

FORMATION AND PROPERTIES OF ZnS AND CdS NANOCRYSTALS IN POTATO STARCH GEL

Karen Khachtryan, Maciej Fiedorowicz, Gohar Khachatryan and Lidia Krzeminska –Fiedorowicz

Department of Chemistry and Physics, University of Agriculture, 31-149 Cracow, Balicka 122, Poland

Introduction

Single-component quantum dots (QDs) could be identified as nanoparticles of sulfides and selenides of metals, most typically of zinc and cadmium. They develop emission when excited with a UV light. The wavelength of emission depends on the size of the nanoparticles [1,2]. Their semiconducting properties originate from their excitons confined in all three spatial dimensions [3]. QDs enjoy a wide range of applications as transistors, components of solar cells, light-emitting devices and diode lasers but also as agents for medical imaging, fluorescent labels, fluorescent probes, and immunosensors. In this paper authors present an original, simple, cheap and nondestructive for the matrix, *in situ* synthesis of ZnS and CdS QDs in aqueous gel of potato starch polysaccharides (Sp). Foils could readily be drawn of the PS/QDs composites. Potentially, such foils could be used as fluorescent labels and probes.

Experimental

Materials

Sp/ZnS and Sp/CdS nanocomposites were prepared from gelatinized potato starch (Polziem, Poznan, Poland) and either $(\text{CH}_3\text{COO})_2\text{Zn}$ (Aldrich, 99.99%) or CdSO_4 (Aldrich, 99.99+% trace metals basis) and Na_2S (Aldrich, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \geq 99.99\%$). Potato starch (1 g) dissolved in deionized then distilled water (19 ml) [5% (v/v)] was heated up to 90°C for 30 minutes, treated with the salt to prepare a 10^{-2} M solution, then a stoichiometric amount of Na_2S in an aqueous solution was added. The resulting suspension after cooling to the room temperature was centrifuged and dried. The centrifuged deposits were applied to a clean, smooth either Teflon or glass surface and left to evaporate in the air. The dry foil was collected and stored in closed vessels.

Apparatus and Procedures

The UV-VIS absorption spectra of PS, PS/Ag and PS/Au nanocomposites were recorded using a Shimadzu 2101 scanning spectrophotometer in the range 200 - 700 nm. Photoluminescence (PL) measurements for Sp/CdS and ZnS QDs films were performed at room temperature using a PerkinElmer Life Sciences LS50B spectrofluorometer (Norwalk, CT) at excitation wavelength of 290 nm and emission wavelength of 300–600 nm. Analyses of sizes and morphologies of the as-prepared nanoparticles were studied using a high resolution JEOL 7550 scanning

electron microscope equipped with EDS analyzer for local chemical analysis.

The differential scanning calorimetry (DSC) experiments were performed in Mettler-Toledo 821e calorimeter equipped with an intracooler Haake in $40\mu\text{l}$ aluminum crucibles under constant flow of argon (80 ml/min) within temperature range $25\text{--}400^\circ\text{C}$. X-ray powder diffractometry was performed according using X'pert type Phillips diffractometer with a cobalt lamp of $\lambda=1.78896 \text{ \AA}$ (30 mA and 40 kV) and in the scanning region of 2θ from 5 to 60° in 0.02° intervals. Molecular weight M_w and radii of gyration R_G of polysaccharide chains from PS and PS/Ag and PS/Au samples were measured by 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) were connected to the columns.

Results and Discussions

The UV-vis absorption spectra of potato starch and Sp/CdS and Sp/ZnS nanocomposites are presented Fig.1.

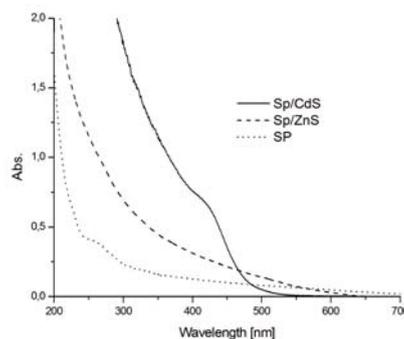


Fig1. UV- Vis absorption spectra of potato starch (Sp), silver (Sp/CdS) gold (Sp/ZnS) nanocomposites.

Formation of nanodots in starch matrix led to shift of absorption band of pure starch from to 320 nm and 450 nm in the case of Sp/ZnS and Sp/CdS nanocomposite respectively. The fluorescence spectra of the Sp/ZnS and Sp/CdS nanocomposites (Fig.2.) are different in shape. In the case of ZnS (Fig2.A) QDs

emission peak was centered around 450 nm. In the case of CdS (Fig. 2. B) two emission peaks with maximum at 450nm and 600nm were observed.

