Effect of Hydrophilic and Hydrophobic Capping Agents on ZnO Nanoparticles: A Structural and Optical Perspective

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Abstract

In this paper, optoelectronic and structural properties of surface-modified zinc oxide nanoparticles (ZnO NPs) were investigated using two capping agents: hexamethylenetetramine (HMTA) and oleic acid. The aim was to compare their impact on nanoparticle morphology and optical behavior relative to uncapped ZnO NPs. By selecting high-purity precursor materials and using a wet chemical synthesis method, ZnO NPs were synthesized, capped, and characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-visible spectroscopy. The XRD results confirmed a wurtzite crystal structure in all samples, with reduced particle sizes upon capping—27 nm for oleic acid and 33 nm for HMTA—compared to 35 nm for uncapped ZnO. SEM analysis revealed that HMTA-capped ZnO formed smaller, more spherical particles with reduced agglomeration compared to the irregular morphology of oleic acid-capped ZnO. UV-visible analysis showed that capping caused a blue shift in the absorption edge, correlating with a size reduction and corresponding bandgap widening. Thus, capping effectively tunes the optical properties of ZnO nanoparticles by controlling their size and dispersion, with HMTA demonstrating superior structural refinement and optoelectronic performance.

Keywords: ZnO, HMTA, Oleic acid, Capping agents, wideband gap material

Introduction

Zinc oxide (ZnO) is a highly versatile wide-bandgap semiconductor, extensively employed in nanotechnology and energy-related applications, including catalysis, energy harvesting, and photovoltaics. Compared to its bulk counterpart, ZnO nanoparticles (NPs) offer enhanced functional properties, making them a key material in diverse technological domains [1–2]. Their synthesis is relatively straightforward, with established techniques such as gas-phase plasma synthesis, hydrothermal growth, sol-gel processing, co-precipitation (wet methods), and microwave-assisted approaches enabling controlled fabrication [3–4]. Recent advances in nanotechnology have popularized the colloidal synthesis of ZnO NPs, where the nanoparticles' stability is significantly influenced by factors like solvent composition and ionic strength. Capping agents—molecules that bind to the nanoparticle surface—play a crucial role in enhancing stability, solubility, reactivity, and biocompatibility. Hydrophilic agents like hexamethylenetetramine (HMTA) improve dispersion in aqueous media, while hydrophobic agents such as oleic acid enhance stability in non-polar solvents [5]. Beyond stabilization, these surface modifiers alter surface charge and chemistry, offering tailored control over nanoparticle interactions for specific applications [6–7]. The optimization of capping agent concentration and synthesis conditions is critical to achieving the desired physicochemical properties of ZnO NPs.

Capping agents are also pivotal in determining the structure, morphology, particle size, and overall stability of ZnO NPs. A wide range of materials—including polymers, amino acids, organic ligands, and dendrimers—have been employed for surface modification [8–9]. Literature reports show that ZnO nanorods synthesized via hydrothermal methods exhibit varying morphology and size depending on the capping agent used, such as polyethylene glycol (PEG), polyvinyl alcohol (PVA), sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB) [10–11]. Among these, PVA has demonstrated superior ability in producing nanoparticles with stable and uniform morphology. Similarly, co-precipitation methods using gelatin, PVA, polyvinylpyrrolidone (PVP), and ethylene glycol (EG) have shown variations in photoluminescence and UV absorption properties, depending on the capping agent employed [12–16].

ZnO NPs also find applications in cosmetics and optoelectronics. For instance, agents like tetraethyl orthosilicate (TEOS) and dimethyldiethoxysilane (DMDES) enhance ZnO compatibility in cosmetic formulations. In the field of electronics, oleic acid-capped, iron-doped ZnO NPs have shown potential in polymer light-emitting diodes (PLEDs). Other surfactants—such as hexamine, tetraethylammonium bromide (TEAB), CTAB, and tetraoctylammonium bromide (TOAB)—have been investigated for tuning ZnO's optoelectronic properties [16–20]. Moreover, bio-based stabilizers like carboxymethyl cellulose (CMC), citrus extracts, and potato starch have also demonstrated reduced nanoparticle aggregation and improved optical properties [21–29].

