Journal of Alloys and Compounds 607 (2014) 39–43

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Formation and properties of selected quantum dots in maize amylopectin matrix

Karen Khachatryan [a,*], Gohar Khachatryan [a], Maciej Fiedorowicz [a], Piotr Tomasik [b]

[a] Department of Chemistry and Physics, Agricultural University, Balicka Street 122, 30 149 Krakow, Poland
[b] Krakow College of Health Promotion, Krowoderska Street 73, 31 158 Krakow, Poland

ARTICLE INFO

Article history:
Received 16 February 2014
Received in revised form 30 March 2014
Accepted 12 April 2014
Available online 20 April 2014

Keywords:
Cadmium sulfide
Calcium sulfide
Cesium sulfide
Gallium sulfide
Light emission
Zinc sulfide

ABSTRACT

CdS, ZnS, Ga_2S_3, CaS and Cs_2S quantum dots (QDs) were generated in the amylopectin (Ap) matrix. They all emitted a light between 460 (ZnS) and 475 (CdS) nm. Sizes of Ga_2S_3 and CdS QDs were 7–9 nm and 5–7 nm, respectively. Single ZnS QDs had 6–7 nm but they readily aggregated. The CaS and Cs_2S appeared mainly as 30–100 nm aggregates. There were no significant interactions between QDs and the Ap matrix. Presented method appeared unsuitable for the generation of CaS and Cs_2S QDs as they as well as their substrates [$Ca(NO_3)_2$] hydrolyzed. Calcium compounds formed complexes with Ap and alkaline solution from CsOH could produce cesium salts of Ap as well as cause oxidation of Ap.

1. Introduction

Luminescent semiconducting quantum dots (QDs), also called nanocrystals, have gained increasing attention in the past decade [1]. In comparison with organic dyes, QDs provide a high quantum yield of fluorescence, broad excitation spectrum and narrow, symmetric emission spectrum [2–4]. Moreover, QDs exhibit high photobleaching threshold and excellent photostability. When excited with UV light, they develop considerable emission of the wavelength depending on the size of the nanoparticles [5,6]. Their semiconducting properties originate from their excitons confined in all three spatial dimensions [7]. QDs enjoy a wide range of applications such as transistors, components of solar cells, light-emitting devices, diode lasers and agents for medical imaging [8–11], fluorescent labels [12–14], fluorescent probes [15–19] and immunosensors [20,21]. Success in applications of QDs in biological studies have frequently been associated with their conjugation with proteins [22–26], peptides [27], amino acids [28], and polysaccharides, for instance, chitosan [29–34], and other saccharides [35–41].

Because the optical properties of QDs depend on their size and shape, a controlled generation of QDs should be a task. Generation of QDs in solid matrices presents one of possible ways for such control. Moreover, such approach attracts attention as a path towards manufacture of materials of interesting optical and mechanical properties.

In this paper, authors present an original *in situ* synthesis of QDs in aqueous gel of amylopectin (Ap). The synthesis is simple, cheap and nondestructive for the matrix. Ap appeared a to be a good dispersion medium offering stable QDs. The hydroxyl groups of polysaccharides act as a passivation center for stabilization of the nanoparticles [42]. Foils could readily be drawn of the Ap/QDs composites. Potentially, such foils could be used as fluorescent labels and probes. QDs/Ap nanocomposites were characterized involving photoluminescence, IR and UV spectra and TEM microscopy. Thermal properties (DSC, TG) of the biocomposites were also recognized. In order to check impact of the QDs formation upon the structure of polysaccharide chains, the absolute molecular weights, M_w, and radii of gyration, R_G, of the resulting foils were taken using the size exclusion chromatography with a dual detection (SEC-MALLS-RI).

