



OPTOELECTRONICS INVESTIGATIONS OF AMINOPROPYLTRIETHOXYSILANE (APTES) FUNCTIONALIZED SEMICONDUCTOR ZNO NANOPARTICLES

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Abstract: The functionalized ZnO nanoparticles with Aminopropyltriethoxysilane (APTES) using the precipitation method were studied here. APTES modification of the ZnO nanoparticles was achieved by carrying out a condensation reaction. By means of FTIR spectroscopy, the presence of imine bonds in the APTES-covered nanoparticles was demonstrated. For complete understanding of APTES functionalized ZnO nanoparticles, X-ray diffraction (XRD), photoluminescence (PL), UV-Visible absorption spectroscopy and FTIR were all used. Polymer capping the ZnO nanoparticles caused their surface to change which made their UV emission brighter and cut down on the green light produced due to defects in PL spectra. It was established that the annealing temperature annealing for fixed time greatly affected the optical qualities of the APTES-ZnO nanoparticle-based system. Since the UV-Visible spectra shifted towards blue wavelengths in the UV region, it can be seen that the APTES functionalized ZnO nanoparticles are smaller in size than uncoated or uncapped ZnO nanoparticles.

IndexTerms-APTES functionalized, SEM, XRD, ZnO nanoparticles, photoluminescence, UV-Vis, optoelectronic properties, annealing time etc.

I. INTRODUCTION

Because of their superior electronics, optics and electrical properties, Group II–VI nanoparticles have caught the attention of many scientists, optoelectronic specialists and researchers. Such qualities are mainly due to the quantum confinement effect that appears at nanoscale levels. It is zinc oxide (ZnO) that, among all these materials, impresses the most with its great photon and electron characteristics that are sought after for electronics technology. It is commonly applied in solar cells, light-emitting screens, sensors, processors of picture images, certain transducers and communication technologies in space [8] [1,2,3,4,5,6,7]. There is a strong relationship between the optoelectronic behavior of ZnO nanoparticles and the ways particles are synthesized, how big or small they are and how their surfaces are modified. Unlike other nanocomposites, ZnO is chemically and optically safe, less expensive and has fewer health risks. Because ZnO is stable in conditions like air, water and light, it becomes an interesting option for many uses. Due to its big band gap of 3.4 eV and a high energy for exciton formation (60 meV), ZnO is mostly found as a wurtzite crystal [9–11]. Scientists have tried many ways to make ZnO nanoparticles such as homogeneous precipitation, the sol–gel process, spray pyrolysis, thermal evaporation, organometallic synthesis and methods using microwaves [12,13]. Among all the methods, precipitation is the most popular option because it requires little skill and is not costly. Even so, it is still very hard to achieve uniform particles, reliable chemical properties and successful passivation during ZnO nanoparticle synthesis. To improve the optical properties of nanoparticles or nanocomposites—particularly by minimizing non-selective absorption—surface modification or capping techniques are widely employed. A variety of capping agents have been utilized for such surface modifications [14–17]. Capping plays a crucial role in enhancing the quantum efficiency of nanoparticles by passivating surface sites that facilitate non-radiative recombination. In recent years, diverse ZnO nanostructures—including nanoparticles, nanocomposites, nanotubes, and nanorings—have been synthesized. Among these, APTES -based nanocomposites have garnered significant attention due to their stable and unique thermal, mechanical, and electronic properties [19–21]. The APTES coatings effectively inhibit the abnormal growth and aggregation of ZnO nanoparticles, thereby enhancing their potential applicability in electronics and computer science. Among the available synthesis methods, chemical approaches are generally preferred over physical ones for producing capped ZnO nanoparticles. While physical methods, such as directly mixing polymers with nanoparticles, are relatively straightforward, they often lead to aggregation and increased production costs [22–25]. Conversely, chemical routes enable the formation of more stable and non-aggregated nanocomposites in a cost-effective manner. In chemical surface modification, surface-initiated polymerization can be achieved by covalently bonding polymer chains to the surface of ZnO nanoparticles—a process known as surface grafting. This approach is particularly promising due to the strong covalent interactions formed between the grafted polymer and the nanoparticle surface.

