

SUB MICROMETER AND NANO ZnO AS FILLER IN PMMA MATERIALS

SUBMIKROMETRSKI IN NANO ZnO KOT POLNILO V PMMA-MATERIALIH

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A review of synthetic approaches towards zinc(II) oxide – ZnO of various particle sizes, shapes, morphology and surface modifications is given as well as a review of preparation procedures for ZnO/poly(methyl methacrylate) – ZnO/PMMA nanocomposites. ZnO nanostructures were prepared from various precursors, media and catalysts and homogeneous nanocomposites were prepared by various preparation procedures using ZnO, modified by various surface active agents and also unmodified ZnO. In our lab, ZnO nano and sub micrometer particles with organophilic surface were prepared in various diols. Homogeneous ZnO/PMMA nanocomposites were formed by the radical chain polymerization of methyl methacrylate – MMA in bulk by optimizing the preparation method. Resulting nanocomposite materials showed high UV absorption and high transparency for visible light as well as enhanced thermal stability. Such materials have high potential as UV stabilized PMMA materials for various outdoor applications with high sun light loads.

Key words: nano ZnO, ZnO quantum dots, PMMA, nanocomposites, NMR spectroscopy, STEM microscopy, TGA analysis, photoluminescence spectroscopy

Podan je pregled sintetskih načinov za pripravo cinkovega(II) oksida – ZnO z različnimi velikostmi delcev, oblikami, morfologijo in s površinsko modifikacijo in tudi pregled postopkov priprave nanokompozitov ZnO/poli(metil metakrilat) – ZnO/PMMA. Nanostrukture ZnO so sintetizirali iz različnih prekurzorjev, medijev in z uporabo različnih katalizatorjev. Istočasno so potekale intenzivne aktivnosti pri pripravi ZnO/PMMA nanokompozitov. Homogene nanokompozite tega tipa so pripravili po različnih postopkih z uporabo ZnO, modificiranega z različnimi površinsko aktivnimi sredstvi in tudi z uporabo nemodificiranega ZnO. V našem laboratoriju smo sintetizirali ZnO nano- in submikrometrške delce z organofilno površino v različnih diolih in pripravili homogene nanokompozite ZnO/PMMA z radikalsko verižno polimerizacijo MMA v masi. Pripravljeni nanokompoziti absorbirajo UV-svetlobo in prepuščajo vidno ter imajo izboljšano termično stabilnost. Takšni materiali so potencialno uporabni kot UV stabilizirani PMMA-materiali za zunanjo uporabo pri veliki izpostavljenosti sončni svetlobi.

Ključne besede: nano ZnO, ZnO kvantne točke, PMMA, nanokompoziti, NMR-spektroskopija, STEM-mikroskopija, TGA-analiza, fotoluminiscenčna spektroskopija

1 INTRODUCTION

Nano and micro structured materials are one of the fastest growing fields in modern materials science, especially the preparation of semiconductor materials. Zinc oxide is very promising semiconductor due to unique properties in near-UV region, electric conductivity and optical transparency and has drawn a considerable attention of scientists in last few years.¹ ZnO has large direct band gap and high exciton binding energy and it shows potential applications in catalysis, optoelectronic devices, sensors, and photovoltaic. ZnO can be synthesized in various shapes and particle sizes²⁻⁶ and also by various synthetic approaches.⁷ ZnO is also an environmentally friendly material, at least in the micrometer particle size range. Because of all this, it has attracted high attention in various fields of science.

2 SUBMICROMETER AND NANO ZnO

The solution phase approach to the preparation of nano-to-sub micrometer ZnO particles presents the low

cost preparation method and recently attracted a lot of interest due to the low temperature particle growth temperature (85–95 °C). It is much more favorable for large-scale synthesis, especially nowadays, since the consumption of energy is very low. ZnO nanoparticles with controllable morphology have been prepared with chemical precipitation method via a solution route. Unfortunately, with this method either much different morphology was obtained or the distribution range of diameter is wide. From that reason the preparation of ZnO nanostructures under low and moderate temperature conditions still presents a great challenge. Below, we list some representative routes of the preparation of ZnO nanostructures.