2. Experimental

2.1. Generation of quantum dots and preparation of films

Ap/ZnS, CdS, Ga_2S_3, Cs_2S, CaS nanocomposites were prepared from gelatinized maize amylopectin (Ap) and either zinc acetate (Aldrich, 99.99%), cadmium acetate (Aldrich, 99.99%), gallium(III) nitrate (Aldrich, 99.9%), cesium chloride (Sigma–Aldrich, 99.9%), calcium nitrate (Aldrich, 99.9%) and Na_2S (Aldrich, $Na_2S{\cdot}9H_2O \geqslant 99.99\%$). Amylopectin (Ap) (1 g) dissolved in deionized water

* Corresponding author. Tel.: +48 12 6624139; fax: +48 12 6624336.
E-mail address: rrchacza@cyf-kr.edu.pl (K. Khachatryan).

http://dx.doi.org/10.1016/j.jallcom.2014.04.082
0925-8388/

(19 mL) [5% (v/v)] was 30 min heated at 90 °C, treated with a given salt to prepare a 10^{-2} M solution, then a stoichiometric amount of 0.01 M aq. $Na_2S{\cdot}9H_2O$ solution was added. The resulting suspension brought to room temperature was centrifuged. The deposit was applied to a clean, smooth either Teflon or glass surface and left for evaporation in the air. The dry foils were collected and stored in closed vessels.

2.2. Transmission electron microscopy (TEM)

Analyses of the size and morphology of the as-prepared nanoparticles were studied using a high resolution JEOL 7550 equipped with a TEM detector.

2.3. Photoluminescence spectrometry

Photoluminescence measurements for films were performed at room temperature using a F7000 HITACHI spectrophotometer using excitation at 290 and 360 nm.

2.4. FTIR-ATR spectrophotometry

The FTIR-ATR spectra of the film were recorded in the range of 4000–500 cm^{-1} at resolution of 4 cm^{-1} using a MATTSON 3000 FT-IR (Madison, Wisconsin, USA) spectrophotometer. That instrument was equipped with a 30SPEC 30° reflectance adapter fitted with the MIRacle ATR accessory from PIKE Technologies Inc., Madison, Wisconsin, USA.

2.5. Thermogravimetry

Thermogravimetric analysis coupled with mass spectrometry analyses (MS-TG/DTG/SDTA) was performed with a Mettler-Toledo 851e apparatus in 150 μL corundum crucibles, closed by a lid with a hole. The experiments were run in a flow of argon and in the air (80 mL/min) within the temperature range of 30–1000 and 30–600 °C, respectively. In both cases the heating rate was 10 °C/min.

2.6. Differential scanning calorimetry

The differential scanning calorimetry (DSC) was performed in a Mettler-Toledo 821e calorimeter equipped with an Haake intracooler in 40 μL aluminum crucibles at a constant flow of argon (80 mL/min) within temperature range of 25–400 °C.

2.7. High performance size exclusion chromatography (HPSEC-MALLS-RI)

Molecular weight, M_w, and radii of gyration, R_G, of the polysaccharide chains from the nanocomposite samples were estimated with the system consisting of a pump (Shimadzu 10AC, Tokyo, Japan), an injection valve (model 7021, Rheodyne, Palo Alto, CA, USA), two connected size exclusion columns TSKgel GMPWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan) and TSKgel 2500 PWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan), a multiangle laser light scattering detector (MALLS) (Dawn-DSP-F, Wyatt Technology, Santa Barbara, CA, USA) and a differential refractive index detector (L-7490, Merck, Darmstadt, Germany).

2.8. α-Amylolysis

α-Amylase from porcine pancreas (EC.3.2.1.1,Merck, Darmstadt, Germany) was reconstituted in 20 mM phosphate buffer (pH 6.5–7.0) containing 2 mM NaCl and 0.25 mM $CaCl_2$ to obtain a stock solution with an enzyme activity of 250 units/mL. Nanocomposites were precisely weighed into Erlenmeyer flasks and suspended in the phosphate buffer (38 mL). Aliquots of the enzyme stock solution (2 mL) were added to achieve a 1 mg/mL final concentration of amylopectin and a final enzyme activity of 12.5 units/mg substrate. The Erlenmeyer flasks were incubated at 37 °C. The amount of maltose was determined by the 3,5-dinitrosalicylic acid method [43]. The extent of amylopectin amylolysis was calculated as the ratio of the amounts of hydrolyzed amylopectin and total dry substrate.