Numerous researchers have explored the synthesis and characterization of polymer-based ZnO nanocomposites. For example, Guo and Yang [3] synthesized highly monodisperse ZnO nanoparticles functionalized with APTES and examined their optical properties. Their results demonstrated an enhanced near-band-edge ultraviolet (UV) emission and a notable suppression of the defect-related green emission in photoluminescence (PL) spectra. The surface modification in this case was found to alter the Ostwald ripening kinetics, thereby reducing the growth rate of ZnO nanoparticles. Tachikawa et al. [18] looked at the process of using different polymeric precursors, PEG and PVP, as capping agents for ZnO nanoparticles. They produced ZnO nanoparticles by using the sol-gel method. But our process which uses APTES-treated ZnO nanoparticles, is different and more beneficial than these well-known strategies. It should be noted that silica seals the defects (trap states) on the nanowires' surface which means that ultraviolet (UV) emission is the main peak in the PL spectrum and green luminescence due to defects is significantly reduced. All things considered, capping ZnO nanoparticles with APTES yields several advantages, as we see from the above discussion. (i) It stops nanoparticles from gathering by using steric hindrance. (ii) It helps coat or passivate the intrinsic flaws which are often non-radiative and produce unwanted visible light in the emitted spectra.

We chose to cap ZnO nanoparticles with an APTES receptor in the study. Because of this modification, the surface of ZnO nanoparticles is covered, meaning less oxygen vacancy-related issues and higher stability. Moreover, having imine linkages stops nanoparticles from gathering by cutting down surface hydroxyl interactions and getting rid of hydrogen bonding between the nanoparticles. So, this stops oxygen crosslinking which helps to keep nanoparticle dispersions stable.

2. Experimental Details

2.1 This study used the following materials and methods

II. Every reagent was purchased as “analytical grade” and added directly to the experiments. Samples that had dried were checked through Fourier transform infrared (FTIR) spectroscopy using a Bruker Tensor 27 spectrophotometer in KBr pellet mode. A variety of diluted solutions in a 1 cm path length quartz cell were scanned using an Analytik Jena Specord 250 Plus spectrometer to study cation recognition. The materials were put between two quartz plates so they could be finely coated for UV measurements. To get fluorescence spectra, PerkinElmer LS55 fluorescence spectrophotometer was used with 1 cm quartz cuvettes to collect the data. The fluorescence profile of sensor solutions was recorded on Perkin Elmer L55 Fluorescence spectrophotometer using 1 cm path length of quartz cells. The excitation and emission slit widths were both fixed at 10 nm, and all measurements were collected at a scan speed of 200 nm s⁻¹. Solid-state photoluminescence (PL) spectra were obtained with a solid-sample holder. Scanning-electron-microscopy (SEM) analysis was carried out on aqueous dispersions of the materials at a concentration of 200 µM, using a JEOL JSM-6610 LV microscope operated at 15 kV. X-ray diffraction (XRD) patterns of the annealed ZnO samples were recorded on an X'Pert PRO (MPD) diffractometer equipped with a Cu Kα source ($\lambda = 1.546 \text{ \AA}$) operating at 45 kV and 45 mA.

2.2 Synthesis of Aminopropyltriethoxysilane (APTES) ZnO Nanoparticles

Quantum-sized ZnO nanoparticles were synthesized in a round-bottom flask using zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (1 g, 5.0 mmol) and APTES (4.30 g, 6.0 mmol). A sodium hydroxide solution was added slowly and dropwise to the reaction mixture via a dropping funnel. The resulting mixture was then stirred in an ultrasonic bath for 2 hours, during which a stable dispersion of ZnO nanoparticles gradually formed. The resulting dispersion was collected by centrifugal filtration and washed multiple times (4–5 times) with methanol and deionized water to remove any residual impurities. The purified product was subsequently dried at 50 °C for 20 hours. After drying, the ZnO nanoparticles were annealed under vacuum at various temperatures. The annealing process was carried out for a fixed duration of 2 hours at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C, and the resulting samples were labeled A, B, C, D, and E, respectively, according to their annealing temperature.

3. Results and discussion

We discussed here various characterization techniques and also highlighted the optical studies of APTES functionalized ZnO nanoparticles.

3.1 Characterization of APTES functionalized Nanoparticles

Synthesized (modified ZnO nanoparticle samples were characterized using the X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Visible spectroscopy, photoluminescence spectroscopy and FTIR spectroscopy.