Zinc oxide nanocrystals were prepared by homogeneous precipitation method using urea and zinc nitrate as raw materials. The orientation/adhesion of nanocrystallites was discussed by the growth unit model of anionic coordination polyhedrons. It was shown that zinc oxide nanocrystal growth was more easily to occur along c-axis, which was primarily formed by the connection of positive hexagonal cone faces $p(1\ 0\ 1\ 1)$ and negative

hexagonal cone faces $p(1\ 0\ 1\ 1)$, secondly by the positive polar faces $c(0\ 0\ 0\ 1)$ and negative polar faces $c(0\ 0\ 0\ 1)$.⁸ Not only does the microwave irradiation of solutions of $Zn(NO_3)_2$ and urea yield ZnO micro particles much more rapidly than conventional heating methods, it also produces ZnO with a quite different well-defined needle-like morphology based on an unusual and unexpected a-axis.³

The large-scale synthesis of uniform-sized hexagonal pyramid-shaped ZnO nanocrystals can be performed by the thermolysis of Zn-oleate complex, which was prepared from the reaction of inexpensive and environmentally friendly reagents such as zinc chloride and sodium oleate.⁹ ZnO microspheres and hexagonal micro rods with sheet like and plate like nanostructures were prepared by the hydrothermal synthesis approach by using trisodium citrate which plays a key role in directing the formation of these microstructures. By increasing the reaction time, these microspheres gradually dissolved to form short hexagonal micro rods with stacked nanoplate or nanosheet structure.¹⁰ The disk-like, flower-like and nanorod flower-like ZnO nanostructures have been controllably fabricated by citric acid assisted hydrothermal process.^{11,12} Different shapes of ZnO micro crystals have been controllably prepared by a capping-molecule-assisted hydrothermal process. The flowerlike, disk-like, and dumbbell-like ZnO micro crystals of hexagonal phase have been obtained respectively using ammonia, citric acid, and poly(vinyl alcohol) as the capping molecules.¹³ A unique method was developed to produce ZnO by kinetically controlled catalytic hydrolysis of a molecular precursor (Zn nitrate) at low temperature, operating in conjunction with the vectorial control of crystal growth. Nucleation and growth of ZnO was controlled by the local variation in the chemical potential of Zn^{2+} resulting from accumulation of OH groups at the gas-liquid interface.¹⁴ Anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate – NaAOT can be made to form micelles with diverse shapes by adjusting experimental parameters. The self-assembled AOT-layers at the interface of water and oil could act as template for growing ZnO.¹⁵

ZnO nanostructures of different morphologies (nanoparticles, nanorods, and flowerlike ZnO structures) could be synthesized by controlling the content of ethylenediamine, hexamethylenetetramine and triethanolamine (soft surfactant) and the pH of the reaction mixture.^{16,17} Possible mechanisms for the variation of morphology with synthesis parameters have been discussed.¹⁸ With maleic anhydride-modified polystyrene (m-PS) microspheres as a template (core) and zinc nitrate and diethanolamine (DEA) as the starting materials the m-PS/ZnO core-shell structure was synthesized by a wet chemical route; the preferential growth of ZnO nuclei resulted in a cup-shape shell around the m-PS core.¹⁹ Polymer-assisted control of particle morphology and particle size of zinc oxide is another important synthetic

route to prepare ZnO nanostructures.²⁰ For example, water-soluble poly(ethylene oxide-block-methacrylic acid) (P(EO-b-MAA) and poly(ethylene oxide-block-styrene sulphonic acid) (P(EO-b-SSH)) diblock copolymers,^{21,22} polyacrylamide,²³ poly(vinyl alcohol),²⁴ acrylates,²⁵ PVP²⁶ or even gelatin²⁷ were used. In the latest time dendritic²⁸ and hyperbranched²⁹ polymer structures or mixed ligand coordination polymer³⁰ were also used in the controlled synthesis of nano ZnO. A highly important ZnO structures are ZnO quantum dots which are synthesized in various media such as alcohols^{31,32} or other solvents.³³