3. Results and discussion

Our recent paper [41] described generation of ZnS and CdS QDs in solution of hyaluronic acid. These 10–20 nm QDs, emitting at ~410 and 400–450 nm at the excitation with 360 (ZnS) and 290 nm (CdS) wavelength, respectively, were formed preferably at the anionic sites of the polysaccharide. That circumstance could influence the kinetics of the crystal formation and, hence, properties of the crystals. In this project, QDs were generated in the matrix of maize amylopectin (Ap) which was non-ionic polysaccharide.

Sizes of Ga_2S_3 and CdS QDs were 7–9 nm and 5–7 nm, respectively. Single ZnS QDs had 6–7 nm but they readily aggregated as show in Fig. 1. The CaS and Cs_2S appeared mainly as 30–100 nm aggregates. Compared to QDs recently prepared in the hyaluronic acid matrix [41] these prepared in the Ap matrix are slightly smaller.

Emission bands of the QDs resulting from excitation at 290 and 360 nm are shown in Fig. 2a and b, respectively.

One could see in Fig. 2a lack of any emission maximum in the Ap spectrum and emission maxima of all sulfides between 340 (Cs_2S) and 350 nm (the other sulfides). The maximum in the spectrum of Cs_2S was least intensive, and the intensity of remaining sulfides was almost identical. Among them the intensity of the maximum in the spectrum of ZnS was the highest. In the spectra of dots excited at 360 nm, the first peak around 418 nm reflected emission from Ap. The spectrum of plain matrix exhibited also a broad low emission between 450 and 475 nm with a shoulder descending around 475 nm. Emission spectra of Ga_2S_3 and Cs_2S QDs in Ap also showed this band in addition to the 418 nm band as the sole maxima in the spectrum. The intensity ratio of the band

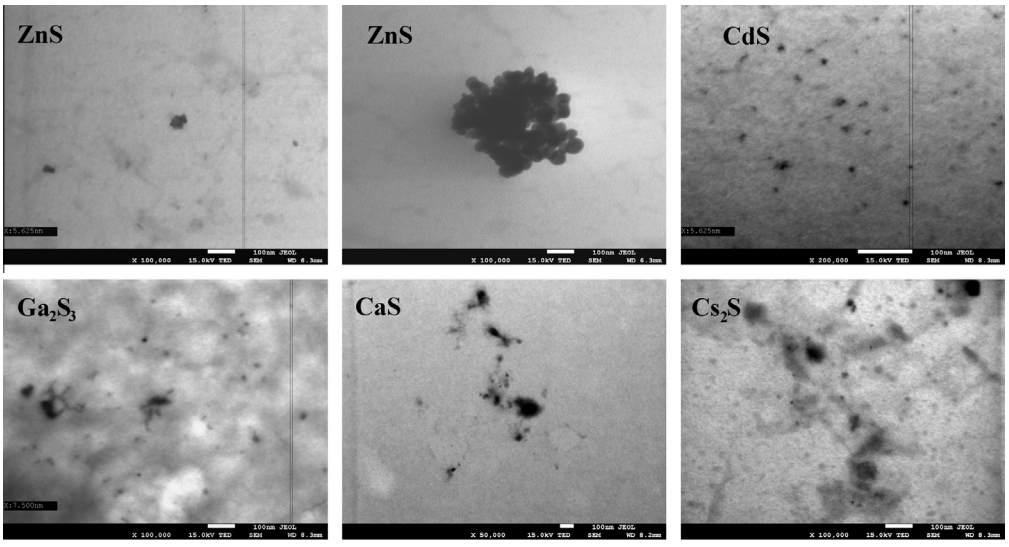

Fig. 1. Taken at 1,00,000 magnification TEM micrographs of ZnS, CdS, Ga_2S_3,CaS, and Cs_2S embedded in the Ap matrix. The central micrograph in the upper row shows magnified detail from the center of the micrograph shown in the left in the same row.