In the present study, we investigate the effect of two chemically distinct capping agents—hydrophilic HMTA and hydrophobic oleic acid (derived from castor beans)—on ZnO nanoparticles synthesized via a wet chemical route. The resulting nanoparticles were comprehensively characterized using structural (XRD, SEM) and optical (UV–Vis) techniques to assess the impact of surface modification on their morphology and optoelectronic behaviour.

2. MATERIALS USED FOR SYNTHESIS AND METHOD OF SYNTHESIS

2.1. Materials used

For the synthesis of ZnO nanoparticles we have followed or used wet chemical process. Initial material for the synthesis of ZnO NPs include various chemicals such as zinc acetate dihydrate, ethanol sodium hydroxide and deionized water. Additionally, capping agents such as HMTA and then hydrophobic oleic acid were added to utilize them as capping agents. In this method of synthesis all chemicals (reagents) have been sourced & purchased from Aldrich (leading company in purity) which does not require any further purification for its use in the synthesis. In this investigation we have synthesised ZnO nanoparticles (uncapped) and capped ZnO nanoparticles by using two capping agents (HMTA and then Oleic acid).

2.2. Synthesis or preparation of ZnO Nanoparticles

ZnO nanostructures could be tailored by adjusting reaction conditions such as temperature, duration, and thermal treatment. So, this study followed a controlled wet synthesis approach. Initially, a 0.5 M solution of Zn $(CH_3COO)_2$ was prepared in deionized water, along with a separate 1.5 M of NaOH solution. These two solutions were combined gradually at room temperature while being continuously stirred, leading to the formation of a white precipitate. In order to regulate the growth of the nanoparticles, the resulting mixture was stirred for an additional two hours at 70°C. The slurry or precipitates (white) formed are then centrifuged then filtered and washed three or four times using deionized water and then further washed with ethanol, and dried at 100°C for 2 hours to get powdered form of ZnO NPs. In order to get better or much enhanced crystallinity of ZnO NPs, the obtained ZnO powder was further subjected to a sintering process at 400°C for 3 hours. It results in formation of fine white powdered form of ZnO NPs.

2.3. Surface capping (Modification) of ZnO Nanoparticles by using HMTA and Oleic acid Capping Agents

In order to modify or capping the ZnO nanoparticle's surface we employed hydrophilic HMTA and then hydrophobic oleic acid as capping agents. This modification aimed to prevent nanoparticle agglomeration while controlling growth rate and further limiting the particle size. In this study both capping agents i.e. HMTA and then oleic acid was prepared in 20 mM ethanol solution. A fixed amount of ZnO powder was dispersed in ethanol solution which is further stirred magnetically for 20 minutes. The prepared mixture will be obtained in ZnO suspension form. This white formed suspension is then given ultrasonic treatment for 50 minutes by using ultrasonic bath. The resulting colloidal suspension formed was then further heated on hot plate for 40°C for approximately 3 hours and subsequently left undisturbed for 30 hours. In order to remove any residual formation in synthesis process or excess residue of surfactant (capping agent), the synthesized capped ZnO nanoparticles were then filtered and washed three or four times using a pure deionized water and ethanol mixture. Finally, the functionalized capped ZnO nanoparticles were dried at 100°C for 2 hours.