Over the past years polyol method was used for synthesis of different inorganic compounds as well as pure metals.^{34–37} In case of less electropositive metal such as cobalt, nickel copper and silver the reduction reaction takes place and metallic nanoparticles are obtained while the addition of water causes the hydrolysis reaction resulting in the formation of oxides or hydroxides.³⁵ Polyol acts simultaneously as solvent, reducing and stabilizing agent, and medium for preventing particle growth.³⁷ Due to the mild reducing power, polyols are unable to reduce a cation of an electropositive metal such as zinc. Reaction of hydrolysis takes place in these systems resulting in formation of ZnO. Using polyol method nano ZnO was synthesized in various diols from various precursors but DEG appears to be most suitable medium and Zn(II) acetate most suitable precursor for the preparation of ZnO with particle size between 50 nm

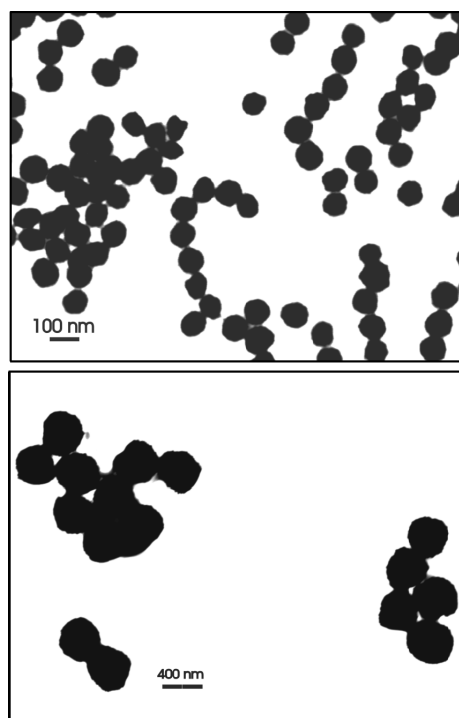


Figure 1: STEM micrographs ZnO nanoparticles synthesized by the polyol method in: a) DEG b) TEG

Slika 1: STEM-mikrografije ZnO-nanodelcev, sintetiziranih po polioli metodi v: a) DEG, b) TEG

and 100 nm.^{34,38} Besides the choice of medium, heating rate is crucial parameter which mostly determines the particle size.

In our study, ZnO sub micrometer and nanoparticles were synthesized in polyol media (di(ethylene glycol) – DEG and tetra(ethylene glycol) – TEG) using zinc(II) acetate as a precursor³⁹. STEM micrographs of ZnO particles, synthesized in DEG and TEG without p-TSA, are given in **Figure 1**. Micrographs show that 75 nm ZnO particles formed in DEG, while those formed in TEG have average particle size of 340 nm. Both ZnO particles are actually agglomerates of smaller (10–30 nm) crystallites.³⁹ Particle sizes and morphologies are similar to the reported results.^{34,38} In other diols no particulate ZnO was obtained and resulting agglomerates were unsuitable for the preparation of nanocomposites. IR spectra showed characteristic absorption band of ZnO in the range of 430–470 cm⁻¹ and weak absorption bands of oxoacetate reaction intermediates at (1590, 1415 and 1340) cm⁻¹. XRD diffractograms of the ZnO, synthesized in TEG, shows characteristic diffraction pattern of crystalline ZnO with hexagonal wurtzite structure (**Figure 2**). Wide diffraction maxima indicate small size of crystallites (18 nm – DEG, 25 nm – TEG) confirming the observations from electron micrographs.³⁹

3 ZnO/PMMA NANOCOMPOSITES

For organic-inorganic composites it is known that they possess improved properties in comparison to pure polymers such as better optical properties, thermal stability, chemical resistance, mechanical properties as well as flame-retardancy. The preferences in using ZnO in the preparation of polymeric nanocomposites, are in high transparency of the polymeric matrix in visible spectral region as well as its UV-protection. Development of simple procedures for the production of transparent UV-protective coatings or the preparation of transparent plates still represents a great scientific challenge since complete compatibility of ZnO nano-

