Biotechnology and Food Sciences

Review article

ZnS Cu-doped quantum dots

Paulina Ziółczyk,[*] Ewa Miller, Małgorzata Przybyt

Institute of General Food Chemistry, Lodz University of Technology
Wólczańska 171/173, 90-924 Lodz, Poland

*ziolczykp@gmail.com

***Abstract**: The paper presents a survey of literature on the structure and optical properties of ZnS and copper ion-doped ZnS quantum dots. The effect of other metal dopants on the spectral properties of ZnS:Cu quantum dots was also considered. The influence of such parameters as dopant concentration, temperature of the synthesis and compounds which form or modify the additional layer on dots on spectral properties of the quantum dots was described. Examples of application of ZnS:Cu quantum dots are also given.*

***Keywords**: quantum dots, photoluminescence, fluorophores, fluorescence, chemosensor, biosensor.*

Introduction

The continuous development of biotechnology, food production and medicine requires new methods of medical diagnostics and food analysis. Considerable attention is paid to analytical methods for fast, easy and selective determination of many chemical substances, such as hydrogen peroxide, carbon monoxide and oxygen [1], or physicochemical parameters, such as pH [2] and temperature [3].

A response to the existing demand may be optical sensors characterized by high sensitivity and selectivity [1, 4, 5]. The main component of a fluorescence optical sensor is fluorophore immobilized on a carrier whose emission varies in the presence of a determined substance or under the influence of physicochemical parameters [6]. Operation of this type of sensor is based on the detection of fluorescence changes which take place under the influence of the agent being determined [2, 7, 8]. The biosensor is formed as a result of applying in the carrier, beside the fluorophore, a biological receptor such as an enzyme, antibody or microorganism which greatly extends the range of determined substances with important biological compounds such as glucose and urea [4, 6, 9, 10]. However, organic fluorophores are often unstable in solution and can exhibit toxicity which prevents their use *in vivo*. They are characterized by a broad emission band making interpretation of results difficult [11]. These drawbacks have contributed to the search for new solutions.

Quantum dots have become an attractive alternative to organic fluorophores. Due to unique spectral properties they are in the focus of research of many centers in the world [12-14].

Structure and properties of quantum dots

The structure of quantum dots

Quantum dots are semiconductor nanocrystals with a size of 1 to 100 nm, where the quantum confinement effect occurs. Therefore, it is possible to modify their spectral properties by changing the quantum dot size or by introducing into its structure a dopant in the form of metal ion. Due to unique optical properties, quantum dots may find application as fluorophores in sensor systems in such areas as food analysis, biotechnology or biomedicine [14,15]. Quantum dots are made up of elements from groups II – VI and III – V [16]. The most commonly used quantum dots include these composed of CdSe [17], ZnSe [18] and ZnS [19].

A quantum dot consists of a semiconductor core (Figure 1A), with a diameter of 2 nm to 5 nm, responsible for the dot luminescence [19,20]. The most common core-forming compounds include CdTe [21], CdSe [22], ZnSe [23] and ZnS [19]. The luminescence of quantum dots is caused by the quantum confinement effect and defects in the crystalline structure of quantum dots [24], which is particularly important in the case of ZnS dots. However, defects on the surface can also reduce luminescence of the dots because atoms on the quantum dot surface have dangling bonds which trap electrons after absorbing a quantum of energy. Relaxation of the electron-hole system occurs in this case by non-radiative way and as a result the luminescence quantum yield of quantum dots is significantly reduced. For these reasons it is important to control the quality of a quantum dot surface [24]. For this purpose the dot core is covered with the second, semiconductor layer (Figure 1C, D). This modification leads also to strengthening of the quantum confinement effect which enables quantum dots to reach higher emission intensity or shift the maximum in the emission spectrum toward longer wavelengths. The compounds used most commonly as quantum dot coatings are semiconductors such as ZnS, ZnSe and InP, and dot size is reaching 10 nm [20].

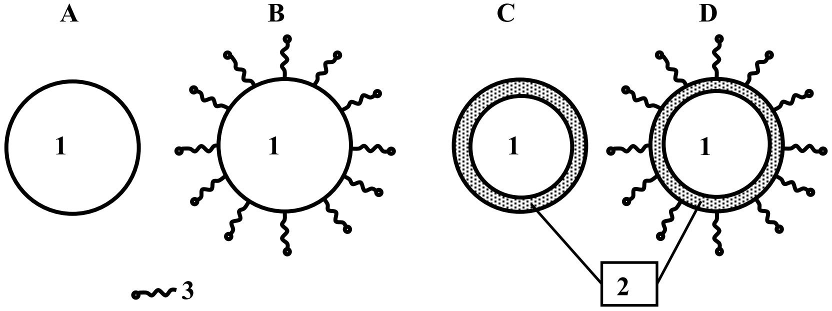

Figure 1. Scheme of quantum dot structure
1 – core, 2 – shell, 3 – organic molecule, A, B, C, D – described in text

To be used in biological systems, i.e. in aqueous media, quantum dots are covered with an additional hydrophilic organic layer (Figure 1B or 1D) whose aim is to give hydrophilic character to the dot surface in order to allow its solubilization in water [24, 25]. The coating can be composed of amino acids, e.g. cysteine, methionine or glycine [26] and compounds containing the –SH group, such as mercaptopropionic acid (MPA) [19, 25], 2-mercaptoethylamine [27] or 2-mercaptoethanol [27]. These compounds are extremely easily bonded to the surface of chalcogens, since the sulfur atom is incorporated into their crystalline structure. In addition, the organic layer which covers the quantum dot surface can also have a protective character, preventing degradation of the dots and their aggregation. Polymers used most commonly for this purpose include sodium polyphosphate [28], polyethylene oxide [29] and polystyrene [29].

Application of organic compounds with functional groups such as –COOH or $–NH_2$ on the dot surface allows for another modification of the surface of quantum dots by binding various ligands to the dot surface (Figure 1C). The ligands are typically biologically active compounds such as proteins [9, 15], antibodies [30, 31], enzymes [5] or amino acids [32]. Their selection is directly related to the use of quantum dots in a particular system. The quantum dot-bonded biological material system becomes a biochemical (nanobiosensor) or chemical nanosensor for the determination of biologically important compounds (glucose, urea) [5, 19], ions such as Na^+, K^+, Cu^{2+}, Mg^{2+} [19, 32], enzymes [15], cancer cells [15, 16] or for measuring the amount of microorganisms [30, 31]. The size of ligand-modified quantum dots can reach even 100 nm [20].

