

THE WET-CHEMICAL SYNTHESIS OF FUNCTIONALIZED $Zn_{1-x}OMn_x$ QUANTUM DOTS UTILIZABLE IN OPTICAL BIOSENSORS

MOKRA KEMIJSKA SINTEZA FUNKCIONALIZIRANIH KVANTNIH DELCEV $Zn_{1-x}OMn_x$, UPORABNIH V OPTIČNIH BIOSENZORJIH

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ZnO quantum dots (QDs) were successfully synthesized via the precipitation technique, and the effect of the Mn^{2+} ion concentration as dopant on the optical properties was studied. In order to control the particle size by limiting the growth of the particles after the nucleation and to provide a side group on the surface, which can be further conjugated to bio-cells, polyethylene glycol (PEG) was used as a bio-compatible capping agent. XRD analyses revealed a single-phase ZnO wurtzite crystal structure. A TEM micrograph illustrates that the final QDs were about 15 nm in diameter and had a spherical shape. Also, the organic groups on the surface of nano-particles (NPs) were characterized with Fourier transform infrared spectroscopy (FTIR). It is clear from the photo-luminescence spectra that doping Mn^{2+} ions in the host lattice led to an appearance of a new visible emission band in the range of 410–450 nm because of the ${}^4T_1 \rightarrow {}^6A_1$ transition. The results show that the final QDs have a potential for biochemical optical sensing.

Keywords: quantum dots, surface modification, biosensor, photoluminescence

Kvantni delci (QD) ZnO so bili uspešno sintetizirani s tehniko izločanja in preučevan je bil učinek koncentracije ionov Mn^{2+} kot dopantov na optične lastnosti. Polietilen glikol (PEG) kot omejitveno sredstvo je bil uporabljen za kontrolo velikosti delcev z omejevanjem rasti delcev po nukleaciji in za zagotovitev posebne skupine na površini, ki jo je mogoče naprej združevati z biocelicami. XRD-analize so odkrile enofazni ZnO s kristalno strukturo wurtzita. Posnetek s TEM pokaže, da so končni QDs okrogle oblike s premerom okrog 15 nm. Organske skupine na površini nanodelcev (NPs) so bile določene s FTIR-spektroskopijo. Iz fotoluminiscenčnega spektra izhaja, da dopiranje ionov Mn^{2+} v gostujočo mrežo povzroči prehod ${}^4T_1 \rightarrow {}^6A_1$ in zato pojav novega vidnega emisijskega pasu v območju 410–450 nm. Rezultati kažejo, da imajo končni QDs potencial biokemičnega optičnega zaznavanja.

Ključne besede: kvantni delci, modifikacija površine, biosensor, fotoluminiscenca

1 INTRODUCTION

The synthesis of semiconductor quantum dots (QDs) has received a great deal of interest because of their potential for biomedical applications in imaging, drug targeting and delivery. Compared with the conventional organic fluorophores, QDs have significant advantages, for example, a narrow and size-tunable emission spectrum, broadband excitation, a high resistance against photo-bleaching and a good chemical stability^{1,2}. Due to their size-dependent properties and dimensional similarities to biomolecules, these bio-conjugate QDs are well suited as contrast agents for the in-vivo magnetic resonance imaging (MRI) as carriers for drug delivery, and as structural scaffolds for tissue engineering³. ZnO nano-particles are environment friendly and have a wide band-gap of 3.37 eV and a rather large exciton binding energy, which makes the exciton state stable even at room temperature. Therefore, wide band-gap semiconductor nanocrystals can be doped with transition metal

ions^{4,5}. An important section of synthesising NPs is surface modification. Most surface modifications of NPs for bio-imaging applications are based on chemisorption since it offers a stronger and more robust bond and a more stable surface ligand, compared with physisorption. A successful conjugation of biomolecules to NPs depends on a proper surface modification. Poly ethylene glycol (PEG) has been commonly conjugated to various drugs, liposomes, polymeric micelles and nanoparticles to prolong their blood-circulation time by reducing the nonspecific adsorption of proteins via a steric stabilization effect^{6,7}. In this paper, we report on a wet chemical synthesis of $Zn_{1-x}OMn_x$ QDs and functionalizing them with PEG to achieve the appropriate particle size and good optical properties used in biological labelling. The main advantages of this process are the ability to control the ZnO purity and the use of biocompatible capping agents that provide triple functions: (1) to control the particle size by limiting the growth of the particles after the nucleation, (2) to provide a side group on a surface

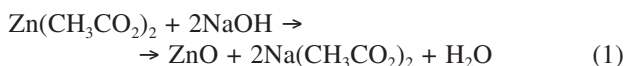
that can be further conjugated to a bio-cell, (3) to eliminate surface defects that would affect the optical properties of ZnO nanocrystals.