to-sub micrometer particles with the polymeric matrix has not been achieved yet. Simply mixing nanoparticles with most polymers leads to aggregation in most cases. Small particles typically aggregate, thus nullifying any benefits of nanoscopic dimensions. The particles are frequently surface-modified or compounded in the polymer in presence of surfactants although few authors also report preparation of stable nano ZnO dispersions without any surface modification^{40,41}. To obtain miscibility of the inorganic particles and polymers usually hydrophobic ligands are used such as: alkyl silanes, oligomeric alkyl silicones, alkylphosphonic acid, hydroxy propyl methyl cellulose, fatty acids, amphiphilic statistical copolymer or block copolymers (diblock copolymers, double-hydrophilic block and grafted copolymers)⁴²⁻⁴⁹. Frequently used method of ZnO/poly(methyl methacrylate) (ZnO/PMMA) nanocomposite preparation is surface modification of ZnO nanoparticle using one of the mentioned ligands followed by the subsequent grafting of methyl methacrylate or mixtures of acrylic monomers on the modified surface of particles.⁵⁰⁻⁵⁵ Possible route towards ZnO/PMMA nanocomposites is by coating the ZnO particles with PMMA polymerized by gamma or electron radiation.⁵⁶ ZnO/PMMA nanocomposites were prepared also by the sol-gel synthesis of nano ZnO in the presence of PMMA.⁵⁷ Transparent ZnO/PMMA with high concentration of nano ZnO (up to 10 %) nanocomposites

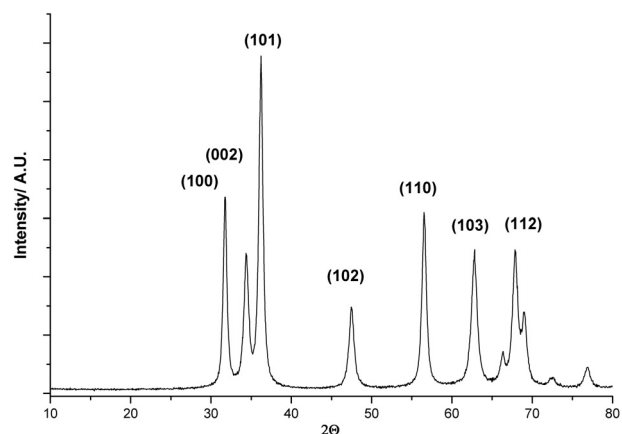


Figure 2: XRD diffractogram of nano ZnO synthesized in TEG
Slika 2: XRD-difraktogram nano ZnO, sintetiziranega v TEG

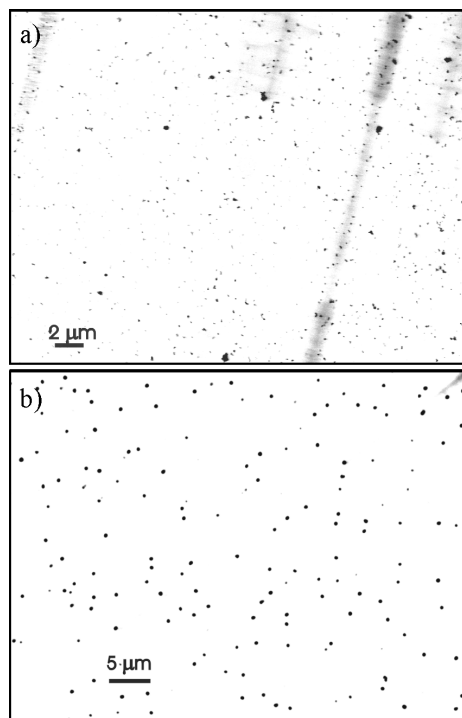


Figure 3: STEM micrographs of ultra microtome sections of ZnO/PMMA nanocomposites using ZnO synthesized in: a) DEG (part. size = 75 nm), b) TEG (part. size = 340 nm)

Slika 3: STEM-mikrografije ultramikrotomskih rezin ZnO/PMMA-nanokompozitov, pripravljenih z ZnO, sintetiziranim v: a) DEG (vel. delcev = 75 nm), b) TEG (vel. delcev = 340 nm)

