SYNTHESIS AND CHARACTERIZATION OF PURE AND SURFACTANT ASSISTED ZnO NANOPARTICLES

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ABSTRACT: Pure and surfactant (EDTA) assisted zinc oxide (ZnO) nanoparticles have been synthesized *via* chemical precipitation method using zinc acetate dihydrate and sodium hydroxide in aqueous solutions and EDTA as surfactant agent. The thermal behaviour of the pure and EDTA capped ZnO nanoparticles are determined by thermo gravimetric and differential thermal analysis (TG-DTA). The formation of ZnO from the precursor and its functional group have been confirmed using X-ray diffraction (XRD) and Fourier transform infra-red (FT-IR) analysis, respectively. The optical properties have been analyzed through UV-visible (UV-vis) and photoluminescence (PL) studies. The morphology of ZnO and the surface morphology have been studied by field emission-scanning electron microscope (FE-SEM) and atomic force microscopy (AFM) technique, respectively.

***Keywords* – ZnO, EDTA, nanoparticles, surfactant.**

1. INTRODUCTION

Zinc oxide (ZnO) is a wide band gap semiconductor material with an energy gap of 3.37 eV at room temperature. It has higher breakdown voltage, ability to sustain large electric fields, lower electronic noise and high-temperature and high-power operation [1,2]. ZnO is much more resistant to radiation damage than other common semiconductor materials, such as Si, GaAs and CdS. The reactivity of ZnO makes it ideal to be used as a precursor for obtaining other compounds of Zn. ZnO has proved to be a boon for materials science as it has got a combination of unique properties like UV absorption, antimicrobial properties and steady thermal and optical properties. Nanostructures of ZnO can be synthesized into a variety of morphologies including nanowires, nanorods, tetrapods, nanobelts, nanoflowers, nanoparticles etc. [3,4]. The morphology of the resulting nanostructures can be tuned by changing the parameters relating to the precursor composition (such as the zinc concentration and pH) or to the thermal treatment (such as the temperature and heating ratio) [5]. Rajeswari Yogamalar et al. [6] found the use of multi capping agents in size confinement of ZnO nanostructured particles by simple chemical process. Several researchers have studied the effect of annealing and capping agent on structural, optical and morphological properties of ZnO nanoparticles [7,8]. In the present study the effect of EDTA capping on ZnO nanoparticles are investigated.

2. MATERIALS AND INSTRUMENTATION

2.1. Materials

All chemicals used in the present work *viz.*, zinc acetate dihydrate, sodium hydroxide and ethylenediaminetetraacetic acid (EDTA) were analytical reagent grade (Aldrich) and used without further purification. Solutions were prepared using deionized water.

2.2. Instrumentation

Thermo gravimetric and differential thermal analysis (TG-DTA) was carried out on TA instruments, model: Q600SDT TG-DTA in the temperature range of 20–1000 °C in nitrogen atmosphere at a heating rate of 20 °C/min. X-ray diffraction (XRD) pattern was recorded at room temperature by using X'Pert-Pro diffractometer system (scan step 0.05° (2θ), counting time of 10.16s per data point) equipped with Cu tube for generating Cu-Kα radiation (λ = 1.5406 Å). The morphology of the sample was recorded by field emission-scanning electron microscopy (FE-SEM) using Zeiss scanning electron micrometer. The Fourier transform infra-red (FT-IR) spectra of the nanoparticles were recorded on Avatar 330 FT-IR in the range of 4000–400 cm^{-1} using KBr pellets. The UV-visible (UV-vis) spectra were recorded on a Shimadzu UV-1650 PC spectrophotometer in the range of 200–800 nm. The photoluminescence (PL) measurements were recorded using a Varian spectrophotometer. The structural properties of the nanopowder were analyzed using Agilent-5500 AFM.

2.3. Synthesis of pure ZnO nanoparticles

Zinc acetate dihydrate (1 g) was dissolved in 50 mL distilled water with stirring. Sodium hydroxide solution (1 g NaOH in 50 mL water) was added drop by drop to zinc source precursor with constant stirring for 3 h at room temperature until it becomes homogeneous solution. After co-precipitation the synthesized ZnO were collected by distilled water washing. The washed precipitate was subsequently dried at 80 °C for 24 h and the obtained ZnO powder was calcined at 650 °C for 4 h.

2.4. Synthesis of surfactant assisted ZnO nanoparticles

Zinc acetate dihydrate (1 g) and 1 g of sodium hydroxide (NaOH) was dissolved in 100 mL of distilled water and stirred well. Then, 0.1 g of EDTA was added to zinc source precursor. The solution was stirred for 3 h at room temperature to get a homogeneous solution. The washed co-precipitates were subsequently dried at 80 °C for 24 h and finally, the synthesized surfactant assisted ZnO powders were calcined at 450 °C for 4 h.