3.1.1 X-ray diffraction (XRD)

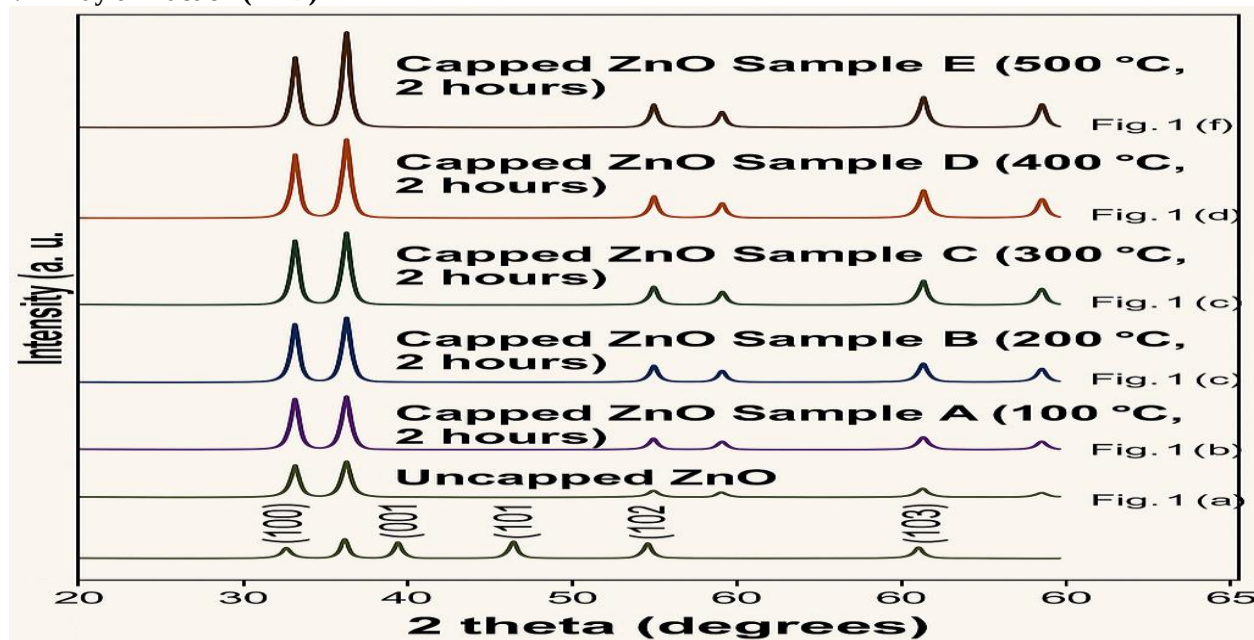
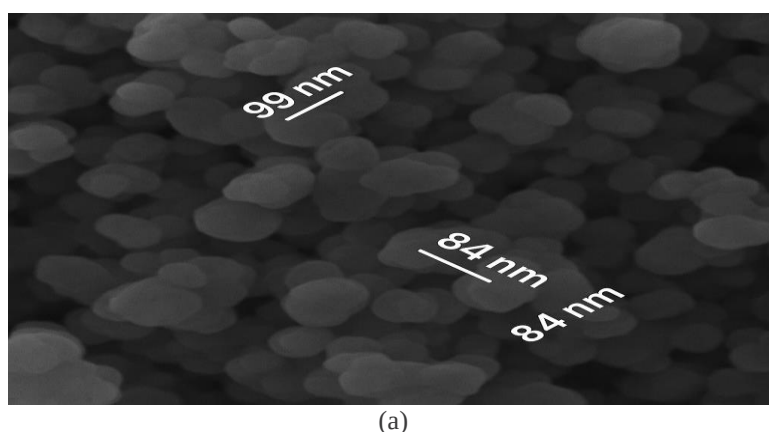


Fig. 1 XRD spectra of (a) uncapped (b) (c), (d), (e), (f) APTES functionalized ZnO nanoparticles at different annealing temperature

