Chapter-6

Summary and future suggestions
6.1. Summary and important findings

A facile solution method is used for the synthesis of ZnO nanostructures viz. nanosheets, flower-like structures and nanoparticles. The variety of ZnO nanostructures and their crystal structures were analyzed by using Scanning electron microscope and X-ray Diffraction studies. All the three morphologies of as synthesized ZnO structures possessed wurtzite-hexagonal structure as confirmed by XRD analysis. The studies of concentrations and molar ratios of ZnAc₂ and KOH solutions indicated that the thickness and roughness of ZnO structures decreases with the increasing concentration of precursor and alkali solution in the reaction chamber. In this study we used two different solvents i.e. water and ethanol. While varying the ratio OH⁻/Zn²⁺ along with concentration of precursor and alkali solution, show an impact on the morphologies in both of the solvents cases. To analyzed the growth, we used Transmission electron microscopy which shows that the ZnO nanostructures viz. nanosheets and flower-like structures synthesized in ethanol and water as solvent, respectively have faceted edges, and grow via oriented attachment of the particles along the (002) direction. The observed similar growth direction (002) for both of the synthesized ZnO nanostructures indicates that the mediums affect the aggregation tendencies of initially formed nanocrystals only. All the synthesized ZnO morphologies have different band gap due to their different size range as observed by UV-Vis spectroscopy. The Fourier transform infrared spectroscopy shows that both the nanosheets and flower-like structures have hydroxyl (chemisorbed and/or physisorbed H₂O molecules) and carboxylate group of acetate coordinated to the surface of ZnO nanocrystals along with other remnant species.

The whole process of formation of ZnO nanostructures i.e. nanosheets and flower-like structures with reaction time may be described to proceed via the nucleation of ZnO nanocrystals and their different aggregation in respective mediums. After aggregation of nanocrystals, the anisotropic growth leading to the formation of nanosheets and flower-like structures may occur either by collision (due to random Brownian motion), oriented attachment of nanocrystals or Ostwald ripening. The reason behind the different aggregation tendencies of initially nucleated ZnO nanocrystals in H₂O and C₂H₅OH medium leading to the formation of nanosheets and flower-like structures with the reaction time is attributed to the extent of hydrogen bonding. The solvent facilitating the adhesion among the ZnO centres through hydrogen bonding leads into the complex interwoven morphologies like nanoflowers. Strong hydrogen bonding networking takes place between the adjacent ZnO
nuclei in water than alcohol medium due to the +I effect of the alkyl chain. Hydrogen bonding was confirmed by symmetry distortion in both of the mediums. And the symmetry distortion is found to be higher in case of nanocrystals from H₂O medium revealing the strong inter hydrogen bonding among these ZnO nanocrystals as compared to the nanocrystals obtained from C₂H₅OH medium. Therefore, the alcohol medium prevents nanoparticles from aggregation while water medium favors their aggregation.

We know that the wide band gap of ZnO restricts its use only in UV region, but in the present study we have used as synthesized ZnO structures in visible regime as well by creating the defects during synthesis at room temperature. The defects were created by fast addition of the precursor solutions, therefore during the reaction the precursor ions do not have sufficient time to orient themselves in completely oriented manner, and hence defects are created in the structures. The defects were confirmed by photoluminescence spectroscopy, which showed emissions peaks around 390 nm (UV), 420 nm (violet), 466 nm (blue), 485 nm (blue-green) and 520 nm (green) for all structures, confirming the visible emission. The observed emission in photoluminescence spectroscopy indicated the existence of oxygen and zinc vacancies which expands its use in UV as well as visible regions also. The existence of oxygen and zinc vacancies could be used for environmental and opto-electronics applications. Taking advantage of the induced defects, we applied ZnO structures for photocatalytic activities under sunlight illumination. However, both the nanosheets and flower-like structures performed the photocatalytic activity in sunlight irradiation but the nanosheets due to large surface area as compared with the flower-like structures showed better performance as a catalyst. In other words, the flower-like structures due to aggregation tendencies do not completely expose their surfaces when irradiated in sunlight irradiation, resulting in less production of OH⁻ and O₂⁻ radicals and hence a lower degradation efficiency of dye as compared with the nanosheets. Therefore, nanosheets can be used as an efficient material for water purification in photocatalytic mechanism under sunlight irradiation.