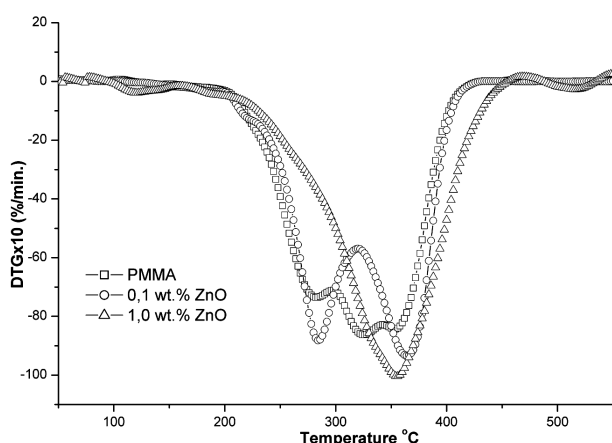


Figure 4: DTG curves of ZnO/PMMA nanocomposite using nano ZnO, synthesized in TEG (part. size = 86 nm), in dependence of ZnO concentration

Slika 4: DTG-krivulje ZnO/PMMA-nanokompozitov na osnovi nano ZnO, sintetiziranega v TEG (vel. delcev = 86 nm), v odvisnosti od koncentracije ZnO

have been also prepared by in-situ bulk polymerization in the presence of the prepared nanoparticles, which gives improved dispersion of nanoparticles compared to simple mixing.^{58–60} Bulk polymerization is the only synthetic method of PMMA which gives material with excellent optical properties (plexi glass) and is a widely used industrial process giving this method a very high potential in large scale production of ZnO/PMMA nanocomposite materials. Alternative method of ZnO/PMMA preparation is simultaneous formation of ZnO nanoparticles and PMMA polymerization³¹ or ATRP polymerization of MMA initiated from the surface of the ZnO.⁶¹ In the latest time homogeneous ZnO QDs nanocomposites were prepared by simply casting from solution^{41,62–64} or even by melt processing.⁶⁵

In our research work we focused on preparation of nanocomposites using synthesized nano ZnO particles with organophilic surface, synthesized by the polyol method. ZnO/PMMA nanocomposites were prepared by dispersing the unmodified ZnO nanoparticles in methyl methacrylate and by the subsequent in-situ chain polymerization of MMA. ZnO nanoparticles were dispersed in MMA by mixing and sonication. The dispersion was subsequently transferred into a glass mold and MMA was polymerized in a temperature controlled water bath for 20 h. The ZnO particle size, surface modification and concentration were varied.

The prepared nanocomposites were characterized by the thermo gravimetric analysis – TGA, TEM microscopy, UV-VIS spectroscopy and PLS – photoluminescence spectroscopy. STEM electron micrographs confirmed that nano ZnO is uniformly distributed in the PMMA matrix. (Figure 3).³⁹ Thermal stability of ZnO/PMMA nanocomposites was studied by the TGA. Results showed that thermal stability is enhanced at ZnO concentrations of 1 % and more (Figure 4). Enhanced thermal stability was explained by the influence of nano

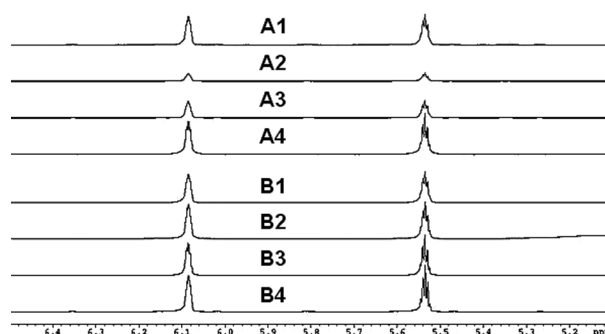


Figure 5: The intensity of vinylidene proton peaks in ^1H NMR spectra of PMMA in dependence of the ZnO concentration and size: A-ZnO (75nm); A1) 0 %, A2) 1 %, A3) 0.1 %, A4) 0.01 % and B-ZnO (340 nm); B1) 0 %, B2) 1 %, B3) 0.1 %, B4) 0.01 %

Slika 5: Intenziteta signalov vinilidenskih protonov v ^1H NMR-spektrih PMMA v odvisnosti od ZnO-koncentracije in velikosti delcev: A-ZnO (75 nm); A1) 0 %, A2) 1 %, A3) 0,1 %, A4) 0,01 % and B-ZnO (340 nm); B1) 0 %, B2) 1 %, B3) 0,1 %, B4) 0,01 %