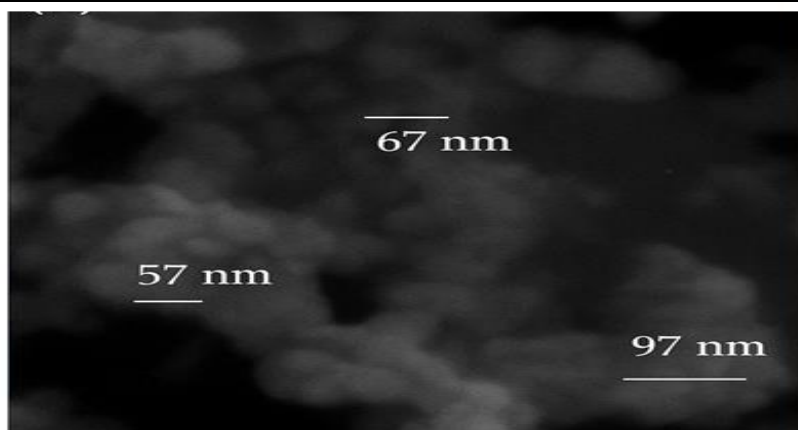
III. Crystallite size of the synthesized APTES functionalized ZnO nanoparticles were characterized and analysed by using XRD technique. By using Scherrer's equation, the particle size of uncapped ZnO nanoparticles was found to be 31 nm which correspond to different peaks in different planes (100), (101), (002), (102), (110), (103) and (112) as shown in figure 1 (a). While figure 1 (a) and (b), (c), (d), (e), (f) shows the comparison of XRD spectra of the uncapped and Aminopropyltriethoxysilane (APTES) ZnO nanoparticles for one of the samples (E), i.e., at an annealing temperature 500 (C), which again confirms the formation of the stable wurtzite structure for the APTES modified ZnO nanoparticle for the sample E. The size of the crystallite of the APTES based ZnO nanoparticles sample was computed and calculated using the Debye-Scherrer formula $= 0.9\lambda / (\beta \cos \theta)$, where D is g the diameter of the crystallite, β is the full width at half maximum (FWHM), λ is the value of the wavelength of the copper (Cu) radiation. XRD spectra show the presence of broad peaks at 32.65°, 34.6°, 37.48°, 48.56°, 63.85°, 66.96°, and 69.93°. The broadening of large XRD peaks confirms that the size of APTES modified ZnO nanoparticles were found to be smaller than uncapped ZnO nanoparticles. By comparing with respect to the JCPDS card (36-1452), the particle size was found to be 27 nm. Peaks corresponding to different impurities were not found to be present in the XRD spectra of figure 1 (b), (c), (d), (e) and (f) confirming the high purity of the synthesized polymer-based ZnO samples. Figure illustrates that with surface modifications, the peaks of the XRD pattern of APTES functionalized ZnO nanoparticles have been seen to be broadened.

3.1.2 Morphology of the Aminopropyltriethoxysilane (APTES) capped ZnO nanoparticles

SEM images generally used to examine the morphology of the modified (APTES) ZnO nanoparticles. Figure 2 (b) shows the SEM image of the APTES -based ZnO nanoparticles, which appear to be homogeneous, distinct, and non-aggregated while figure 2 (a) represent the SEM for capped ZnO nanoparticles.



(a)
Fig. 2 (a) SEM images of uncapped ZnO nanoparticles



(b)

Fig. 2 (b) SEM images APTES capped ZnO nanoparticles at 100 deg.

Therefore, in XRD measurements, we used to get a size of ZnO nanoparticle smaller than the SEM measurements. The APTES-based ZnO nanoparticle size in SEM measurements was found to be less than 100 nm. It is evident from the SEM micrograph that the modified ZnO nanoparticles are very well dispersed with a sphere-shape morphology.

3.1.3 PL spectra of APTES based ZnO nanoparticles

Photoluminescence (PL) spectra of APTES-functionalized ZnO nanoparticles were obtained using an excitation wavelength of 325 nm. Typically, ZnO nanoparticles exhibit a strong ultraviolet (UV) emission near the band edge, accompanied by broad visible emissions that originate from intrinsic defects. Among these visible emissions, green luminescence is the most prominent, although emissions in the blue, yellow, and bluish-yellow regions are also frequently observed. For optoelectronic applications such as UV lasers, minimizing or eliminating the visible emission is crucial. The UV luminescence is commonly attributed to free exciton recombination processes. Despite extensive research, the exact mechanism responsible for green luminescence remains debated. Various hypotheses have been proposed, suggesting that this emission arises from structural defects such as oxygen vacancies, zinc vacancies, or the formation of donor-acceptor pairs during synthesis. Numerous studies have also highlighted a strong correlation between the intensity of visible emissions and the surface characteristics of colloidal ZnO nanoparticles.