3. CHARACTERIZATION TECHNIQUES

To analyze the structural and chemical properties of the synthesized nanoparticles (uncapped & capped) ZnO NPs, several characterization techniques were used but, in this paper, will investigate XRD & SEM measurement, while UV-visible spectroscopic technique is employed for optical measurements

4. RESULTS

4.1 X-ray Diffraction (XRD)

In this study comparative study of XRD obtained from synthesized pure ZnO NPs and modified ZnO or capped ZnO NPs have been studied. The synthesized crystalline powder of ZnO nanoparticles and modified (Oleic acid & HMTA) ZnO NPs were assessed using a Rotating diffractometer (Brunker, Germany) attached with the monochromator (Graphite) which is then rotating with the Cu-Kα radiation lase (λ = 1.5405 Å). This set up was kept at high voltage of 40 KV and current rating of 75 mA. The X-ray diffraction (XRD) patterns were recorded at 2 theta value which is in the range of 20° to 95°. The set up was scanning the target at angle of 1-5 degrees. The synthesized ZnO nanoparticles (NPs) were prepared by using wet chemical synthesis method. This synthesis process is then followed by synthesis of capped or modified ZnO nanoparticles by employing both oleic acid and HMTA as capping agents for comparative study.

For the hexagonal formation of ZnO nanostructure, the d_{hkl} parameter (d-spacing) and the lattice parameters are related to the lattice constants which are respectively be highlighted as (a, c) [33] the equation governing all these parameters is given as under [33]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

By using this equation in conjunction with Braggs law ($2d_{hkl} \sin\theta = n\lambda$) and by subsequently using the miller indices (h, k, l) the lattice parameters a and c can be easily be determined.