ZnO on the termination mechanism of MMA radical polymerization causing reduced content vinylidene double bonds in PMMA chains as confirmed by ^1H NMR spectroscopy (Figure 5).³⁹ Double bonds are weak points of MMA chains where decomposition starts and reducing their content causes enhanced thermal stability. UV-VIS spectroscopic measurements confirmed that nano ZnO is extremely efficient UV absorber since 3 mm thick plates containing the mass fraction of ZnO 0.01 % absorb more than 90 % of the incident UV light (Figure 6). At the same time more than 70–80 % of the visible light is transmitted through the material when material is prepared by the prepolymer procedure. Our results are different to those reported in the literature;^{61,62} concentrations of nano ZnO filler were much lower; mainly because we used unmodified ZnO while in reported nanocomposites ZnO, modified with t-butyl phosphonic acid, was used. Nevertheless, changes in thermal stability and UV-VIS absorption are similar to the reported ones. Due to the absence of surface modification our ZnO

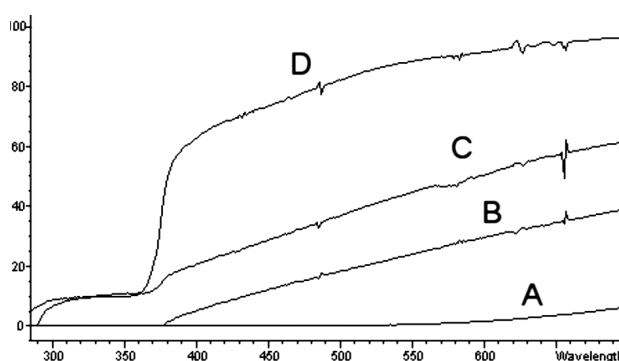


Figure 6: UV-VIS spectra of ZnO/PMMA nanocomposites using ZnO prepared in DEG in dependence of ZnO concentration: A) 1.0 %, B) 0.1 %, C) 0.01 %, D) 0.01 % – prepolymer procedure

Slika 6: UV-VIS-spektri ZnO/PMMA-nanokompozitov na osnovi ZnO, pripravljenega v DEG, v odvisnosti od masne koncentracije ZnO: A) 1.0 %, B) 0.1 %, C) 0.01 %, D) 0.01 % – postopek preko predpolimera

nanofiller is, due to lower production costs, more price competitive. Despite rather low ZnO concentration, there is a substantial effect on UV absorption as well as on the thermal stability of the prepared nanocomposites. Comparison with ZnO/PMMA nanocomposites, prepared by other procedures, is rather difficult because those nanocomposites are mostly in the form of powder or thin films while our materials are 3.5 mm thick plates.^{52–59} Prepared ZnO/PMMA nanocomposites have, due to high UV absorption, potential application as UV stabilized PMMA materials for various outdoor applications.

4 CONCLUSIONS

Syntheses of sub micrometer and nano ZnO structures as well as processing methods towards homogeneous ZnO/PMMA nanocomposites have been reviewed. ZnO nanostructures were synthesized by various hydrothermal and solvothermal synthetic routes, using various precursors, media and catalysts, and we showed that nano ZnO with organophilic surface can be successfully prepared in gram quantities in various diol media. Homogeneous ZnO/PMMA nanocomposites were prepared by different synthetic strategies using surface modified and unmodified nano ZnO. In our study, homogeneous ZnO/PMMA nanocomposites were prepared, using unmodified nano ZnO, by the radical chain polymerization of MMA in bulk and by optimizing the preparation procedure. Prepared nanocomposites showed enhanced thermal stability, when the concentration of ZnO is at least 1 %. Enhanced thermal stability, when ZnO is added in concentration of 1 % and higher, was explained, using ¹H NMR spectroscopy, as a consequence of reduced concentration of vinylidene double bonds in PMMA chains. Resulting nanocomposite materials absorbed from 80–98 % of the incident UV light by adding only the mass fraction of nano ZnO filler 0.01 %. Such materials have potential as UV stabilized PMMA materials for various outdoor applications with high sun light loads.

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