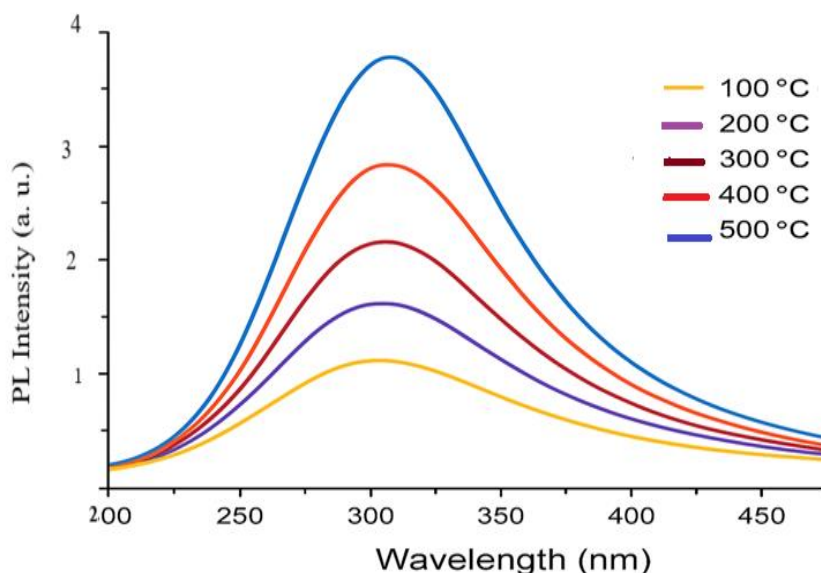


Fig. 3 PL spectra of the APTES based ZnO nanoparticles at different annealing temperature

We have observed the effect of annealing time on the PL intensity in PL spectra. PL spectra have been shown for different annealing times in APTES functionalized ZnO nanoparticles at different steps i.e. at 100°C, 200°C, 300°C, 400°C, 500 °C for fixed 2 hours respectively. Photoluminescence intensity of the PL spectra has been increased as annealing temperature is varied from 100°C, 200°C, 300°C, 400°C, 500 °C for fixed 2 hours. This will be due to increased size of APTES functionalized ZnO nanoparticles as temperature is increased from 100 degree to 500-degree centigrade. Corresponding PL intensity value will be highest for the highest temperature due to maximum increase in size of the capped ZnO nanoparticles i.e. for 500 degrees centigrade. In this case, PL intensity will be least for minimum temperatures i.e. 100 degrees centigrade, due to smaller size of modified ZnO nanoparticles. Similarly, figure 3 shows the PL spectra of APTES capped nanoparticles at different annealing temperature.

3.1.4 UV-Visible absorption spectra of the Aminopropyltriethoxysilane (APTES) capped ZnO nanoparticles

The optoelectronic behavior of ZnO nanoparticles becomes increasingly significant as their size is reduced to the nanoscale. In this study, we investigated the radiative absorption behavior of APTES based ZnO nanoparticles using UV-Visible (UV-Vis) spectroscopy. The UV-Vis absorption spectra of APTES ZnO nanoparticles were recorded across various annealing temperatures ranging from 100°C to 500°C in colloidal solution, as presented in Figure 4.