Optical properties of quantum dots

Quantum dots owe their unique properties to the quantum confinement effect which results from limitation of the movement of electrons in a quantum dot through a potential energy barrier. A quantum dot, as said, is essentially a semiconductor crystal with a size in the nanometer range. In the bulk semiconductor energy levels of atoms overlay and form, as a result, conduction band (empty) and valence band occupied by the valence electrons of atoms (Figure 2). They are separated by a bandgap (forbidden gap), where electrons cannot be present. The bandgap energy in semiconductors is relatively low (e.g. for ZnSe about 2.5 eV [33] and 3.7 eV for ZnS [19]), which allows for the passage of an electron from the valence band to the conduction band and is responsible for electrical conductivity of semiconductors. In a quantum dot, which is a nanocrystal built from a finite and small number of atoms, energy bands are again split into different energy levels, and the width of the bandgap increases compared to the bulk semiconductor. This effect is the stronger the smaller the size of the semiconductor crystal. As a result, the movement of electrons is confined to the area determined by the dot edge and quantum confinement occurs.

The optical properties of quantum dots are determined by the transfer of an electron from the valence to conduction band due to absorption of light quanta. Since the bandgap in semiconductors is relatively narrow, they absorb light in the ultraviolet and visible spectrum. As a result of electron transfer to the conduction band, an ‘empty’ place (a so-called hole) remains in the valence band. The return of the electron from the conduction to valence band is accompanied by the emission of light quantum with energy close to bandgap energy. The smaller the quantum dot, the wider the energy bandgap. Thus, in this case the size of nanoparticles directly affects the wavelength of the emitted light [19, 34]. This dependence is a big advantage of quantum dots. An additional option allowing us to ‘adjust’ the energy bandgap and thus the wavelength of the emitted light is the application of dopants in the form of metal ions in the quantum dot. The dopants form additional energy levels within the forbidden gap (Figure 2).

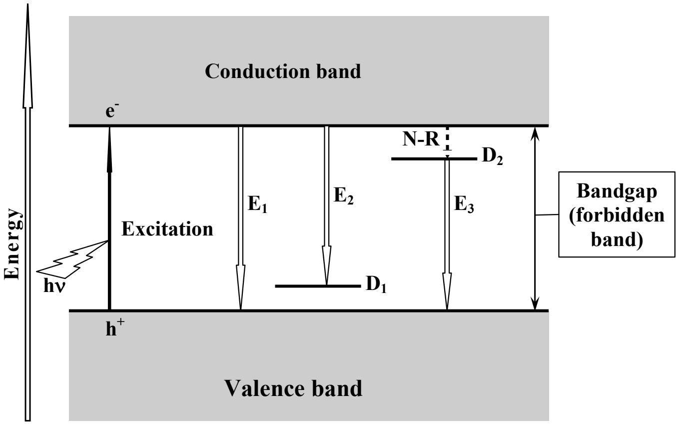

Figure 2. Schematic energy level diagram of quantum dots
D_1, D_2 – dopant levels, E_1, E_2, E_3 – emission of light, N-R – nonradiative process

Other advantages of quantum dots as fluorophores can also include high quantum yield, broad absorption band, narrow emission band with a large Stokes shift, high photostability and resistance to photobleaching [35-37].

The article addresses the synthesis and properties of zinc sulfide quantum dots doped with copper ions (ZnS:Cu) and covers researches carried out in the Chemical Biophysics Team in the Institute of General Food Chemistry.

ZnS quantum dots, synthesis and optical properties

Quantum dots used most frequently, *inter alia*, in optoelectronic devices include CdSe [22,38], CdS [33] or CdTe dots [22]. They are characterized by high quantum yield and fluorescence [39, 40]. However, these dots contain cadmium which is highly toxic to living organisms, so it is not advisable to use them in sensor systems for clinical diagnostics [15, 41]. Therefore, ZnS quantum dots with low toxicity [19] are of interest to many research centers. Zinc sulfide is one of the earliest discovered semiconductor materials and has long been used in optoelectronic devices [19]. ZnS has two possible structures: cubic and hexagonal, with the bandgap energy amounting to 3.68 eV for the regular form and 3.8 eV for the hexagonal one [42]. Depending on such factors as pH of the environment or temperature, ZnS quantum dots exhibit absorbance in the range from 250 to 375 nm, and photoluminescence with a maximum of about 360 – 545 nm [19, 43, 44]. Bindu *et al.* [42] showed that pure ZnS is characterized by a strong quantum confinement effect. They recorded two bands in the excitation spectrum at 246 nm and 375 nm and corresponding photoluminescence bands at 362 nm (λ_{exc} 245 nm) and 455 nm (λ_{exc} 362 nm) for ZnS quantum dots in dry form. The first band was broad and irregular, and the second one narrow and symmetrical.

For ZnS quantum dots coated with mercaptoethanol Li *et al.* [45] found that with the increase of dots aging time at temperature 80°C their radius grows which changes the shape of absorption spectrum and causes a shift of its maximum from 290 nm toward longer wavelengths. On the other hand, in the photoluminescence emission spectrum only an increase of intensity was observed with a maximum persisting at 423 nm. Presumably, the increase of photoluminescence intensity was caused by the increased crystallinity of dots and disappearance of defects on their surface as a result of aging. Li *et al.* [46] synthesized ZnS quantum dots coated with 3-mercaptopropionic acid (MPA), which was then partly exchanged to (3-mercaptopropyl) trimethoxysilane (MPS). This modification led to an increase of both the intensity of photoluminescence emission and the quantum yield. Senthilkumar *et al.* [47] immobilized ZnS quantum dots on a polyvinyl alcohol substrate. In the photoluminescence spectrum which they recorded there were two overlapping emission bands with peaks at 415 nm and 440 nm, which the authors explained by the presence of the sulphur and zinc ions vacancies. In general, it is observed that for pure ZnS quantum dots its size has no significant effect on the position of the photoluminescence emission peak, and defects of crystalline lattice (sulphur and zinc ions vacancies) are responsible for light emissions (Figure 3).