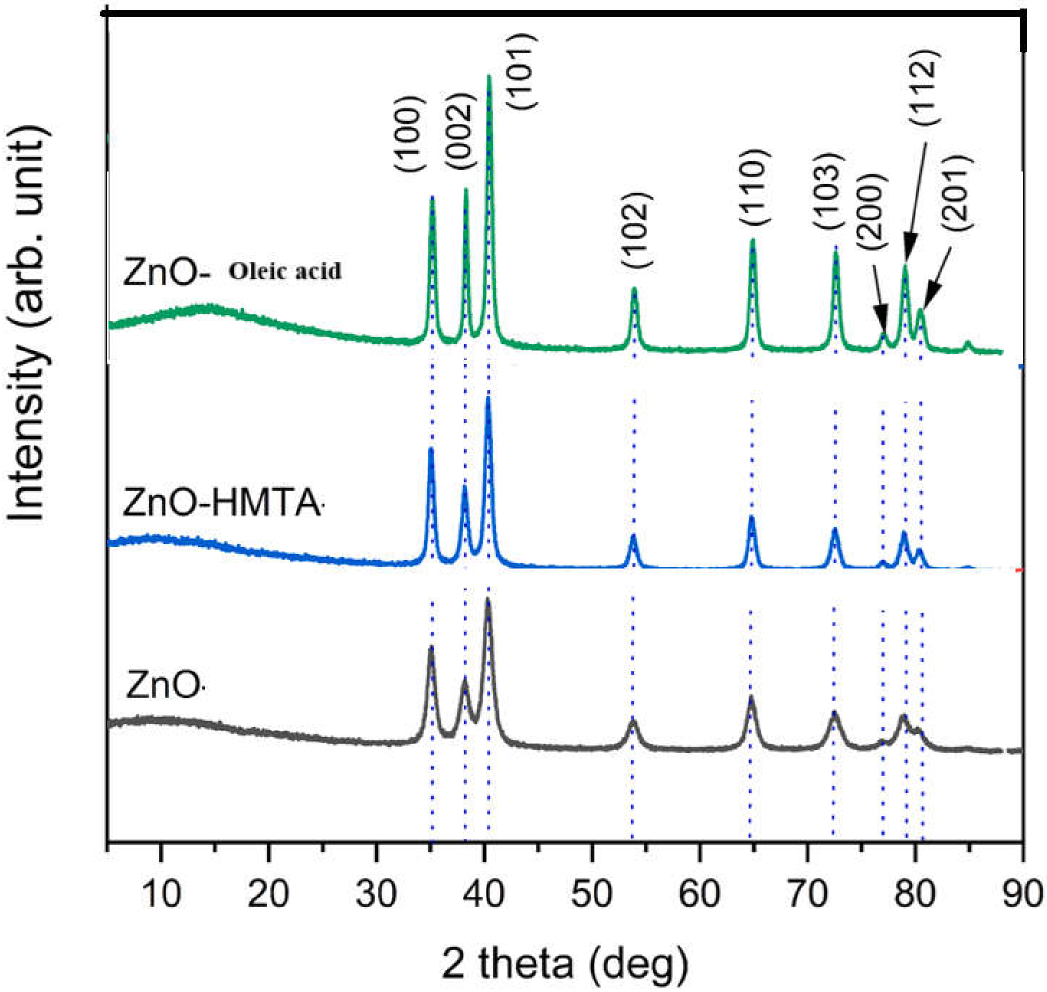

Figure 2: XRD pattern of syntheized pure or uncapped ZnO, Oleic acid capped ZnO NPs and HMTA modified or capped ZnO NPs

Table1. Particles size of ZnO and Oleic acid and HMTA capped ZnO NPs

Samples	**size (nm)**	**Lattice Parameter**		
		a(Å)	**c(Å)**	**c/a**
ZnO	**35**	**3.246**	**5.205**	**1.603**
OA capped	**27**	**3.247**	**5.201**	**1.601**
HMTA capped	**33**	**3.243**	**5.196**	**1.602**

X-ray diffraction (XRD) pattern or spectra of ZnO nanoparticles (Figure 2) exhibits a set of well-defined peaks at 2theta = 32.75°, 33.14°, 35.29°, 47.53°, 56.58°, 62.83° and 66.91°corresponding to the ZnO crystalline planes with Miller indices (100), (002), (101), (102), (110), (103) and (112). These peaks further confirm the presence of a hexagonal wurtzite structure. The sharp and narrow diffraction peaks indicate the high crystallinity and purity of synthesized ZnO nanoparticles with no impurities or secondary phases.

The average crystallite size (D) was then determined from the Scherrer formula or equation as:

$D= K\lambda /\beta\times\cos\theta$………(A)

In equation (A) the K signifies the Scherrer constant whose value lies in range of 0.9, and theta is the Bragg angle. While particle size ZnO capped with oleic acid i.e. (oleic acid capped ZnO) was found to be 27 nm while particle size of HMTA capped with ZnO NPs was found to be 33 nm as shown in Table 1.

4.2 SE M Measurements

From the SEM micrographs, major differences of the degree of agglomeration were noted in two capped ZnO NPs. As illustrated, the particle agglomeration was greater for ZnO-oleic acid capped ZnO sample (which formed irregularly shaped) than that for ZnO-HMTA capped ZnO (which formed smaller spherical ZnO) which agglomerates less (Figure 3(A) versus 3(B)). It needs to be noted that most solvent ZnO syntheses result in the creation of crystals with so-called inactive surfaces. These measurements are consistent with XRD measurements.