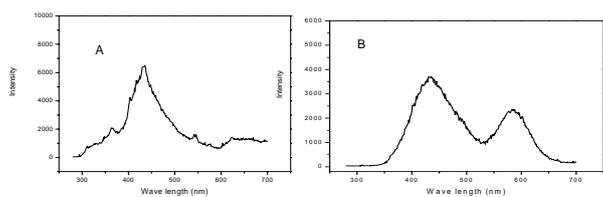


Fig.2. The fluorescence spectra of the Sp/ZnS (A) and Sp/CdS (B) nanocomposites.

Typical TEM images of CdS (A) and ZnS (B) nanoparticles embedded in the starch matrix are displayed on Fig.2. In the case of foil embedded with CdS QDs formation of channels filled with amorphous phase, containing shorter polysaccharide chains, surrounded by semicrystalline phase could be observed. It is clearly visible that Cds QDs are embedded in the amorphous phase. In the contrary, in the case of foils containing ZnS QDs such structures are not visible, and ZnS Qds are evenly distributed in the polysaccharide foil.

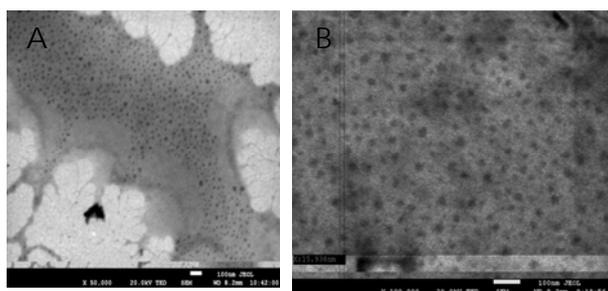


Fig.3. SEM image of potato starch foils embedded with CdS (A) and ZnS (B) quantum dots

Size exclusion chromatography showed (Table 1) a decrease in the molecular weight of potato starch polysaccharide chains after generation of QDs in its solution.. Formation of ZnS QDs was more destructive for polysaccharides from amylopectin fraction, whereas formation of CdS QDs led to significant destruction of polysaccharide chains from amylose fraction. In the effect potato starch foil embedded with CdS QDs contained more polysaccharide molecules with small molecular weight, and in the same time more big amylopectin molecules than foil embedded with ZnS QDs. Such differences in molecular weight distribution of polysaccharide chains between foils embedded with CdS and ZnS QDs could explain differences in foil morphology and distribution of QDs observed on SEM images.

Table 1. Absolute molecular weight of the original starch fractions and their changes after generation of nano Ag (Sp/Ag) and nano Au crystals inside starch gel. (R_G , radius of gyration).

| Sample | M_w Fraction I | M_w Fraction II | R_G Fraction I (nm) | R_G Fraction II (nm) |
|--------|---------------------|----------------------|--------------------------|---------------------------|
| Starch | 3.87×10^7 | 3.64×10^6 | 105.8 | 122 |
| PS/ZnS | 1.63×10^6 | 3.07×10^5 | 48.5 | 108.3 |
| PS/CdS | 2.91×10^6 | 1.70×10^5 | 44.7 | 90.8 |

Conclusions

Nanometer-sized semiconductor ZnS and CdS particles have been successfully prepared within potato starch film matrix. Because of involvement of potato starch phosphate group acting as coordination centers, this polysaccharide was proven to be efficient in preventing aggregation and controlling growth for ZnS and CdS nanocrystals.

Acknowledgment

This work was financed by grant: N R12 0015 06. The National Centre for Research and Development (NCBiR) Republic of Poland.

References

1. A.F. van Driel, G. Allan, C. Delerue, P. Lodahl, W.L. Vos, D. Vanmaekelbergh. Frequency-Dependent Spontaneous Emission Rate from CdSe and CdTe Nanocrystals: Influence of Dark States. *Phys.Rev. Lett.* 95 (2005). 236804-236808
2. L.L. Yang, J.H. Yang, X.Y. Liu, Y.J. Zhang, Y.X. Wang, H.G. Fan, D.D. Wang, J.H. Lang. Low-temperature synthesis and characterization of ZnO quantum dots *J. Alloys Compd.* 463 (2008) 92–95.
3. C.B. Murray, C.R. Kagan, M.G. Bawendi. SYNTHESIS AND CHARACTERIZATION OF MONODISPERSE NANOCRYSTALS AND CLOSE-PACKED NANOCRYSTAL ASSEMBLIES. *Annu. Rev. Mater. Sci.* 30 (2000) 545–610.