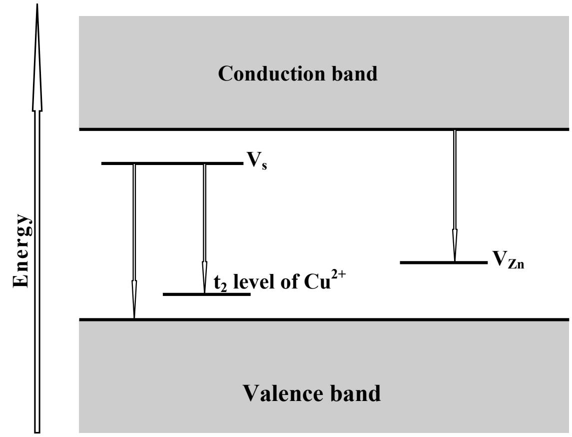

Figure 3. Schematic energy level diagram of ZnS and ZnS:Cu quantum dots according to [55]
V_s – sulphur vacancy, V_{Zn} – zinc vacancy

The addition of transition metal ions to the ZnS quantum dots often causes quenching of the photoluminescence of ZnS matrix by itself and at the same time the emission properties of dots. It was found that doping the ZnS quantum dots with metal ions, e.g. Mn^{2+} [48, 49], Co^{2+} [50], Fe^{3+} [51], Cu^{2+} [52] caused modification of their optical properties, in particular shifted the emission maximum toward longer wavelengths, and could also increase the quantum yield of photoluminescence and emission intensity. Best known are the dots doped with Mn^{2+} ions which are characterized by a very narrow emission band with maximum at about 595 nm almost independent of the dot size. In this case, the $^4T_1 \rightarrow {}^6A_1$ transition in Mn^{2+} ions is responsible for light emission and the observed photoemission has the character of phosphorescence [48, 49].

ZnS:Cu quantum dots

In the case of Cu-doped ZnS quantum dots there are still questions about their properties to which the current researches give only a partial response. The basic problems are:

- The oxidation state of copper ions in doped nanocrystal (Cu^+ or Cu^{2+}),
- The exact location of dopant levels in the forbidden gap,
- The nature of photoemission from doping centers (fluorescence or phosphorescence),
- Selective adsorption of copper ions on the surface of nanocrystals.

Synthesis of ZnS:Cu^{2+} quantum dots

There are two basic types of quantum dot synthesis: a high-temperature synthesis in organic medium and low-temperature synthesis in aqueous medium. In the case of ZnS:Cu dots the latter is mainly used and it will be discussed here in detail.

ZnS is known to be a hardly soluble salt which is formed by mixing the salts which contain Zn^{2+} and S^{2-} ions in a solution. In the case of its doping the solution must contain dopant ions, i.e. Cu^{2+}. By choosing appropriate conditions of synthesis such as reagent concentration, pH and temperature, one can obtain ZnS in the form of nanocrystals and not as a precipitate. As a zinc source water-soluble salts $Zn(CH_3COO)_2$ [28, 53-56], $ZnCl_2$ [57-60] or $ZnSO_4$ [61] are used. Copper ions are doped using $Cu(CH_3COO)_2$ [28, 53, 55, 56], $CuCl_2$ [57-59] or $CuSO_4$ [54, 61]. A source of sulfide ions is usually Na_2S [28, 54-59] and organic compounds, hydrolysing in water forming S^{2-} ions, such as thiourea [53, 64] or thioacetoamide [67, 76].

The applied conditions of synthesis such as pH, heating time and temperature of the solution, differ depending on source cited. Thus, the pH of the synthesis medium may range from 7 [53] to 11.5 [62, 63], with high pH leading to the formation of dots exhibiting high photoemission [71]. When using Na_2S the process of synthesis is usually carried out at room temperature [28], while in the case of thiourea high temperature is applied, reaching even 180°C [64] when the synthesis is performed in the autoclave. Lee *et al.* [65] examined the effect of temperature on quantum dot synthesis with the use of thiourea. In all cases the nanoparticles which they obtained have a crystalline structure and their photoluminescence intensity increases as a function of synthesis temperature from 70 to 85°C, and then decreases. In the photoluminescence emission spectrum two bands were observed: first, weak with a maximum at 420 nm from zinc sulfide, and a second, strong with a maximum at 520 nm for which copper ions are responsible. The decrease of emission intensity, when the temperature of synthesis was higher than 85ºC the authors explained by the formation of CuO which created centers of non-radiative recombination of electrons and holes.

The applied time of synthesis and aging of ZnS:Cu quantum dots varied from 30 minutes [54] to several hours [52, 59, 62, 64]. In some cases the synthesis was carried out under anaerobic conditions by purging the solutions with nitrogen [59, 62].

All these parameters of synthesis affect optical properties of quantum dots, as will be discussed in more detail below.

The effect of dopant concentration on spectral properties of Cu^{2+}-doped quantum dots

The concentration of dopant metal ions in the starting solution during synthesis is one of the most important factors affecting the optical properties of quantum dots. Jayanthi *et al.* [53] examined the effect of copper addition in the range 0.001% M-0.1% M on the emission of quantum dots in the form of dried films. In the emission spectrum three bands were distinguished, the first two with maxima at about 390-420 nm and 480 nm for which defects in the ZnS structure are responsible, and the third one at about 520 nm caused by the presence of Cu^{2+} ions. Intensity of the fluorescence emission increased at Cu^{2+} concentration from 0.001% M to 0.01% M, and then it decreased to 0.1% M. According to the authors, the reason of reduction of the fluorescence intensity in this range was the formation of copper sulfide resulting in a decrease in the amount of Cu^{2+} ions which may serve as active luminescence centers in ZnS. Peng *et al.* [55] studied ZnS:Cu quantum dots with 0.5% to 2% addition of copper (molar ratio of copper to zinc ions). In the emission spectrum of dry powders they recorded one band for which the maximum was shifting toward longer wavelengths (from about 411 nm to 500 nm) with an increasing content of copper ions, and the highest emission intensity corresponded to quantum dots containing 1% of copper ions. Peng [55], like Jayanthi *et al.* [53], attributed photoluminescence quenching in the dots which contained more than 1% of copper ions Cu^{2+} to the formation of CuS. Kole *et al.* [56] studied optical properties of ZnS:Cu quantum dots with addition of copper ions in the range from 0.25 to 1.00% in methanol solution. They found that the absorbance spectrum was the same regardless of the concentration of copper added with a maximum at 305 nm and band edge at 334 nm. This indicated that the resulting dots were characterized by a low degree of polydispersity and their sizes did not depend on the amount of copper added. Photoluminescence emission spectra of the dots can be separated into three bands with maxima at 407 nm, 460 nm and the third one at about 495-518 nm depending on the concentration of copper ions added. The first two bands appear also in the dots of pure ZnS. The last band is related to the emission during the transition of an electron from the conduction band to dopant level within the band gap formed as a result of doping with Cu^{2+} ions. It was also found that there was an optimal concentration of the dopant (in this case 0.75%) over which the photoluminescence of quantum dots decreased. Like Jayanthi *et al.* [53], the authors attributed this phenomenon to the formation of copper sulfide.