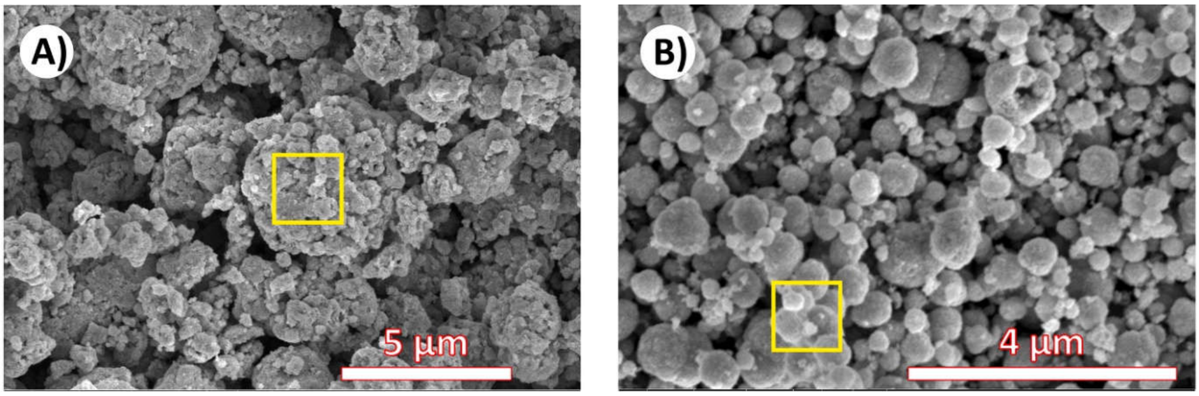

Fig 3 (A): SEM of Oleic acid capped ZnO NPs (B) SEM of HMTA capped ZnO NPs

4.3 Optoelectronics investigation (optical properties) of ZnO and capped or modified ZnO NPs (UV-Visible instigation)

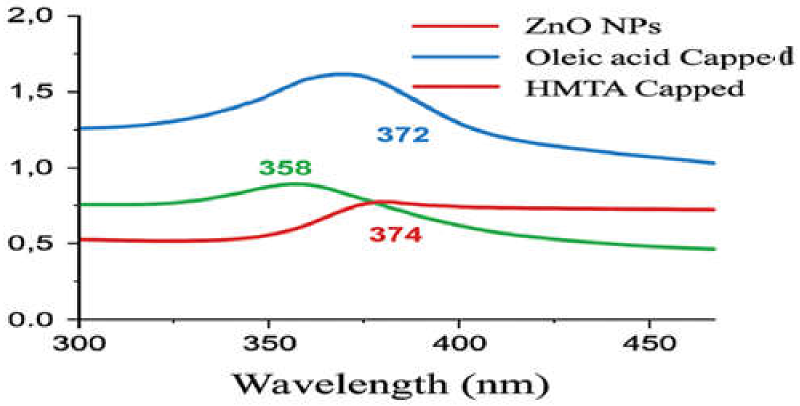

Figure 3: Absorbance spectra of ZnO, Oleic acid and HMTA capped ZnO NPs

The UV–visible absorbance spectra of pure ZnO, oleic acid-capped ZnO, and HMTA-capped ZnO nanoparticles (NPs) are presented in Figure 3, within the wavelength range of 300–420 nm (full spectrum: 200–800 nm). The absorbance peaks in the spectra correspond to the fundamental absorption edge, where the incident photons with energy E=hv are sufficient to excite electrons from the valence band across the Zn–O bond. Among the samples, HMTA-capped ZnO NPs exhibit a sharper and more distinct absorbance peak compared to those capped with oleic acid, indicating improved optical definition. Furthermore, the absorption edge for HMTA-capped ZnO occurs at a lower wavelength, signifying smaller particle size and a wider band gap—consistent with the size reduction observed in structural analyses (XRD and SEM). Overall, both capped samples demonstrate a blue shift relative to pure ZnO, reinforcing the correlation between nanoparticle size and optical behavior.

5. CONCLUSION

In this study, ZnO nanoparticles were successfully synthesized using a wet chemical route and subsequently modified with two distinct types of capping agents: hydrophilic hexamethylenetetramine (HMTA) and hydrophobic oleic acid. XRD analysis confirmed the formation of a hexagonal wurtzite structure in all samples, with no evidence of secondary phases, indicating phase purity throughout the synthesis. The use of both capping agents led to a noticeable reduction in nanoparticle size—27 nm for oleic acid-capped and 33 nm for HMTA-capped ZnO—compared to the 35 nm size of uncapped ZnO. SEM analysis further revealed that the hydrophilic HMTA facilitated the formation of smaller, more uniformly spherical particles with reduced agglomeration, while the hydrophobic oleic acid resulted in more irregularly shaped, aggregated structures. UV–visible spectroscopy demonstrated a blue shift in the absorption edge for both capped samples, indicating an increase in bandgap energy consistent with quantum size effects. This shift confirms the influence of capping on particle size and optical behaviour. Overall, the study highlights how hydrophilic and hydrophobic capping agents distinctly affect the structural and optoelectronic properties of ZnO nanoparticles. HMTA, in particular, was more effective in achieving uniform morphology and enhanced optical performance, making it a promising candidate for applications requiring fine control over nanoparticle characteristics.

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