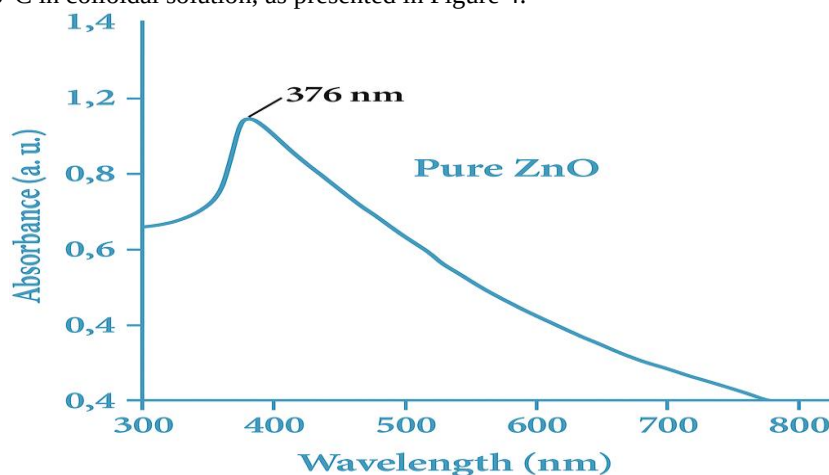


Figure 4 :UV-visible spectra of Uncapped ZnO Nanoparticles

It is noteworthy that the absorption wavelength of 373 nm (corresponding to 3.37 eV) represents the band edge of uncapped ZnO nanoparticles. In contrast, the APTES-functionalized ZnO nanoparticles exhibited absorption in the range of 346 nm to 357 nm for all five temperatures, indicating a blue shift compared to the uncapped sample. This blue shift is attributed to the quantum confinement effect, which becomes more pronounced in smaller nanoparticles.

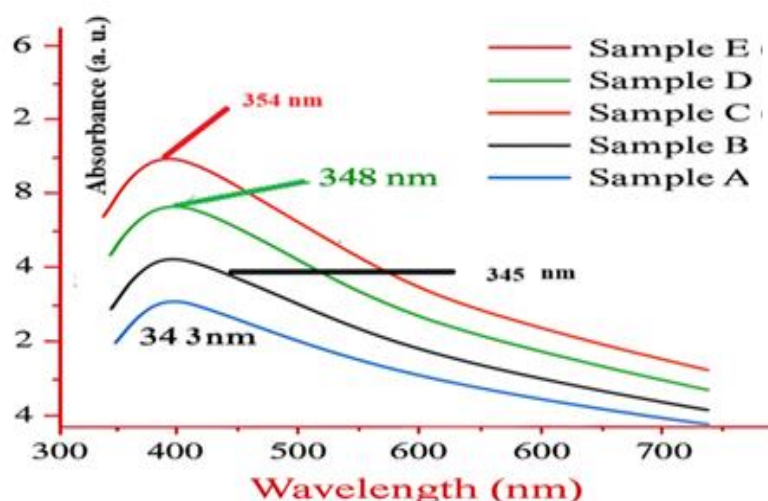


Figure 5: Comparison of UV-Visible spectra of APTES-functionalized ZnO nanoparticles from 100°C to 500 °C (Sample A to E)

As shown in Figure 5, a comparative analysis between uncapped and APTES-functionalized ZnO nanoparticles (Sample E) reveals a notable blue shift in the capped sample. This shift, with absorption peaking at 357 nm for APTES-functionalized ZnO nanoparticles is indicative of smaller particle size relative to the uncapped ZnO nanoparticles. The enhanced absorbance at shorter wavelengths for the capped sample is again attributed to the quantum confinement effect, which dominates as nanoparticle size decreases.

3.1.5 FTIR Spectroscopy of APTES-Functionalized ZnO Nanoparticles

The FTIR spectra of APTES-functionalized ZnO nanoparticles, recorded over the 1000–4000 cm^{-1} range, offer valuable information about the surface functionalities and chemical composition. A broad absorption band near 3500 cm^{-1} is attributed to O–H stretching vibrations, confirming the presence of hydroxyl groups on the nanoparticle surface. The absorption peaks in the region of 2840 to 3000 cm^{-1} correspond to C–H stretching vibrations associated with alkyl chains. Additionally, distinct bands appearing between 1639 and 1387 cm^{-1} are characteristic of symmetric and asymmetric stretching of carboxylate (COO^-) groups coordinated with zinc. These carboxylate features likely stem from carbon-containing byproducts formed during synthesis, while the hydroxyl groups are commonly attributed to the moisture-absorbing nature of ZnO nanoparticles. Figure 6 shows the FTIR spectra of uncapped ZnO nanoparticles.