All authors agree to the fact that with an increasing concentration of copper ions in the quantum dots, the photoluminescence emission maximum shifts systematically toward longer wavelengths and the intensity of photoluminescence increases to a certain concentration limit. Too high amount of copper dopant causes a decrease of emission which is caused probably by copper sulfide formation during the synthesis. In the results obtained by various authors one may observe some differences between the shape of emission spectra, position of the recorded maxima of each band and copper ions concentration optimal for a maximum emission. This is due to differences in the methods of dots synthesis and measurement methods used to study them, in particular whether the dots were tested in a dry form or in solution [53, 55, 56].

The degree of oxidation of copper in dots – Cu^{2+} or Cu^{+} ?

The degree of oxidation of a dopant in the form of Cu^{+} or Cu^{2+} ions has an influence on the optical properties of quantum dots [62, 66-71]. In order to receive quantum dots doped with Cu^{+} ions, the reducing agent is used during synthesis and the most commonly used ones are sodium sulfite Na_2SO_3 [66, 67] and sodium borohydride $NaBH_4$ [70]. The role of a reducing agent may play also sulfide ions S^{2-}. Here, the ESR measurements can be helpful because Cu^{+} ions are paramagnetic, while Cu^{2+} are not. Labiadh *et al.* [62] basing on X-ray photoelectrons measurements and ESR found that in the quantum dots which they obtained copper was present in the form of Cu^{+} ions and sulfide ions were a reducing agent. Similar conclusions were reached by Corrado *et al.* [71].

Since Cu^{+} ions in an aqueous medium are unstable, to prevent their oxidation they may be complexed with appropriate ligands [60, 67]. In the synthesis of $ZnS:Cu^{+}$ dots Yang *et al.* [67] used stable complexes with SCN^{-} ions. On the other hand, Sun *et al.* [60] used as ligands complexing Cu^{+} ions thiourea and thiosulfate ions. Comparing the fluorescence spectra of quantum dots doped with Cu^{2+} and Cu^{+} ions, Yang *et al.* [67] observed significant differences between them which demonstrates different mechanisms of fluorescence. They proposed the following mechanism of fluorescence of Cu^{+}-doped ZnS dots. Once photons are absorbed by ZnS, electrons from the valence band, transferred to the conduction band, are trapped by defects in the crystalline lattice of the quantum dot. Then, recombination occurs between the defects and energy level t_2 introduced by Cu^{+} ions and light is emitted. Manzoor *et al.* [66] examining the effect of the amount of Cu^{+} ions on photoluminescence emission spectra, found two acceptor centers. The first is formed as a result of exchanging Zn^{2+} by Cu^{+} ion in the crystalline lattice of ZnS and is responsible for the emission with a maximum at 470 nm. The second type of centers is formed with an increasing amount of copper ions. This results in a close binding of copper ions which replace Zn^{2+} ions with Cu^{+} ions in the interstitial position. The centers exhibit a maximum emission at 500 nm. The mechanism of fluorescence emission for Cu^{2+} is explained as the transfer of an electron from the conduction band to the energy level t_2 of Cu^{2+} ion (Figure 3) [55, 56, 72].

Modifications in the structure of ZnS:Cu quantum dots

During the synthesis of ZnS:Cu quantum dots, to water solutions of inorganic salts containing Zn^{2+} [28, 53-56, 60], Cu^{2+} [28, 53-56] or Cu^{+} [60, 67] and S^{2-} ions [28, 53-55, 60] compounds are added to modify properties of the dots. Acids such as α-methacrylic [55] or mercaptopropionic (MPA) [62, 63] are used to increase solubilization of quantum dots [62, 73] and their stability in a solution [55]. For ZnS:Cu quantum dots coated with MPA Labiadh *et al.* [62] observed increased photoluminescence emission during irradiation with UV light. They attributed this effect to MPA photooxidation on the dot surface. This led to the release of sulfide ions binding with Zn^{2+} ions and forming an additional ZnS coating around the existing ZnS:Cu quantum dot. In the synthesis of ZnS:Cu quantum dots Wang *et al.* [58] used glycine as a ligand to reduce the difference in solubility of ZnS and CuS, which allowed them to incorporate a larger amount of copper into ZnS:Cu quantum dots. Sun *et al.* [60] used thiourea or sodium thiosulfate as ligands in the synthesis of ZnS nanocrystals doped with Cu^{+}. Both of these ligands were used to reduce the difference between the solubility of Cu_2S and ZnS, and also by forming complexes with Cu^{+} ions to stabilize them in the aqueous medium. The type of ligand applied had an effect on the size of quantum dots obtained. When using thiourea the dot diameter was 3.4 nm, and in the case of thiosulfate it was 3.8 nm. The photoluminescence emission spectra of the dots were similar for both applied ligands.

As film-forming compounds covering the core of quantum dots which were intended to protect the quantum dot against degradation and aggregation, also such polymers as polymethacrylic acid [54], polyvinylpyrrolidone [73] as well as inorganic compounds such as sodium polyphosphate [28] were used.

Immobilization of ZnS:Cu quantum dots

For repeated use of ZnS:Cu quantum dots or their application in optoelectronics, the dots must be immobilized. For this purpose research regarding their immobilization on various media are conducted. The dots can be simply applied as thin layers on a substrate like glass or quartz plate [53], but in this case they can be used only in dry form. Bodo et al. [61] immobilized ZnS and ZnS:Cu quantum dots in polyvinyl alcohol in the form of thin films on glass plates. On the other hand, Huang et al. [72] immobilized ZnS:Cu quantum dots in sulfonated polystyrene. Quantum dots in this case were characterized by a very narrow photoluminescence emission spectrum with a maximum at 415 nm. Thin films obtained from a polymer containing quantum dots were used as an emitter in the light-emitting diode (LED) whose electroluminescence showed a maximum at about 440 nm [72]. For the same purpose Nath et al. [59] immobilized dots in the zeolite.

ZnS:Cu quantum dots doped by other ions

ZnS:Cu, X (X-F$^-$, Br$^-$, Cl$^-$) quantum dots

Halogens are among the most popular elements used as co-dopants for ZnS:Cu quantum dots. Quantum dots doped with halogens are characterized by a higher photoluminescence intensity as compared to ZnS:Cu dots and a shift of the emission spectrum generated by zinc sulfide toward longer wavelengths [66]. Manzoor *et al.* [66] studied the effect of addition of halide anions on ZnS and ZnS:Cu dots containing Cu^+ ions. In the case of pure ZnS the addition of halide anions did not change optical properties of the dots. However, in the case of Cu^+ doped dots it caused an increase of photoluminescence intensity and a shift of the maximum toward longer wavelengths, with the best activator being the F^- ions. The authors attributed this effect to the increase Cu^+ ion solubility in the ZnS lattice under the influence of halides. By appropriate selection of the amount of added Cu^+ and F^- ions one can obtain quantum dots with maximum emission ranging from 434 to 514 nm.

