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Quantum dots as a possible oxygen sensor

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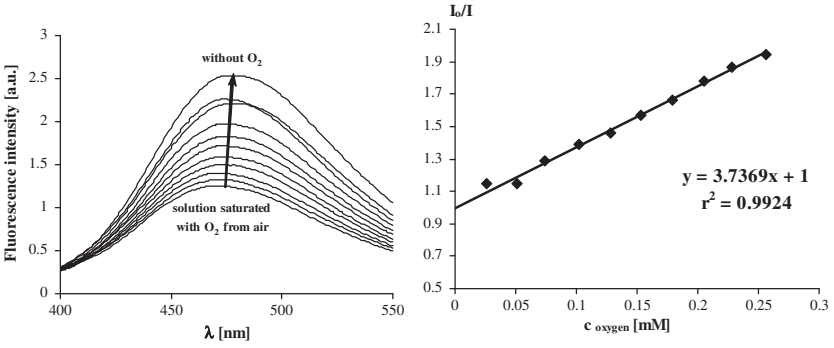
HIGHLIGHTS

- Fluorescence properties of ZnS:Cu quantum dots depend on amount of added copper.
- Fluorescence intensity of ZnS:Cu quantum dots is increasing with increasing pH.
- Elimination of oxygen increases fluorescence of quantum dots 3–4 times.
- Fluorescence of ZnS:Cu quantum dots is quenched by oxygen.
- Quenching constants varies from 2.7 to 4.6 mM^{-1} depending on copper addition and pH.

GRAPHICAL ABSTRACT



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ABSTRACT

Results of studies on optical properties of low toxicity quantum dots (QDs) obtained from copper doped zinc sulfate are discussed in the paper. The effect of copper admixture concentration and solution pH on the fluorescence emission intensity of QDs was investigated. Quenching of QDs fluorescence by oxygen was reported and removal of the oxygen from the environment by two methods was described. In the chemical method oxygen was eliminated by adding sodium sulfite, in the other method oxygen was removed from the solution using nitrogen gas. For elimination of oxygen by purging the solution with nitrogen the increase of fluorescence intensity with decreasing oxygen concentration obeyed Stern–Volmer equation indicating quenching. For the chemical method Stern–Volmer equation was not fulfilled. The fluorescence decays lifetimes were determined and the increase of mean lifetimes at the absence of oxygen support hypothesis that QDs fluorescence is quenched by oxygen.

Introduction

Development of biotechnology and biomedicine requires still new, quick, sensitive and selective analytical and diagnostic methods. Hence, optical biosensors due to their interesting properties have become a subject of studies in many research centers in the world. Particularly noteworthy are the sensors with the use of fluorescence techniques because of their very high sensitivity and selectivity. The essence of this type of sensors is an immobilization in the sensor layer fluorophores whose emission is sensitive to the presence of a determined reagent or to a change in the tested system properties [1–4]. Oxygen is a very important element involved in biological and chemical processes, so there is special group of sensors based on photoluminescence, which enable determination of its concentration [5–7]. In many reactions catalyzed by enzymes, oxygen is also one of substrates. Due to this, by determining O_2 concentration it is also possible to determine indirectly the presence and concentration of many biologically significant substrates, e.g. glucose, in the reaction of its oxidation by glucose oxidase [8,9].

For several years, there has been growing interest in quantum dots (QDs) because of their unique optical properties caused by quantum confinement [10,11]. Quantum dots are semiconductor

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nanocrystals of dimensions ranging from several do tenths of nanometres. They are composed of elements from groups II–VI or III–V. Their photoluminescence depends on their dimensions and the maximum of it is growing with the increasing radius. QDs have interesting optical properties such as broad excitation band and narrow emission band and are characterized by high Stokes shift. Additionally, good photostability of quantum dots and their resistance to metabolic degradation and photobleaching makes them applicable in bioanalysis [12–15].

The use of quantum dots and their conjugates with enzymes enables the observation of biochemical reactions on the cell level in living organisms in the time range from a second to over several days [16]. Moreover, quantum dots can find application in protein detection, DNA sequencing and in immunological tests. QDs play also an important role in testing new medicines, allowing researchers to follow the way in which their particles are transported to a relevant receptor [16,17].

The core of quantum dots is usually composed of elements belonging to groups II and VI, e.g. toxic quantum CdSe dots [12] or low-toxic ZnS ones [11]. Contrary to cadmium selenide, which due to the toxicity of cadmium cannot be applied *in vivo* determination, a promising material is just quantum ZnS dots. Interesting and relatively poorly known are optical properties of these luminophores doped with various transient metal ions such as Mn^{2+} [18,19], Cu^{2+} and Cu^{+} [20,21], Ag^{+} [22] and Co^{2+} [23]. The presence of these metals causes a modification of spectral properties of quantum dots. Hence, they have become the subject of studies in many research centers in the world. The most often used dopants are Mn^{2+} ions [14,24,25]. Martínez-Castañón et al. [24] described a simple method of synthesis and optical characteristic of ZnS, ZnS:Mn particles and their equivalents with CdS coating. The ZnS:Mn quantum dots obtained by them showed the fluorescence emission with a maximum shifted towards longer wavelengths (580 nm) in relation to pure ZnS quantum dots. The ZnS:Mn dots with CdS coating synthesized by them were characterized by an increased fluorescence emission at 580 nm as compared to quantum dots without coating. On the other hand, Khosravi et al. [25] described the maximum emission of ZnS quantum dots doped with Mn^{2+} ions at 600 nm.

