with 360 W for 2 min to initiate the nucleation of Ag_2S core particles with a paled yellow color. The irradiated solution was stirred to be cooled down to room temperature. In second step, tin chloride (0.04, 0.067 and 0.1 g) was dissolved in 50 ml DI-water and then added to the cooled solution. Thereafter, the final solution was exposed again to microwave irradiation (MI) at 180 W up to 40 min with 2 min of pulse duration and 1 min rest time. To monitor the growth of the core-shells, aliquots were taken at different irradiation times for absorption and PL measurements and they were subtracted from the solution and re-dispersed in water for absorption and PL measurements for stability check. The solution was centrifuged and re-dispersed in water and dried at room temperature (25 °C) for different

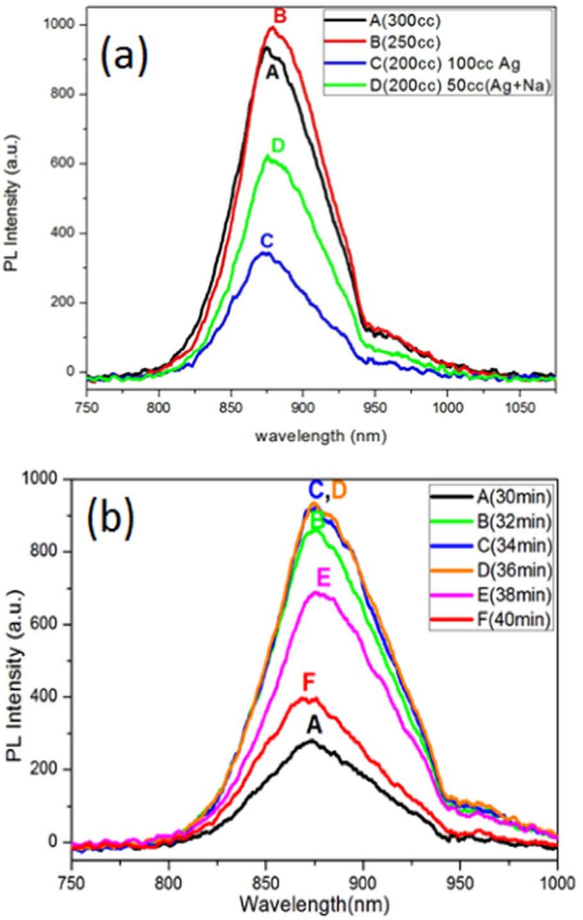

Fig. 1. PL emission of (a) the samples prepared with different total volumes of the solution: C and D have equal total volume but silver nitrate was dissolved in 100 and 150 ml DI water, respectively (b) The sample with volume 250 cc for different times of microwave exposure.

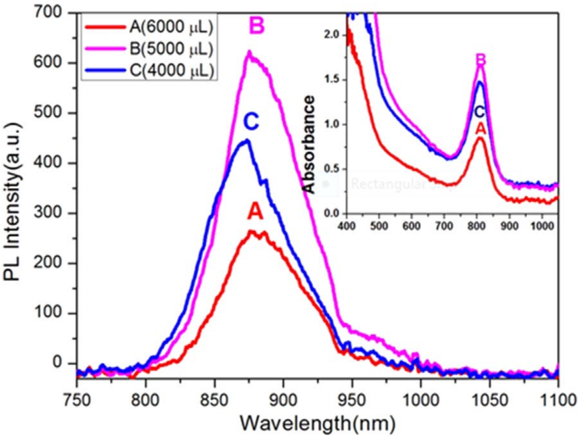

Fig. 2. Highest PL emission of samples with different TGA values (inset: Their correspondence absorption spectrum).