Corrado *et al.* [69] described the high-temperature synthesis of ZnS:Cu quantum dots in an organic medium with the use of Br^- as a co-dopant. The ZnS:Cu dots doped with Br^- obtained in the optimized conditions showed approximately 5 times greater emission than the dots without this co-dopant. They attributed the strengthening of emission to the increase of solubility of the copper ions in the ZnS structure in the presence of Br^- ions and to the donor-acceptor transition between the electron trapped on the dopant level formed by Br atoms and the hole on the dopant level formed by the Cu atoms.

While studying the synthesis of ZnS:Cu quantum dots in the aqueous medium with the use of $CuCl_2$ as a source of copper ions, Corrado *et al.* [71] found that at the same time chloride ions were incorporated into the structure of synthesized dots. This caused an increase of photoluminescnce emission intensity as a result of formation of additional donor levels.

The authors of the above studies agreed that the mechanism of donor-acceptor transition was most probably responsible for the photoluminescence emission of quantum dots doped additionally with halogens, with a donor being the halide ions and acceptor the copper ions [66, 69, 71].

ZnS:Cu quantum dots with a metallic co-dopant

Addition of the second metal ion to ZnS:Cu dots makes it possible to change their optical properties. Begun *et al.* [70] synthesized ZnS quantum dots co-doped with Cu^{2+} and Mn^{2+} ions stabilized with chitosan. In the emission spectrum of these dots two separated bands were observed, a weak one with a maximum at 460 nm connected with a Cu dopant and the other at 592 nm related to the presence of manganese ions. Addition of a reducing agent ($NaBH_4$) resulted in a decay of the band with a maximum at 460 nm and formation of a new strong band at about 520 nm. The authors attributed this to the reduction of Cu^{2+} ions to Cu^{+}. Position of the band originating from Mn^{2+} ions as a result of the reduction was virtually unchanged, only an increase of emission was observed.

Similar results were recorded by Ummartyotin *et al.* [68] who synthesized powdered, ceramic ZnS quantum dots doped with Mn^{2+} and Cu^{+} ions. For ZnS quantum dots they observed the maximum of emission at 452 nm, for ZnS:Cu quantum dots at 517 nm, and for ZnS:Mn dots at 595 nm. For zinc sulfide quantum dots doped with copper and manganese together they obtained two emission bands: one at 457 nm, which corresponding to the shifted ZnS band, and another one at 595 nm, for which manganese ions were responsible. The band emitted by copper was not recorded for these dots. The authors presumed that due to a higher degree of oxidation, the Mn^{2+} ions replaced the Zn^{2+} ions in ZnS, easier than Cu^{+} ions. However this conversion was not complete, as evidenced by the presence of emission band at 457 nm corresponding to the emission of pure zinc sulfide.

In the case of other co-dopants their mutual interaction in a nanocrystal is observed. One of such co-dopants is lead. Lead ions exhibit higher activity than copper ions, so they react with zinc sulfide more easily than Cu^{2+} ions. In zinc sulfide quantum dots doped with Cu^{2+} and Pb^{2+} ions the so called composite luminescence centers are formed for which the energy gap is smaller than in the case of quantum dots doped only with copper ions or lead ions. The quantum yield of emission also increases, since more electron – hole pairs can be created [74, 75]. Yang *et al.* [75] synthesized crystalline ZnS:Cu:Pb nanoparticles of a size from 2 to 4 nm, with a broad emission band with the maximum ranging from 500 nm to 550 nm. The spectrum differs from the spectra of quantum dots doped only with Cu or only with Pb, which indicates that distinct composite centers are formed. By appropriate selection of the Cu:Pb ratio and concentration of these elements in the dots they reached nearly eightfold increase of the emission as compared to pure ZnS, while the separate addition of either Cu or Pb resulted in reduced emissions.

Ehlert *et al.* [74] obtained ZnS:Cu:Pb quantum dots by the high-temperature method in an organic medium. They tested the effect of an additional shell of pure ZnS on the emission properties of nanocrystals obtained in dry form. They found that the emission spectrum of ZnS:Cu:Pb nanocrystals was a combination of emission spectra derived from the same ZnS matrix and both dopants. In the case of dots of the core/shell type with the ZnS shell they observed a decay of emission component at high wavelengths (about 700 nm) associated with the presence of Pb^{2+} ions.

Another co-dopant may be Co^{2+} ions. Addition of the cobalt ions alone to ZnS usually results in reduction of the fluorescence intensity of quantum dots. Yang *et al.* [76] were the first to describe the properties of zinc sulfide nanocrystals doped with Co^{2+} and Cu^{2+} ions. Co-doped quantum dots obtained in this way exhibited strong fluorescence, much higher than that of pure ZnS with a maximum in the range from 515 nm to 560 nm with both peak position and emission increase dependent on the Cu:Pb ratio and the concentration of these elements in the ZnS matrix. The authors attributed strengthening of the emission by co-doping with Cu^{2+} and Co^{2+} ions to the formation of composite centers like in the case of co-doping with Pb^{2+} ions [75]. Similar results were obtained by this research group for co-doping with In^{3+} ions [78]. For copper and cobalt-doped quantum dots Iqubal and Iftekhar [77] observed a non-symmetric emission spectrum with a maximum at 480 nm much different from the results obtained by Yang et al. [76]. This was caused by a different synthesis method, in this case in an anhydrous medium (acetonitrile).

Applications of ZnS:Cu quantum dots

So far Cu ion-doped ZnS quantum dots have found a few applications. Most research on the synthesis of such dots and their optical properties is conducted with respect to their application in optoelectronics in the construction of light-emitting diodes (LED) [59, 72], therefore their properties are tested in the solid state, when the dots are applied in the form of powder on the medium or immobilized in the polymer [53, 61]. As is known, semiconductors of the ZnS type are used as photocatalysts. In an aqueous medium, after absorbing a quantum of light, the generated electron-hole pair initiates further reactions leading to the formation of free radicals, and as a result to the oxidation of organic compounds dissolved in water. This process can be widely used in environmental protection in water and sewage treatment. Due to high extension of surface area, nanocrystals (quantum dots) are very effective photocatalysts. The ZnS:Cu dots were used as photocatalysts in model reactions of dye oxidation in water solutions [62, 79]. The ability of quantum dots to emit visible light under the UV illumination makes it possible to use them as markers applied on various media (paper, cotton fabric) by the screen-printing method [80] in order to protect documents or form smart packages or to detect fingermarks in blood on non-porous surfaces [81]. Begum et al. [52] used ZnS:Cu dots coated with chitosan to label tissues and cells.

