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Glutathione-assisted synthesis of star-shaped zinc oxide nanostructures and their photoluminescence behavior

Kavita^{a,*}, Karamjit Singh^a, Sunil Kumar^b, H.S. Bhatti^a

^a Department of Physics, Punjabi University, Patiala-147002, Punjab, India

^b Quantum Functional Semiconductor Research Center, Dongguk University, Seoul-100715, South Korea

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ABSTRACT

Star-shaped ZnO nanostructures have been synthesized by facile chemical co-precipitation method in the presence of glutathione. Glutathione, a reducing agent, shape modifier and an entirely benign antioxidant; acts as a capping agent in the present study. The powder X-ray diffraction patterns indicate that the novel star-shaped ZnO nanostructures exhibit hexagonal structure. Fourier transform infra-red spectroscopic studies confirmed the anchoring of glutathione on ZnO nanocrystals. Transmission electron microscopy and field emission scanning electron microscopy revealed the star and cube-shaped morphology of the glutathione modified nanocrystals. Optical characterization of synthesized nanocrystals has been done by UV–vis absorption spectroscopy and steady state photoluminescence spectroscopy. Recorded Photoluminescence spectra confirm the multi-chromatic photoluminescence behavior of the synthesized nanostructures.

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1. Introduction

ZnO is a direct band gap (~ 3.37 eV) semiconductor and reported to have the richest family of nanostructures such as, nanoparticles, core/shell nanoparticles, nanowires, nanorods, nanocombs, nanocages etc. [1–4]. Creation of variety of nanostructures results due to the electrostatic interaction energy and diverse chemical doings of the polar surfaces (Zn^{2+} and O^{2-}) of ZnO. Nanostructured ZnO has received broad attention in biomedical science as it is biosafe and due to its distinguishable performance in electronics, optics, and photonics. For biomedical applications, ZnO nanostructures have to be functionalized through surface modification with biocompatible capping molecules. Many of the organic ligands, particularly the thiols, have been utilized for both stabilizing and fine tuning the surface properties of semiconductor nanocrystals [5–7]. The use of organic ligands as chemical treatment holds great promise for controlling the surface electronic properties of semiconductors. By appropriately selecting thiol stabilizers like mercaptopropionic acid [8] or mercaptosuccinic acid [9] the Photoluminescence (PL) of synthesized nanocrystals in aqueous solution could be appreciably improved.

In the present study, glutathione (GSH) is used to treat the surface of synthesized ZnO nanostructures. GSH is a tripeptide

with a gamma peptide linkage between the amine group of cysteine (which is attached by normal peptide group of glycine) and the carboxyl group of the glutamate side-chain. These functional groups have tendency to form a polymerized structure due to their cross-linking and coupling tendency. GSH gained special attention, since it is the most versatile and most powerful of the body's self generated antioxidants. Thiol group of cysteine is very significant in detoxification [10] and it is the active part of molecule which serves as reducing agent. Its thiol group acts as capping agent and each GSH molecule also contains one amine group and two carboxylate groups. GSH has been effectively used to cap Au, ZnS, CdS, CdSe, and CdTe nanostructures [11–15] and appears to work best in terms of promoting PL quantum yield.

The photoluminescence behavior of GSH-capped ZnO nanocrystals is being reported for the first time to the best of our knowledge.

2. Experimental

All the chemicals used in the synthesis were of analytical grade and all the precursor solutions were prepared with ultra high purity and accuracy.

GSH capped ZnO nanostructures were synthesized using chemical co-precipitation method under normal atmospheric conditions [16], originally reported to synthesize ZnO nanorods with some modifications. The capping agent used to passivate the dangling bonds was

* Corresponding author. Tel.: +91 9988027574.

E-mail addresses: bhardwajkavita25@gmail.com, kavitaneeraj25@gmail.com (Kavita).

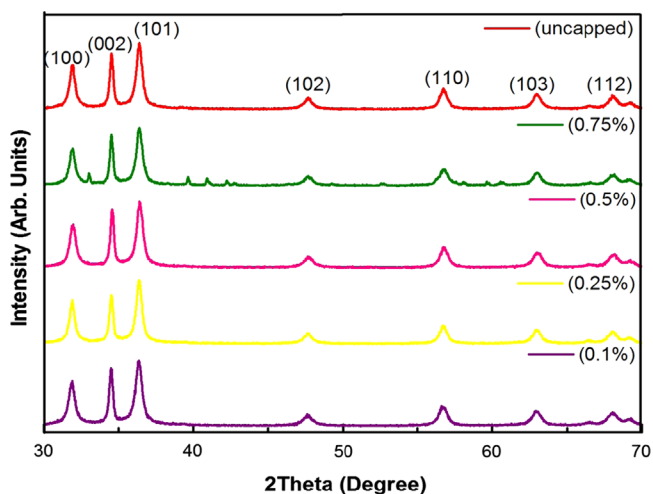


Fig. 1. XRD patterns of uncapped and GSH-capped ZnO nanostructures.

GSH. The pH of the solution was not controlled and the nanostructures synthesized in highly basic media.