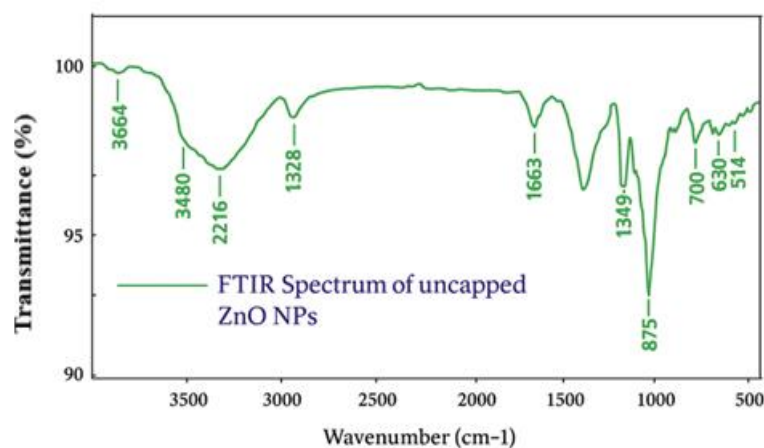
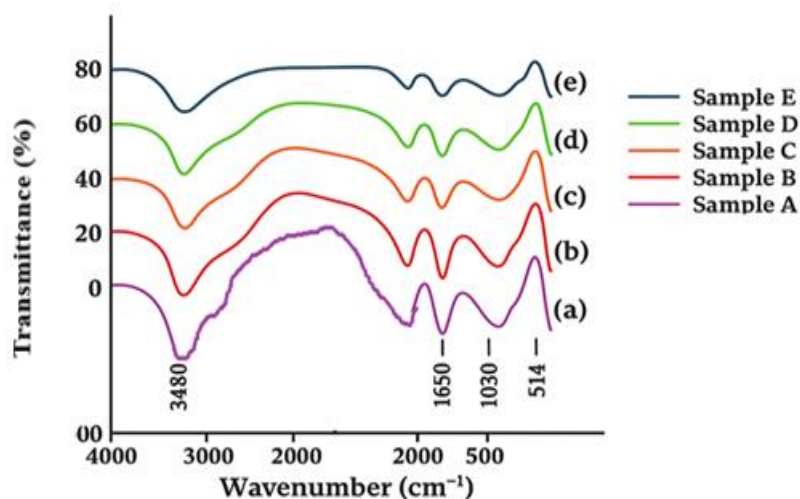


Figure 6: FTIR of uncapped ZnO nanoparticles



V.

Figure 7: FTIR spectra of the APTES functionalized ZnO nanoparticles at different annealing temperature in colloidal solution for (a) 100°C (b) 200°C (c) 300 °C (d) 400°C (e) 500°C respectively.

Figure 7 (a–e) presents the FTIR spectra of APTES-capped ZnO nanoparticles subjected to various annealing temperatures. A noticeable decline in the intensity of peaks associated with hydroxyl and carboxylate groups is observed with increasing annealing temperature, indicating a gradual elimination of surface-bound organic residues. At higher annealing temperatures, the carboxylate-related peaks nearly vanish, implying the decomposition of zinc carboxylate into ZnO. The remaining –OH bands are likely attributed to the re-adsorption of moisture from the surrounding environment.

4. Conclusion

APTES modified ZnO nanoparticles were successfully synthesized using a wet chemical precipitation method. Structural and optical properties of the APTES-functionalized ZnO nanoparticles were examined using XRD, photoluminescence (PL), UV-Vis, and FTIR spectroscopy. The PL spectra revealed enhanced UV emission at 350 nm after 10 hours of annealing, demonstrating the effect of surface capping and thermal treatment on emission behavior. The UV-Vis spectroscopy confirmed a clear blue shift in the absorption edge for capped ZnO nanoparticles compared to uncapped ones, attributed to the quantum confinement effect. These findings highlight that APTES-functionalized ZnO nanoparticles exhibit superior optical tunability, which is beneficial for optoelectronic applications where size-dependent absorption and emission properties are critical.

REFERENCES

- [1] Ü. Özgür et al., "A comprehensive review of ZnO materials and devices," *J. Appl. Phys.*, vol. 98, no. 4, pp. 041301, 2005.
- [2] A. B. Djuricic and Y. H. Leung, "Optical properties of ZnO nanostructures," *Small*, vol. 2, no. 8–9, pp. 944–961, 2006.
- [3] Y. Guo and L. Yang, "Surface functionalization of ZnO nanoparticles with APTES and their enhanced photoluminescence properties," *J. Nanopart. Res.*, vol. 12, no. 7, pp. 2387–2396, 2010.
- [4] Z. L. Wang, "Zinc oxide nanostructures: growth, properties and applications," *J. Phys.: Condens. Matter*, vol. 16, no. 25, pp. R829–R858, 2004.
- [5] M. Willander et al., "Zinc oxide nanorod based photonic devices: recent progress in growth, light emitting diodes and lasers," *Nanotechnology*, vol. 20, no. 33, pp. 332001, 2009.
- [6] A. Janotti and C. G. Van de Walle, "Fundamentals of zinc oxide as a semiconductor," *Rep. Prog. Phys.*, vol. 72, no. 12, pp. 126501, 2009.
- [7] C. Pacholski, A. Kornowski, and H. Weller, "Self-assembly of ZnO: from nanodots to nanorods," *Angew. Chem. Int. Ed.*, vol. 41, no. 7, pp. 1188–1191, 2002.
- [8] C. Klingshirn, "ZnO: from basics towards applications," *Phys. Status Solidi B*, vol. 244, no. 9, pp. 3027–3073, 2007.