Although in general quantum dots are widely used as chemosensors, in the case of specific ZnS:Cu dots only a chemosensor for folic acid determination was described [82]. Quenching of quantum dot photoluminescence by this analyte made it possible to determine folic acid at the least level of 11 μM. From studies performed by our research team it follows that the photoluminescnce of ZnS:Cu dots is quenched by oxygen [83], which may suggest that they can be used in the construction of a biosensor for glucose determination with the use of glucose oxidase by measuring oxygen consumption.

Summary

From the literature on copper-doped zinc sulfide quantum dots it follows that they can have interesting properties when used as fluorophores to form chemical nanosensors or nanobiosensors. On the other hand, as results from the literature data, in the case of these particular ZnS:Cu dots there is little opportunity to change the position of emission maximum by manipulating the composition and size of the dots which can limit their potential applicability as markers in cells and tissues. Most of the above presented studies on the effect of formation conditions of quantum dots on the emission properties refer to measurements conducted for objects in the form of dry powders. A small part concerns ZnS:Cu dots solubilized in water solutions. The influence of solubilization medium parameters (e.g. pH) on the stability of dots in solutions is practically unrecognized. There are also very few results of time-resolved measurements of photoluminescence of these dots which would allow us to better recognize the mechanism of emission. The influence of oxygen on emission properties of these dots offers a prospect of using them in the construction of nanobiosensors to determine glucose with the use of glucose oxidase, or other oxidase substrates dependent on oxygen. As can be seen, in the case of ZnS:Cu dots there is still ample room for further research, which we plan to continue with our team.

References

1. Wolfbeis OS. Materials for fluorescence-based optical chemical sensors. J Mat Chem **2005**, 15:2657-2669.
2. Wencel D, Abel T, McDonagh C. Optical chemical pH sensors. Anal Chem **2014,** 86:15-29.
3. Wang X, Wolfbeis OS, Meier RJ. Luminescent probes and sensors for temperature. Chem Soc Rev **2013**, 43:7834-7869.
4. Pickup JC, Hussain F, Evans ND, Rolinski OJ, Birch DJS. Fluorescence-based glucose sensors. Biosen Bioelectron **2005,** 20:2555-2565.
5. Steiner MS, Duerkop A, Wolfbeis OS. Optical methods for sensing glucose. Chem Soc Rev **2011**, 40:4805-4839.
6. Kołwzan B. Zastosowanie czujników biologicznych (biosensorów) do oceny jakości wody. Ochr Sr **2009**, 4:3-14.
7. Urek ŠK, Francic N, Turel M, Lobnik A. Sensing heavy metals using mesoporous-based optical chemical sensors. J Nanomater **2013**, 1-13.
8. Askim JR, Mahmoudi M, Suslick KS. Optical sensor arrays for chemical sensing: the optoelectronic nose. Chem Soc Rev **2013**, 42:8649-8682.
9. Borisov SM, Wolfbeis OS. Optical Biosensors. Chem Rev **2008**, 108:423-461.
10. Terry LA, White SF, Tigwell LJ. The application of biosensors to fresh produce and the wider food industry. J Agr Food Chem **2005**, 53:1309-1316.
11. Burikov SA, Vervald AM, Vlasov II, Dolenko SA, Laptinskiy KA, Dolenko TA. Use of neural network algorithms for elaboration of fluorescent biosensors on the base of nanoparticles. P Soc Photo-Opt Ins **2013**, 22:156-165.

12. Behbahaninia M, Martirosyan NL, Georges J, Udovich JA, Kalani YMS, Feuerstein BG, Nakaji P, Spetzler RF, Preul MC. Intraoperative fluorescent imaging of intracranial tumors: A review. Clin Neurol Neurosur **2013**, 115:517-528.
13. Kim CS, Tonga GY, Solfiell D, Rotello VM. Inorganic nanosystems for therapeutic delivery: Status and prospects. Adv Drug Deliver Rev **2013**, 65:93-99.
14. Hildebrandt N, Biofunctional quantum dots: controlled conjugation for multiplexed biosensors. ACS Nano **2011**, 7:5286–5290.
15. Valizadeh A, Mikaeili H, Samiei M, Farkhani SM, Zarghami N, Kouhi M, Akbarzadeh A, Davaran S. Quantum dots: synthesis, bioapplications and toxicity. Nanoscale Res Lett **2012**, 7:1-14.
16. Azzazy HME, Mansour MMH, Kazmierczak SC. From diagnostics to therapy: Prospects of quantum dots. Clin Biochem **2007**, 40:917-927.
17. Meulenberg RW, van Buuren T, Hanif KM, Willey TM, Strouse GF, Terminello LJ. Structure and composition of Cu-doped CdSe nanocrystals using soft X-ray absorption spectroscopy. Nano Lett **2004**, 11:2277-2285.
18. Kumar P, Singh K. Ferromagnetism in Cu-doped ZnSe semiconducting quantum dots. J Nanopart Res **2011**, 13:1613-1620.
19. Fang X, Zhai T, Gautam UK, Li L, Wu L, Bando Y, Golberg D. ZnS nanostructures: from synthesis to applications. Prog Mater Sci **2011**, 56:175-287.
20. Ahmad F, Pandey AK, Herzog AB, Rose JB, Gerba CP, Hashsham SA. Environmental applications and potential health implications of quantum dots. J Nanopart Res **2012**, 14:1-24.
21. Kaniyankandy S, Rawalekar S, Verma S, Palit DK, Ghosh HN. Charge carrier dynamics in thiol capped CdTe quantum dots. Phys Chem Chem Phys **2010**, 12:4210-4216.
22. Amelia M, Lincheneau C, Silvi S, Credi A. Electrochemical properties of CdSe and CdTe quantum dots. Chem Soc Rev **2012**, 41:5728-5743.
23. Mahamuni S, Lad AD, Patole S. Photoluminescence properties of manganese-doped zinc selenide quantum dots. J Phys Chem C **2008**, 112:2271-2277.
24. de Mello Donega C. Synthesis and properties of colloidal heteronanocrystals. Chem Soc Rev **2011**, 40:1512-1546.
25. Carrillo-Carrión C, Cardenas S, Simonet BM, Valcarcel M. Quantum dots luminescence enhancement due to illumination with UV/Vis light. Chem Commun **2009**, 5214-5226.
26. Ehrlich H, Shcherba T, Zhilenko M, Lisichkin G. Peculiarities of formation and luminescence of ZnS nanoparticles modified with amino acids. Mater Lett **2011**, 65:107-109.
27. Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowski A, Eychmuller A, Weller H. Thiol-capping of CdTe nanocrystals: an alternative to organometallic synthetic routes. J Phys Chem B **2002,** 106:7177-7185.
28. Bol AA, Ferwerda J, Bergwerff JA, Meijerink A. Luminescence of nanocrystalline ZnS:Cu^{2+}. J Lumin **2002**, 99:325-334.
29. Ehrlich Kloust H, Schmidtke C, Merkl JP, Feld A, Schotten T, Fittschen UEA, Gehring M, Ostermann J, Pöselt E, Weller H. Poly(ethylene oxide) and polystyrene encapsulated quantum dots: highly fluorescent, functionalizable, and ultrastable in aqueous media. J Phys Chem C **2013**, 117:23244-23250.
30. Ku MJ, Dossin FM, Choi Y, Moraes CB, Ryu J, Song R, Freitas-Junior LH. Quantum dots: a new tool for anti-malarial drug assays. Malaria J **2011**, 10:1-5.