2 EXPERIMENTAL WORK

Manganese acetate tetrahydrate (Mn(Ac)₂·4H₂O), zinc acetate dihydrate (Zn(Ac)₂·2.5H₂O), polyethylene glycol (*M_w* = 400 g/mol), extra pure water, ethanol and hydroxide sodium were used as the starting materials. We have developed a room-temperature technique for synthesising semiconductor nanocrystals that employs a capping agent to control both the size and the shape. The manganese precursor (Mn(OAc)₂·4H₂O) dissolved in 1 ml of water and then 100 ml of ethanol was added to the solution. After stirring the solution for 2 h, Zn(OAc)₂·2.5H₂O was added; then the temperature raised to 50 °C and the solution was stirred again. After that the obtained solution was quenched in ice, and the required PEG was added as a capping agent. The mixture was again stirred for 3 h and then hydrolyzed by adding NaOH under ultrasound for 2 h. The solvents were then removed with the rotation vaporization. Eventually, the resulting mixture was washed with water leading to a precipitation of Zn_{1-x}Mn_xO nanocrystals. The resulting powders were analyzed with X-ray diffraction (XRD; Bruker AXS: D8 Advance), transmission electron microscopy (TEM; a Hitachi H-800 electron microscope) and fluorescence spectrophotometer (Perkin-Elmer LS-55, the exciting source: a near-ultraviolet-Xenon lamp) and Fourier transform infrared spectroscopy (Equinox-55).

3 RESULTS AND DISCUSSION

ZnO colloids were prepared with the precipitation from the solution using Zn(CH₃CO₂)₂ and NaOH. The overall reaction of the synthesis of ZnO nanoparticles from Zn(II) acetate can be written as:



The XRD pattern of the ZnO nanocrystals synthesized via precipitation is shown in **Figure 1**. The main

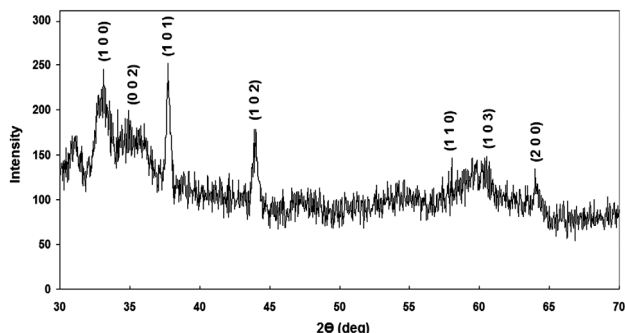


Figure 1: XRD pattern of ZnO prepared with precipitation

Slika 1: Rentgenski praškovni posnetek ZnO, pridobljen z izločanjem

phase can be indexed to the pure phase of zinc oxide according to JCPDS 80-0075. Also, the wurtzite structure of the ZnO lattice of a nanocrystalline sample can be confirmed.

From the FTIR spectrum presented in **Figure 2a**, it is obvious that PEG properly caps the surface of the QDs. The main peaks can be related to different groups as follows: 1) the peaks around 3670 cm⁻¹ and 3407 cm⁻¹ are due to the O-H stretching; 2) the peaks around (2974, 2916 and 1241) cm⁻¹ are attributed to the C-H stretching from the -CH₃ alkanes, the C-H stretching from the -CH₂- alkanes and the R-O-R stretching (the conjugate ether), respectively. In addition, the TEM image of the ZnO:Mn QDs capped with PEG is illustrated in **Figure 2b**. It is clearly observed that nanoparticles are spherical in shape and their average size is approximately 10 nm.

The PL spectrum of the Mn-doped ZnO d-dots with different doping concentrations (from mol fraction 0–7 %) are shown in **Figure 3(a–d)**. It is worth mentioning that by varying the Mn doping concentration, the relative PL intensities of the dual-colour emissions can be well manipulated. The UV emission (356 nm) is characteristics of the ZnO host and usually influenced by the

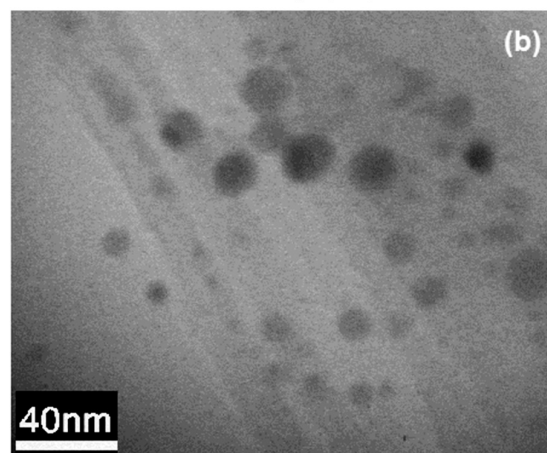
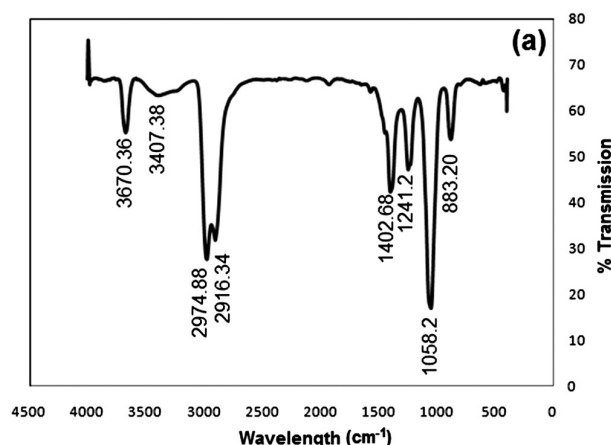


