Preparation and Properties of Luminescent ZnO Nanoparticles in the Mesoporous Silica Matrices


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Modern material science devotes particular attention to studies of new optical materials for a wide range of applications including solar cells, laser sources, electroluminescent devices, tunnel diodes, optical amplifiers, biological luminescent labels, etc. Today the prospects in optics are closely related to highly efficient luminescent semiconductor nanoparticles, or “quantum dots”, which possess unique electronic properties. Further progress in evolution of luminescent materials is associated with enhancement of their stability, simplification of synthetic methods, as well as development of novel procedures for preparation of nanostructures with predefined optical properties. In the same time the possibility to accurately control any functional properties of nanomaterials is affected by three governing factors: the size, shape and dispersity of nanoparticles, the number of structural defects and the uniformity of chemical composition. The ability to prepare quantum dots with narrow size distribution is prerequisite to implement many technological applications such as line emitters, sensing self-assembled arrays, etc.

Binary oxide, sulfide and selenide semiconductors (e.g., ZnO, Cu₂O, ZnS, CdS, PbS, CdSe, PbSe and many others) have attracted great attention because of their specific optical and electronic properties, which differ significantly from the bulk materials. However, rather low chemical and temperature stability of nanoparticles usually results in distortion of originally adjusted parameters due to aggregation processes or chemical reactions with their surrounding, limiting practical application of purely nanocrystalline systems.

A well-known solution of aggregation problem is encapsulation of nanoparticles in a chemically inert matrix. The other important advantage of implementation of matrix techniques is the possibility to accurately control dispersion of nanoparticles. Obviously the dispersity degree of nanoparticles depends of the uniformity of the pores of the matrix. Here one should choose such matrices, which possess uniform pore structure with accurately controlled diameter. The most known and promising solid state nanoreactors possessing uniform pore structure at nanolevel are porous materials (zeolites, mesoporous silica and porous alumina). Mesoporous silica (MCM) seems to be the most challenging system for creation of nanocomposites owing to the possibility of preparing materials with different pore size (2 - 50 nm) and structure.

In this work, we investigate the formation of zinc oxide nanoparticles inside mesoporous silica (MCM-41) matrix. Zinc oxide has been known as a luminescent material for a century and today it is used for various applications such as vacuum fluorescent displays. Usually, ZnO exhibits two primary emission bands in its photoluminescence spectra: near band edge excitonic UV emission around 380 nm and visible deep level emission with a maximum between 500 and 530 nm. High exciton binding energy of ZnO (approx. 60 meV (∼10⁻²⁰ J)) leads to its high stability of the exciton even at room temperature, and attracts considerable technological interest to ZnO-based materials because of their potential application in exciton related electro-optical devices, such as UV light-emitting diodes and laser diodes. In order to achieve high UV emission intensity of ZnO and reduce visible once, one can use passivation technique to bind the surface atoms with inert compound having wider band gap and produce so-called “core-shell” nanoparticles. One can expect that the use of wide band semiconductors
such as SiO\(_2\) as a matrix will allow protecting nanoparticles surface and significantly increasing their UV luminescent efficiencies. Besides, porous system of mesoporous silica possess nanoscale ordering, which makes possible to architect novel position sensitive sensor devices basing on spatially ordered array of semiconductor particles with attached transparent electrodes.

An intercalation of zinc atoms into MCM-41 was performed using the zinc acetylacetonate because this hydrophobic metal complex can be expected to dissolve well in the hydrophobic part of the SiO\(_2\)/surfactant micelles and could be easily thermally decomposed to give zinc oxide. Dried mesoporous silica-surfactant matrix was stirred in Zn(acac)\(_2\) ethanolic solution at 70°C for 6 hours. After filtration the sample was washed with ethanol in order to get rid of Zn(acac)\(_2\) absorbed on the external surface, dried at room temperature and annealed in the oxygen flow at 500 °C for 5 hours (MS_ZnO_1 sample). For comparison, Zn(acac)\(_2\) was also intercalated into preliminarily annealed (550 °C, 10 h, O\(_2\)) mesoporous matrix (MSan_ZnO_1 sample). In order to avoid template removal from SiO\(_2\) during its intensive heating and stirring in ethanol, a part of mesoporous silica-surfactant matrix was soaked without stirring in Zn(acac)\(_2\) ethanolic solution at room temperature for 15 days. Sample was filtrated, washed with ethanol, dried at room temperature and annealed in the oxygen flow at 500 °C for 5 hours (MS_ZnO_2 sample). Another way to avoid removal of CTAB molecules involves the use of water-free solvents for intercalation of Zn(acac)\(_2\) which inhibits the dissolution of template and prevents hydrolysis of acetylacetonate complex with formation of bulk zinc hydroxide. Mesoporous silica-surfactant matrix was stirred in solution of Zn(acac)\(_2\) in dehydrated toluene at room temperature for 3 hours under Ar flow. The sample was washed several times with toluene, dried at room temperature and annealed in the oxygen flow at 500 °C for 10 hours (sample MS_toluene_ZnO).

To prove the presence of mesoporous structure after intercalation of zinc complex and following thermal modification the comparison between the SAXRD patterns for as-synthesized mesoporous silica, samples impregnated by Zn(acac)\(_2\) and the resulted nanocomposites was performed. All the samples correspond to the hexagonal mesoporous silica phases but the lattice parameter of mesoporous silica with surfactant molecules equals \(a = 4.8\) nm, while the lattice parameter of nanocomposites ZnO/SiO\(_2\) was found to be 4.5 nm. Obviously it deals with shrinking of mesoporous framework during thermal modification.

Photoluminescence spectra (at 77 K) of the ZnO/SiO\(_2\) nanocomposites show, that the emission spectrum for MSan_ZnO_1 has two maxima which are typical for ZnO - a narrow intensive exciton peak at 370 nm and broad emission band around 480 - 510 nm. Obviously exciton emission should be ascribed to ZnO nanoparticles with very low diameter which are confined in the channels of mesoporous silica, while the broad emission maxima at 480 - 510 nm appears due to defects in ZnO macrocrystallites. The spectrum of the MS_ZnO_1 sample also contains exciton peak at 370 nm, but its intensity is notably lower comparing with MSan_ZnO_1 composite and the ratio of the UV emission intensity and visible emission intensity for the sample MS_ZnO_1 is almost two times lower. The absence of exciton emission for MS_ZnO_2 nanocomposite probably deals with introduction of Zn atoms into mesoporous silica walls during the impregnation stage with formation of amorphous zinc silicate after thermal modification. The best results were achieved for the MS_toluene_ZnO composite which possess nearly no large particles on the surface of mesoporous silica and therefore shows very low intensity of visible luminescence with high efficiency of UV luminescence. Thus the proposed method results in formation of ZnO nanoclusters within the mesoporous silica channels, which allows to attain \(I_{UV}/I_{Vis}\) emission intensity ratio for ZnO up to 65.