31. Su XL, Li Y. Quantum dot biolabeling coupled with immunomagnetic separation for detection of Escherichia coli O157:H7. Anal Chem **2011**, 76:4806-4810.
32. Koneswaran M, Narayanaswamy R. L-cysteine-capped ZnS quantum dots based fluorescence sensor for Cu^{2+} ion. Sensors Actuat B: Chem **2009,** 139:104-109.
33. Anikin KV, Melnik NN, Simakin AV, Shafeev GA, Voronov VV, Vitukhnovsky AG. Formation of ZnSe and CdS quantum dots via laser ablation in liquids. Chem Phys Lett **2002**, 366:357-360.
34. Frąckowiak D, Staśkowiak E, Łukasiewicz J. Kropki kwantowe w biotechnologii i medycynie. Postępy fizyki **2005**, 1:12-19.
35. Booth M, Brown AP, Evans SD, Critchley K. Determining the concentration of $CuInS_2$ quantum dots from the size-dependent molar extinction coefficient. Chem Mater **2012**, 24:2064-2070.
36. Dong B, Cao L, Su G, Liu W, Qu H, Jiang D. Synthesis and characterization of the water-soluble silica-coated ZnS:Mn nanoparticles as fluorescent sensor for Cu^{2+} ions. J Colloid Interf Sci **2009**, 339:78-82.
37. Jin Z, Hildebrandt N. Semiconductor quantum dots for in vitro diagnostics and cellular imagining. Trends Biotechnol **2012**, 7:394-403.
38. Chen N, He Y, Su Y, Li X, Huang Q, Wang H, Zhang X, Tai R, Fan Ch. The cytotoxicity of cadmium-based quantum dots. Biomaterials **2012**, 33:1238-1244.
39. Mandal P, Talwar SS, Major SS, Srinivasa RS. Orange-red luminescence from Cu doped CdS nanophosphor prepared using mixed Langmuir–Blodgett multilayers. J Chem Phys **2008**, 128:1-7.
40. Singh SB, Limaye MV, Date SK, Kulkarni SK. Room temperature ferromagnetism in thiol-capped CdSe and CdSe:Cu nanoparticles. Chem Phys Lett **2008**, 464:208-210.
41. Bottrill M, Green M. Some aspects of quantum dot toxicity. Chem Commun **2011**, 47:7039-7050.
42. Bindu KR, Martinez AI, Vasudevan P, Unnikrishnan NV, Anila EI. Nanostructured ZnS powders with strong confinement effects prepared by colloidal precipitation method. Physica E **2012**, 46:21-24.
43. Jothi NSN, Joshi AG, Vijay RJ, Muthuvinayagam A, Sagayaraj P. Investigation on one-pot hydrothermal synthesis, structural and optical properties of ZnS quantum dots. Mater Chem Phys **2013**, 138:186-191.
44. Zhang R, Liu Y, Sun S. Facile synthesis of water-soluble ZnS quantum dots with strong luminescent emission and biocompatibility. Appl Surf Sci **2013**, 282:960-964.
45. Li Z, Wang J, Xu X, Ye X. The evolution of optical properties during hydrothermal coarsening of ZnS nanoparticles. Mater Lett **2008**, 62:3862-3864.
46. Li H, Shih WY, Shih WH. Highly photoluminescence and stable aqueous ZnS quantum dots. Ind Eng Chem Res **2010**, 49:578-582.
47. Senthilkumar K, Kalaivani T, Kanagesan S, Balasubramanian V. Low temperature method for synthesis of ZnS quantum dots and its luminescence characterization studies. Appl Surf Sci **2013**, 264:17-20.
48. Xiao Q, Xiao C. Synthesis and photoluminescence of water-soluble Mn^{2+}-doped ZnS quantum dots. Appl Surf Sci **2008**, 254:6432-6435.
49. Sarkar R, Tiwary C, Kumbhakar P, Basu S, Mitra A. Yellow-orange light emission from Mn^{2+}- doped ZnS nanoparticles. Physica E **2008**, 40:3115-3120.
50. Liu L, Yang L, Pu Y, Xiao D, Zhu J. Optical properties of water-soluble Co^{2+}:ZnS semiconductor nanocrystals synthesized by a hydrothermal process. Mater Lett **2012**, 66:121-124.