- [9] C. S. Rout et al., "Hydrothermally synthesized ZnO nanorods for gas sensor applications," *Appl. Phys. Lett.*, vol. 87, no. 26, pp. 262102, 2005.
- [10] C. Jagadish and S. J. Pearton (Eds.), *Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications*, Elsevier, 2006.
- [11] M. B. Cortie et al., "Modified sol–gel synthesis of ZnO nanoparticles using polyols and its application in UV-blocking coatings," *Langmuir*, vol. 23, no. 9, pp. 5270–5275, 2007.
- [12] D. Zhang, Y. Yang, and H. Wang, "Microwave-assisted synthesis of ZnO nanoparticles," *Mater. Lett.*, vol. 61, no. 20, pp. 4290–4293, 2007.
- [13] H. Y. Zhu and Y. Q. Fu, "Low temperature solution route synthesis of ZnO nanoparticles with improved UV emission," *Mater. Sci. Semicond. Process.*, vol. 40, pp. 881–887, 2015.
- [14] J. F. Wang, G. J. Wang, and D. Y. Xing, "Improvement of photoluminescence of ZnO nanoparticles by surface modification with alkanethiols," *J. Phys. Chem. C*, vol. 112, no. 46, pp. 17912–17917, 2008.
- [15] A. E. Aliev et al., "Surface capping of ZnO nanoparticles with organic ligands for light emission applications," *J. Phys. Chem. B*, vol. 110, no. 27, pp. 13333–13338, 2006.
- [16] M. Pourbaix et al., "Functionalization of ZnO nanoparticles for biomedical and optoelectronic applications," *J. Colloid Interface Sci.*, vol. 450, pp. 124–132, 2015.
- [17] R. D. Raccichini et al., "Influence of APTES modification on ZnO surface and its impact on optical properties," *Appl. Surf. Sci.*, vol. 410, pp. 438–446, 2017.
- [18] T. Tachikawa, M. Fujitsuka, and T. Majima, "Mechanistic insight into the photoinduced reaction of nanostructured ZnO using time-resolved spectroscopy," *J. Phys. Chem. B*, vol. 108, no. 7, pp. 2313–2322, 2004.
- [19] S. Bhattacharjee et al., "Multifunctional ZnO-APTES nanocomposites: synthesis, characterization, and application in optoelectronics," *Nanotechnology*, vol. 29, no. 35, pp. 355601, 2018.
- [20] H. T. Vu et al., "Silane-functionalized ZnO nanostructures for enhanced luminescence and dispersion," *J. Mater. Chem. C*, vol. 9, no. 4, pp. 1167–1174, 2021.
- [21] M. Nasrollahzadeh et al., "Green synthesis of ZnO nanostructures and their photocatalytic and optical properties," *Adv. Colloid Interface Sci.*, vol. 291, pp. 102327, 2021.
- [22] M. M. Rashad et al., "Polymer-capped ZnO nanoparticles: synthesis, stability, and optical performance," *J. Nanopart. Res.*, vol. 15, no. 6, pp. 1713, 2013.
- [23] C. Le Droumaguet and D. Velty, "Surface-initiated polymerization of ZnO nanoparticles for nanocomposite fabrication," *Polym. Chem.*, vol. 4, no. 5, pp. 1427–1436, 2013.
- [24] T. Basu et al., "Surface grafting of polymers on ZnO nanoparticles for enhanced dispersion and stability," *Langmuir*, vol. 34, no. 19, pp. 5674–5682, 2018.
- [25] S. Ma et al., "Grafting polymer chains onto ZnO nanoparticles via covalent bonding: towards improved colloidal stability," *J. Mater. Chem.*, vol. 22, no. 25, pp. 12898–12906, 2012.