Figure 2: a) FTIR spectra of the PEG-capped ZnO nanoparticles and b) a TEM image of 5 % Mn-doped ZnO nano-particles

Slika 2: a) FTIR-spekter s PEG omejevanih ZnO-nanodelcev in b) TEM-posnetek s 5 % Mn dopiranih ZnO-nanodelcev

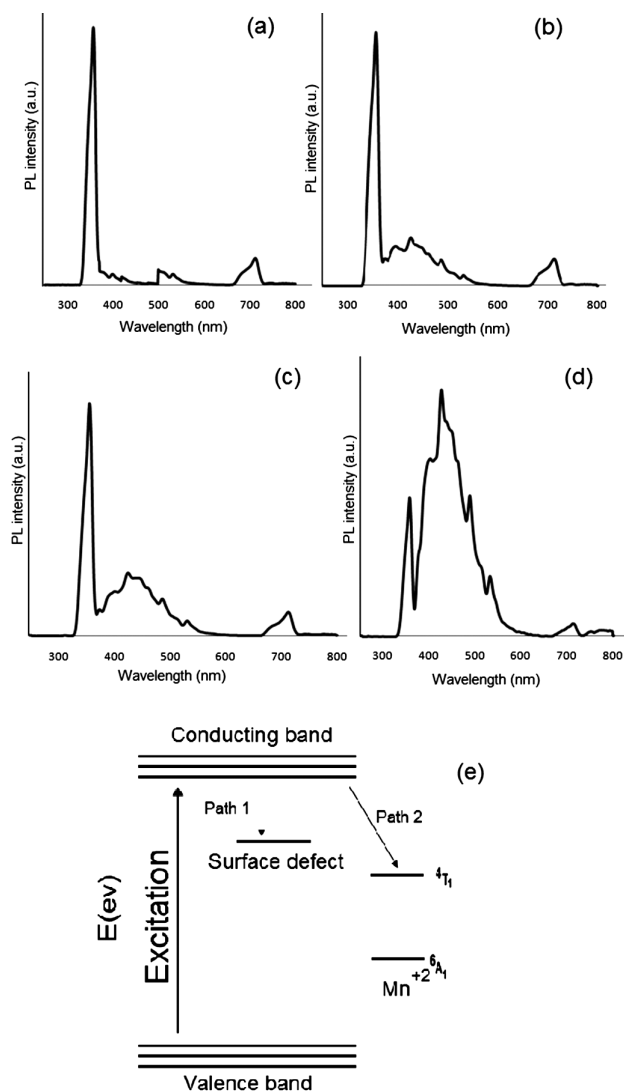


Figure 3: PL emission spectra of the $Zn_{1-x}OM_n_x$ QDs with different doping concentrations: a) $x = 0\%$, b) $x = 2\%$, c) $x = 5\%$, d) $x = 7\%$ excited at 325 nm and e) a schematic representation of the emission levels of the Mn-doped ZnO d-dots

Slika 3: Spekter PL-emisij $Zn_{1-x}OM_n_x$ QD z različnimi koncentracijami dopiranja: a) $x = 0\%$, b) $x = 2\%$, c) $x = 5\%$, d) $x = 7\%$ vzbujenih pri 325 nm in e) shematičen prikaz nivojev emisij z Mn dopiranega ZnO d-delcev

doping situation. Also, the blue emission band, centred at about 426 nm, is attributed to the transition between the ${}^4T_1 \rightarrow {}^6A_1$ energy levels of the Mn^{2+} 3d states. A schematic representation of the emission levels of the Mn-doped ZnO d-dots is briefly illustrated in **Figure 3e**. When an intrinsic q-dot is excited by the photons with the energy higher than its band gap, an exciton (an

electron-hole pair) will be generated. A direct recombination of an electron-hole pair, typically being quantum-confined in the case of nanocrystals, gives the well-known band-edge emission, or exciton emission. However, the emission of a d-dot is fundamentally different. After the exciton is generated by the absorption of the host semiconductor nanocrystal, the energy of a photogenerated electron and a hole pair will be transferred into the electronic levels of the Mn^{2+} ions. The recombination in a Mn^{2+} ion center leads to the characteristic dopant emission from the Mn^{2+} ion, namely the 4T_1 to 6A_1 transition.

4 CONCLUSION

In this research, ZnO:Mn QDs have been successfully synthesized with a precipitation synthesis and then the surface of nanoparticles was covered with hydroxyl groups. In the meantime, the effect of the dopant concentration on the optical characteristics was investigated in detail. According to experimental results, the functionalized QDs can be used as a core of optical biosensors after conjugating with the desired anti-bodies.

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