The as synthesized ZnO structures due to the presence of oxygen and zinc vacancies show good opto-electronics properties in visible light. The photoresponse of these nanostructures was obtained under different color (white, violet and green) illumination using 3V bias voltage. The existence of surface states and large surface area are inferred to be responsible for the photodetection mechanism in the ZnO nanostructures in visible region. The nanosheets show good response to photovoltage, growth time and decay time under
different color light illumination as compared with nanoparticles and flower-like structures, which is attributed to the surface defects and surface area of nanosheets. However, the nanoparticles owing to comparatively large surface area should have fast decay time but in our case, they show slower decay time which is inferred due to the presence of deeper level defects in case of nanoparticles. In case of flower-like structures again due to their aggregated structure do not completely expose their surfaces when irradiated with visible light and hence result in less production of photogenerated electrons which leads to their lower photoresponse. The as synthesized nanosheets could be used as an efficient material for photodetector applications in visible region.

The ZnO being its negligible absorption in the visible region (red light) can be used as a turbid medium to bend the light in optical imaging applications. In our case, we used different ZnO morphologies to bend the light and increased the numerical aperture of an objective lens. We know that for better image resolution in optical microscopy using a turbid lens not only the numerical aperture but also the transmittance of the turbid lens should be high. The greater the transmittance and bending of a turbid medium, the higher the resolution achieved in optical microscopy. In our case, we enhanced both numerical aperture as well as transmittance of a turbid medium using different morphologies of ZnO. By applying ZnO turbid films, the numerical aperture of an objective lens with an initial value 0.906 has been increased to 1.861, 1.939 and 1.971 using the films composed of microstructures, nanoparticles and nanosheets, respectively (44–46 μm film thickness). The variation in NA with different morphologies is attributed to the size-dependent scattering approach. The maximum bending of light is achieved for a turbid film of ZnO nanosheets. ZnO nanosheets based turbid films shows higher value of numerical aperture of objective lens with suitable transmittance. Observed results indicate that the numerical aperture of an objective lens can be further improved by fabricating thicker ZnO nanostructure film, however it will reduce the transmittance.

This is the first report which highlights the creation of defects states during the synthesis of ZnO nanostructures viz. nanosheets, flower-like structures without addition of surfactant, directing agent or template. This approach offers several advantages because of control of synthesis parameters on the properties of the nanostructures. For the opto-electronic application, this is first time we report pure ZnO as a visible-light photodetector without doping, surface modifications, high temperature or expensive equipment. The ZnO
morphologies are firstly applied to enhance the numerical aperture as well as transmittance of turbid lens for improved optical microscopy. The changes observed in the optical and electrical properties of ZnO nanostructures with the variation of solvent suggest that this could be a very useful way to synthesize different morphologies with novel optical and opto-electronic properties.

Future suggestions

➢ In future attempts, this method could develop a synthesis procedure to obtain nanostructures with surface defects and of better quality in smaller time frames. This means these reaction methodologies can be utilized to produce surface defects in materials without doping and surface modifications, and without use of high temperature and expensive equipments.

➢ This synthesis method can be used for the formation of nanostructures of other metal oxide such as Fe₂O₃, NiO, Ce₂O₃, CoO, AZO etc and their properties can be controlled by changing the synthesis parameters.

➢ Further, the luminescence properties suggest that the visible emissions in ZnO nanostructures expand their use in visible region for the environmental and opto-electronics application.

➢ In this thesis, photocatalytic activity of ZnO nanostructures for the removal of organic dye: methylene blue is studied in detail. It would be interesting to study the utilize ZnO nanostructures for other hazardous pollutants such as phenols, malachite green, methyl orange, metronidazole, coliform, E. coli bacteria etc.

➢ Since ZnO thin film and its nanostructures have great application in lithium-ion batteries, sensors and in water purification, the as prepared pure ZnO nanostructures can be further studied for these applications. Also, due to their more surface area and visible emissions they can be used for solar cell, fuel cell, LED, LASER applications etc.