51. Khani O, Rajabi HR, Yousefi MH, Khosravi AA, Jannesari M, Shamsipur M. Synthesis and characterizations of ultra-small ZnS and $Zn_{(1-x)}Fe_xS$ quantum dots in aqueous media and spectroscopic study of their interactions with bovine serum albumin. Spectrochim Acta A **2011**, 79:361-369.
52. Begum R, Sahoo AK, Ghosh SS, Chattopadhyay A. Recovering hidden quanta of Cu^{2+}-doped ZnS quantum dots in reductive environment. Nanoscale **2014**, 6:953-961.
53. Jayanthi K, Chawla S, Chander H, Haranath D. Structural, optical and photoluminescence properties of ZnS:Cu nanoparticle thin films as a function of dopant concentration and quantum confinement effect. Cryst Res Technol **2007**, 10:976-982.
54. Zhang H, Wang Z, Zhang L, Li Y, Yuan J. Chemical synthesis and characterization of Cu doped ZnS nano-powder. J Mater Sci Lett **2002**, 21:1031-1033.
55. Peng WQ, Cong GW, Qu SC, Wang ZG. Synthesis and photoluminescence of ZnS:Cu nanoparticles. Opt Mater **2006**, 29:313-317.
56. Kole AK, Kumbhakar P, Chatterjee U. Observation of nonlinear absorption and visible photoluminescence emission in chemically synthesized Cu^{2+} doped ZnS nanoparticles. Appl Phys Lett **2012**, 100:1-3.
57. Khosravi AA, Kundu M, Jatwa L, Deshpande SK, Bhagwat UA, Sastry M, Kulkarni SK. Green luminescence from copper doped zinc sulphide quantum particles. Appl Phys Lett **1995**, 18:2701-2704.
58. Wang M, Sun L, Fu X, Liao Ch, Yan Ch. Synthesis and optical properties of ZnS:Cu(II) nanoparticles. Solid State Commun **2000**, 115:493-496.
59. Nath SS, Chakdar D, Gope G, Kakati J, Kalita B, Talukdar A, Avasthi DK. Green luminescence of ZnS and ZnS:Cu quantum dots embedded in zeolite matrix. J Appl Phys **2009**, 105:1-4.
60. Sun L, Liu Ch, Liao Ch, Yan Ch. Optical properties of ZnS:Cu colloid prepared with sulfurous ligands. Solid State Commun **1999**, 111:483-488.
61. Bodo B, Kalita PK. Structural and optical properties of ZnS:Cu transparent nanosheets. Research Journal of Physical Sciences **2013**, 1:2-5.
62. Labiadh H, Chaabane TB, Balan L, Becheik N, Corbel S, Medjahdi G, Schneider R. Preparation of Cu-doped ZnS QDs/TiO_2 nanocomposites with high photocatalytic activity. Appl Catal B: Environ **2014**, 144:29-35.
63. Ziółczyk P, Przybyt M, Miller E. Properties of ZnS:Cu quantum dots. PhD Interdisciplinary Journal **2013**, 2:113-118.
64. Wei M, Cao J, Fu H, Yang J, Yan Y, Yang L, Wang D, Han D, Fan L, Wang B. The structure and room temperature ferromagnetism property of the $ZnS:Cu^{2+}$ nanoparticles. Mat Sci Semicon Proc **2013**, 16:928-932.
65. Lee S, Song D, Kim D, Lee J, Kim S, Park IY, Choi YD. Effects of synthesis temperature on particle size/shape and photoluminescence characteristics of ZnS:Cu nanocrystals. Mater Lett **2004**, 58:342-346.
66. Manzoor K, Vadera SR, Kumar N, Kutty TRN. Synthesis and photoluminescent properties of ZnS. Mater Chem Phys **2003**, 82:718-725.
67. Yang P, Song Ch, Lu M, Zhou GJ, Yang Z, Xu D, Yuan D. Photoluminescence of Cu^{+} - doped and Cu^{2+} - doped nanocrystalittes. J Phys Chem Solids **2002**, 63:639-643.
68. Ummartyotin S, Bunnak N, Juntaro J, Sain M, Manuspiya H. Synthesis and luminescence properties of ZnS and metal (Mn, Cu)-doped-ZnS ceramic powder. Solid State Sci **2012**, 14:299-304.

69. Corrado C, Cooper JK, Hawker M, Hensel J, Livingston G, Gul S, Vollbrecht B, Bridges F, Zhang JZ. Synthesis and characterization of organically soluble Cu-doped ZnS nanocrystals with Br co-activator. J Phys Chem C **2011**, 115:14559-14570.
70. Begum R, Chattopadhyay A. Redox-tuned three-color emission in double (Mn and Cu) doped zinc sulfide quantum dots. J Phys Chem Lett **2014**, 5:126-130.
71. Corrado C, Jiang Y, Oba F, Kozina M, Bridges F, Zhang JZ. Synthesis, structural, and optical properties of stable ZnS:Cu,Cl nanocrystals. J Phys Chem A **2009**, 113:3830-3839.
72. Huang J, Yang Y, Xue S, Yang B, Liu S, Shen J. Photoluminescence and electroluminescence of ZnS:Cu nanocrystals in polymeric networks. Appl Phys Lett **1997**, 18:2334-2337.
73. Hou S, Zhang X, Mao H, Wang J, Zhu Z, Jing W. Photoluminescence and XPS investigation of Cu^{2+}- doped ZnS quantum dots capped with polyvinylpyrrolidone. Phys Status Solidi B **2009**, 10:2333-2336.
74. Ehlert O, Osvet A, Batentschu M, Winnacker A, Nann T. Synthesis and spectroscopic investigations of Cu- and Pb-doped colloidal ZnS nanocrystals. J Phys Chem B **2006**, 110:23175-23178.
75. Yang P, Lu M, Xu D, Yuan D, Zhou G. Photoluminescence properies of ZnS nanoparticles co-doped with Pb^{2+} and Cu^{2+}. Chem Phys Lett **2001**, 336:76-80.
76. Yang P, Lu M, Zhou G, Yuan D, Xu D. Photoluminescence characteristics of ZnS nanocrystalittes co-doped with Co^{2+} and Cu^{2+}. Inorg Chem Commun **2001**, 4:734-737.
77. Iqbal MJ, Iftekhar M. Effect on photophysical properies of colloidal ZnS quantum dots by doping with cobalt, copper, and cobalt-copper. J Nanopart Res **2011**, 2139-2145.
78. Yang P, Lu M, Song Ch, Xu D, Yuan D, Cheng X, Zhou G. Luminescence of Cu^{2+} and In^{3+} co-activated ZnS nanoparticles. Opt Mater **2002**, 20:141-145.
79. Pouretedal HR, Norozi A, Keshvarz MH, Semnani A. Nanoparticles of zinc sulfide doped with manganese, nickel and copper as photocatalyst in the degradation of organic dyes. J Hazard Mater **2009**, 162:674-681.
80. Small AC, Johnston JH, Clark N. Inkjet printing of water “soluble” doped ZnS quantum dots. Eur J Inorg Chem **2010**, 242-247.
81. Moret S, Bécue A, Champod C. Cadmium-free quantum dots in aqueous solution: potential for fingermark detection, synthesis and an application to the detection of fingermarks in blood on non-porous surfaces. Forensic Sci Int **2013**, 224:101-110.
82. Geszke-Moritz M, Clavier G, Lulek J, Schneider R. Copper- or manganese-doped ZnS quantum dots as fluorescent probes for detecting folic acid in aqueous media. J Lumin **2012**, 132:987-991.
83. Ziółczyk P, Kur-Kowalska K, Przybyt M, Miller E. Quantum dots as a possible oxygen sensor. Spectrochim Acta A **2014**, 126:28-35.