The crystallographic characteristics of the prepared samples were investigated by Panalytical X'Pert Pro Powder X-ray diffractometer using Cu K_{α} radiation ($\lambda=0.154187$ nm), keeping the step size of 0.02° in the 2θ range 30° – 70° . The morphological characteristics of the synthesized materials were investigated using Hitachi (S-4300), field emission scanning electron microscope (FESEM) and Hitachi (H-7500), transmission electron microscope (TEM) operated at 80 keV TEM study was carried out by dispersing ZnO samples in ethanol followed by ultrasonication before loading the sample on carbon coated copper grid. Fourier Transform Infrared (FT-IR) spectra of synthesized nanopowders mixed with KBr were recorded in the 400 – 4000 cm^{-1} range in transmission mode using Perkin-Elmer spectrum 400 FT-IR/ FT-FIR spectrometer. Absorption spectra (250 – 800 nm) of synthesized ceramic nanostructures dispersed in ethanol were recorded using Perkin Elmer PC-coupled spectrophotometer. Steady state photoluminescence measurements were performed by Spectrofluorometer (Fluorolog version-3; Model FL3-11) in 370 – 650 nm spectral range using an excitation wavelength (λ_{ex}) of 325 nm.

3. Results and discussion

3.1. Crystallographic analysis

The recorded powder X-ray diffraction (XRD) patterns of the synthesized uncapped and GSH-capped ZnO nanostructures are shown in Fig. 1. The detected XRD peaks are characteristic of the ZnO with hexagonal wurtzite crystal structure (JCPDS card no. 36-1451) [17] and no impurity phase has been seen in the XRD patterns except at 0.01% capping concentration. The sharp diffraction peaks indicate that the synthesized nanostructures are highly crystalline and pure. Various crystallographic parameters of the synthesized nanomaterials are calculated analytically and tabulated in Table 1. The lattice constants of the synthesized nanostructures are in good agreement with the values of hexagonal ZnO of the space group P63mc. Variation of lattice parameters with GSH concentration has been shown in Fig. 2. The average crystallite size was calculated using well known Debye-Scherrer equation:

$$D = 0.9\lambda/\beta \cos \theta \quad (1.1)$$

where D , λ , β and θ are average crystallite size, X-ray wavelength, full width half maximum (FWHM) of major diffraction peak and

Table 1

Various measured crystallographic parameters of GSH-capped ZnO nanostructures.

Capping concentration (wt%)	D_{avg} (nm)	Lattice parameter, a (Å)	Lattice parameter, c (Å)	Volume (nm^3)	c/a	No. of unit cells, n
0.00	18.39	3.227	5.1723	0.1400	1.6028	23248
0.1	17.60	3.242	5.1968	0.1419	1.6029	20096
0.25	13.18	3.242	5.1936	0.1418	1.6019	8449
0.5	14.17	3.240	5.1930	0.1416	1.6027	10515
0.75	14.68	3.240	5.1927	0.1416	1.6026	11692

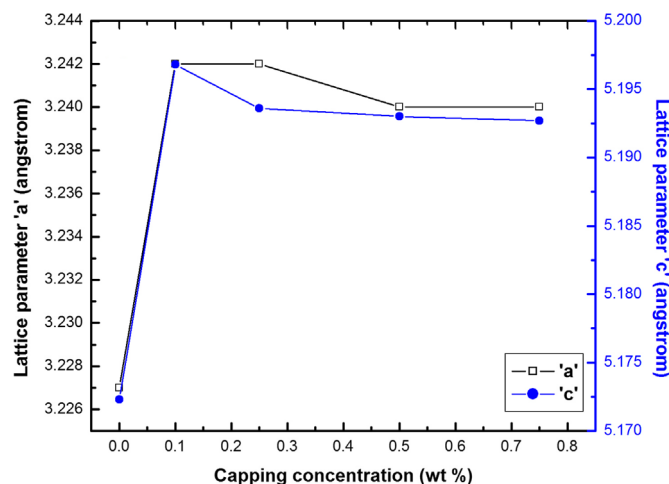


Fig. 2. Variation of lattice parameters with GSH capping concentration.

diffraction angle, respectively. The average crystallite size is found to be 18.39 nm for uncapped ZnO nanocrystals, whereas in the presence of GSH average crystallite size varies between 13.18 nm and 17.60 nm, much lower than the particle size deduced from the TEM. It can be clearly observed from the calculated crystallographic parameters that GSH capping significantly control the crystallography and morphology of the nanocrystals. Capping concentration augmentation upto optimum value (0.25 wt%) causes decrease of average crystallite size and number of unit cells whereas beyond the optimum capping concentration addition of GSH causes crystallite size enhancement. The lattice parameters and unit cell volume values fluctuate with the variation in crystallite size and particle morphology because the variation in surface energy with varying crystallite size strongly effects the crystal structure stability. This obvious discrepancy may be based on the assumption of such crystallization mechanism in which primary nanocrystals have parallel yet spatially separated crystallographic alignment leading to formation of ZnO mesocrystals.

3.2. Morphological analysis

Fig. 3a–g illustrates the TEM micrographs of uncapped (Fig. 3a) and GSH-modified ZnO nanostructures (Fig. 3b and f) and corresponding SAED pattern (Fig. 3g). It is evidenced that the morphology of the ZnO nanostructures obtained is strongly dependent on the GSH, as capping molecule. The cube-like morphology was observed at 0.01% , while at 0.75% GSH concentration star-like morphology was observed. Thus, GSH plays a crucial role in controlling the morphology of the obtained ZnO nanostructures. This is probably due to a preferential interaction between GSH and some crystal facets of ZnO. The TEM micrograph of an individual star (Fig. 3f) shows the tip structure of arms revealing that it is not a single-crystal rod but an assembly of several well-defined nanorods with average size of few nanometers as suggested by XRD measurements. The formation of star by the combination of

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