Khani et al. [14] studied the effect of Fe^{3+} ions on the optical properties of ZnS quantum dots. They found that this addition caused a shift of the fluorescence emission maximum from 427 nm for pure ZnS QDs to 442 nm for doped one. Addition of Fe^{3+} was most probably responsible for the appearance of a next emission band at 532 nm.

Optical properties of quantum dots doped with copper ions are poorly known. The mechanism of their photoemission has not been fully explained. Doping of quantum dots with copper ions causes an increase of fluorescence intensity or its quenching, depending on their concentration [26]. Manzoor et al. [27] found that for ZnS quantum dots the addition of copper only caused a decrease of photoluminescence intensity, however once a co-activator in the form of halide (e.g. F^{-} ions) was added, the fluorescence emission increased. The addition of copper ions causes a shift of the emission maximum of ZnS dots towards longer wavelengths [27,28]. A separate class of studies are the experiments carried out not with solutions but with the use of dry quantum dots. There are reports on the shift of emission bands in a broad range from 466 nm [29] through 490–510 nm [30] to as much as 600 nm [31]. Zheng et al. [32] observed two emission bands for ZnS:Cu, the first one with a maximum at 450 nm and the second one at 526 nm. Similarly, Yang et al. [33] who studied the properties of ZnS quantum dots doped with copper, lead and both of them, reported two emission bands for ZnS:Cu at 450 nm and 530 nm.

The aim of presented paper is the study of factors influencing ZnS quantum dots fluorescence from the point of view of their further application in biosensors. Results of the steady-state and time-resolved fluorescence measurements for synthesized ZnS quantum dots doped with various amounts of copper are presented and discussed. Also the influence of oxygen presence in solution on QDs fluorescence was studied and is reported.

Experimental

Materials

$ZnSO_4{\cdot}7H_2O$ (⩾99.0%) was purchased from Sigma Aldrich (Germany), $CuSO_4{\cdot}5H_2O$, $Na_2S{\cdot}9H_2O$ and Na_2SO_3 were purchased from POCH S.A. (Poland), mercaptopropionic acid (MPA) (⩾99.0%) was purchased from Fluka (Germany). Distilled water was used throughout.

Synthesis of Cu-doped quantum dots

ZnS:Cu quantum dots were prepared according to [22] with slight modifications. Nanoparticles were synthesized with different $CuSO_4$ to $ZnSO_4$ volume ratios: 1:49 (**A**), 2:48 (**B**) and 3:47 (**C**). For example for Cu:Zn ratio 1:49 (sample A), 4.9 mL of 0.1 M $ZnSO_4$ solution was mixed with 0.1 mL of 0.1 M $CuSO_4$ and 0.17 mL of MPA, added with water to obtain the final volume of 50 mL and adjusted to pH 11.5. Then 5 mL of 0.1 M Na_2S was added and this mixture was heated for 30 min at 95 °C. Next, the mixture was cooled to room temperature and QDs were precipitated by adding 75 mL of ethanol. QDs were harvested by centrifugation, washed with ethanol and dried overnight at 40 °C.

The stock solution of QDs was prepared as follows: 10 mg of ZnS:Cu QDs were dissolved in 2 mL of 0.01 M phosphate buffer, pH 7. For measurements 100 μL of stock solution was added to a 10 mL flask and dissolved with buffer giving final concentration of QDs 0.05 mg/mL.

Apparatus and measurements

Absorbance spectra were recorded using a spectrophometer Nicolet Evolution 300 (Thermo Scientific, USA) in 10 mm path length quartz cells.

Steady-state fluorescence measurements were performed using a Fluoromax-4 spectrofluorometer (Jobin Yvon-Spex Instruments S.A., Edison, New Jersey, USA). The fluorescence spectra were measured with 10 mm path length closed quartz cells. The excitation and emission slits were set at 5 nm each. The increment was set at 1 nm and integration time at 0.5 s. The measurements were carried out at ambient room temperature.

Oxygen concentration in solutions expressed as % of saturation with O_2 from air was measured using a galvanic silver–zinc oxygen electrode CTN-920.S (MES-EKO, Wrocław, Poland) connected with a CO-551 oxygen meter (Elmetron, Zabrze, Poland).

Fluorescence emission decays were measured with a time-correlated single photon counting apparatus from the Edinburgh Instruments Co (UK), equipped with a pulsed NanoLED diode (Horiba JobinYvon IBH Ltd., UK) as an excitation light source. The used diode had peak wavelength 395 nm and pulse duration less than 0.01 ns. The measurements were carried out with the emission monitored at a 90° angle to the excitation. The instrument profile was obtained by replacing the sample with Ludox as a scatter. The data were collected in 1023 channels to 10,000 counts in the peak, and the time calibration was 53 ps per channel. The data were analyzed by a tail fit procedure [34] using the software package provided by the Edinburgh Instruments.