Biomaterials 33 (2012) 5130–5135

Contents lists available at SciVerse ScienceDirect

Biomaterials

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

Water-soluble Ag_2S quantum dots for near-infrared fluorescence imaging in vivo

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ARTICLE INFO

Article history:
Received 6 March 2012
Accepted 19 March 2012
Available online 7 April 2012

Keywords:
Fluorescence
Nanocrystals
Near-infrared
In vivo imaging
Silver sulfide

ABSTRACT

A one-step method for synthesizing water-soluble Ag_2S quantum dots terminated with carboxylic acid group has been reported. The crystal structure and surface of the prepared Ag_2S quantum dots were characterized. The prepared Ag_2S quantum dots exhibited bright photoluminescence and excellent photostabilities. The photoluminescence emissions could be tuned from visible region to near-infrared (NIR) region (from 510 nm to 1221 nm). Ultra-small sized Ag_2S nanoclusters were synthesized with high initial monomer concentration in the current system. The in vivo imaging experiments of nude mice showed that the NIR photoluminescence of the prepared Ag_2S quantum dots could penetrate the body of mice. Compared to the conventional NIR quantum dots, the Ag_2S quantum dots don't contain toxic elements to body (such as Cd and Pb), thus, the prepared Ag_2S quantum dots could serve as excellent NIR optical imaging probes and would open the opportunity to study nanodiagnostics and imaging in vivo.

1. Introduction

Colloidal semiconductor nanocrystals (quantum dots, QDs) are of great interest due to their potential applications for biomedical labeling [1,2], especially for in vivo imaging [3,4]. For the application of in vivo imaging, near-infrared (NIR) fluorescent quantum dots exhibits superior properties over the quantum dots emitting in visible region, because NIR fluorescence has large penetration depth and tissues (or cells) emit low auto-fluorescence in this region (which can cover the fluorescence signals of quantum dots) [5]. These superiorities promote the development of NIR fluorescent quantum dots. In the past decades, various Cd-containing or Pb-containing NIR fluorescent quantum dots have been developed, such as CdTe (II–VI) [6], PbS (IV–VI) [7], and type-II heterostructured quantum dots (CdTe/CdSe, CdSe/ZnTe and CdSe/CdTe) [8,9]. However, these quantum dots may be not suitable for in vivo imaging because of their intrinsic toxicity from Cd(II) or Pb(II) [4]. Thus, it is important to develop low-toxicity quantum dots (non-cadmium and non-lead) with emissions in the NIR region for in vivo imaging.

III–V quantum dots (InAs, InP) [10,11] exhibited emissions in the NIR region. However, very expensive and hazard $(TMS)_3P$ and $(TMS)_3As$ were respectively used as phosphorus precursor and arsenic precursor for synthesizing InAs and InP quantum dots. Ternary I–III–VI quantum dots (Cu–In–Se, $CuInS_2$, $AgInS_2$) [12,13] are another class of non-cadmium and non-lead NIR fluorescent nanomaterials developed in recent years. However, it is difficult to control the compositions of the resulting quantum dots due to the different activities of the cation precursor. Moreover, many of these reported non-cadmium and non-lead quantum dots were synthesized in organic phase and could not be directly used in biosystems without phase transfer.

Silver chalcogenides, I–VI semiconductors, are ideal narrow-bandgap (0.9–1.1 eV for bulk Ag_2S, 0.15 eV for Ag_2Se and 0.67 eV for Ag_2Te) [14–16] semiconductor materials for preparing low-toxicity NIR quantum dots [14,15,17,18]. Previous reported NIR fluorescent Ag_2S quantum dots [14,15] was synthesized in organic phase and none of them reported tunable emissions, which are requisite for multicolor imaging in vivo. Recently, we reported the synthesis of emission-tunable NIR Ag_2S quantum dots [17]. However, further phase transfer process that suffered from decreasing the photoluminescence (PL) quantum yield (QY) was needed for studies in biological applications. To our knowledge, there is no report on directly synthesizing water-soluble NIR fluorescent Ag_2S quantum dots.

Herein, we developed a one-step method to synthesize water-soluble Ag_2S quantum dots with tunable emissions. The Ag_2S nanocrystals were terminated with carboxylic acid group and the fluorescence emissions could be tunable from visible to NIR regions by modulating the growth time. In vivo imaging experiment of nude mice was carried out to investigate the potential applications of the as-prepared NIR Ag_2S quantum dots for biomedical labeling.

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0142-9612/$ – see front matter
doi:10.1016/j.biomaterials.2012.03.059