3. RESULTS AND DISCUSSION

3.1. TG-DTA analysis

TG-DTA measurement was carried out to identify the thermal behaviour of ZnO precursors. Fig. 1a and 1b shows the simultaneous TG-DTA curves of the as-prepared ZnO. The TG analysis displays the weight losses in two stages. The first step is in the range of 100 to 180 °C, indicating the dehydration of surface water. The second phase of significant weight loss occurred in the range of 180 to 450°C representing the decomposition of the precursor ZnO. Furthermore, no weight loss and no thermal effect were observed for temperatures above 450 °C, indicating that decomposition does not occur above this temperature and that the stable residues may be ascribed to ZnO nanoparticles. On the DTA curve, a major exothermic peak was observed between 300 and 600 °C with a maximum at about 440 °C, indicating that the thermal events could be ascribed to the decomposition of the precursors of ZnO. Conversely, the TG and DTA curves of ZnO show no major variation on EDTA capping. However, the width of the exothermic peak was reduced in the DTA curve. These results are in agreement with previous reports [9,10].

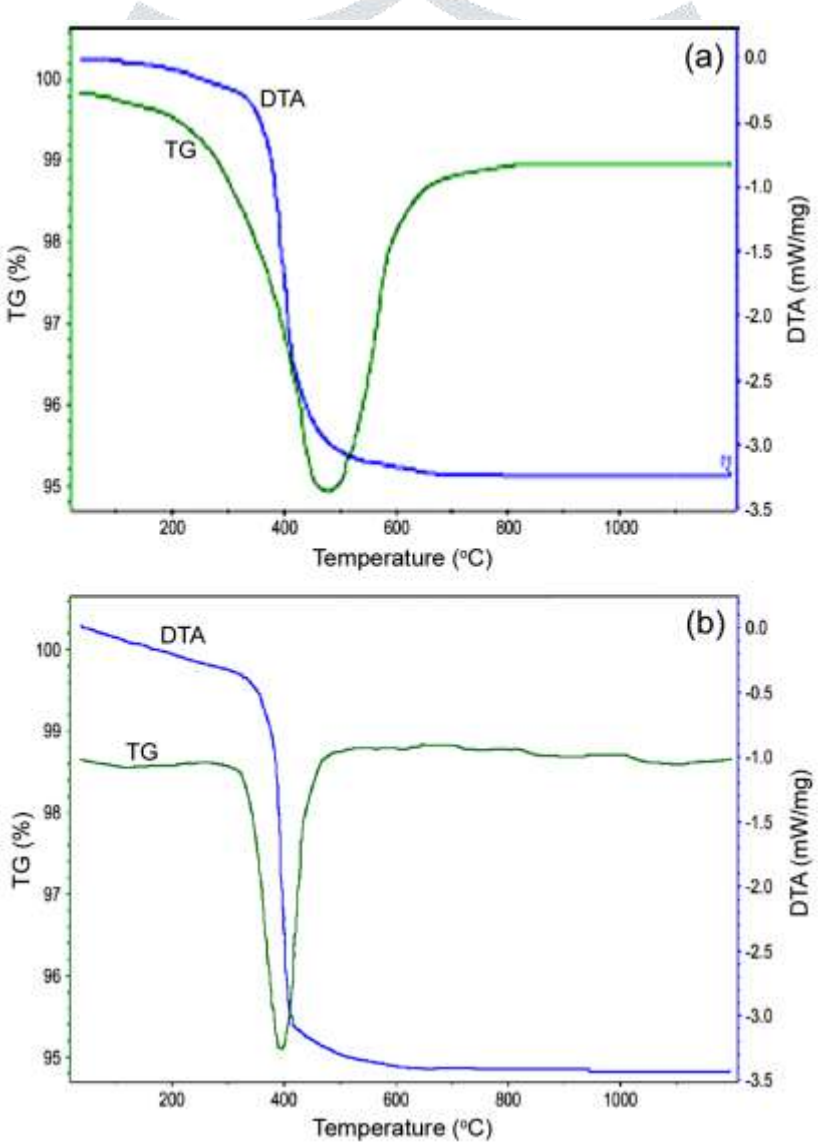

Fig. 1 TG-DTA curves of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.2. XRD analysis

The X-ray diffraction patterns of uncapped and EDTA capped ZnO nanoparticles are shown in Fig. 2a and 2b. All the diffraction peaks can be indexed to ZnO wurtzite hexagonal structure (JCPDS No. 89-7102). Diffraction patterns related to any impurity phases were not seen in the XRD pattern revealing the high purity of the available products. Also, it is considered that

the diffraction peaks of ZnO on EDTA encapsulation show line broadening, indicating the reduced size of the particles. The size of the samples could be evaluated using Scherrer equation $D = 0.89\ \lambda/\beta\ \cos\theta$, where λ is the wavelength (1.5406 Å), β is the full width at half maximum, and θ is the angle of diffraction. The average crystalline size was estimated as 30 and 20 nm for ZnO and EDTA capped ZnO, respectively. This result indicates that EDTA plays a significant role in controlling the ZnO particle. The coordination of Zn^{2+} with EDTA, can control the grain size of ZnO by reducing the reaction rate. Therefore, it is observed that, in the presence of EDTA, smaller grains are formed due to lower crystal growth and aggregation rate.

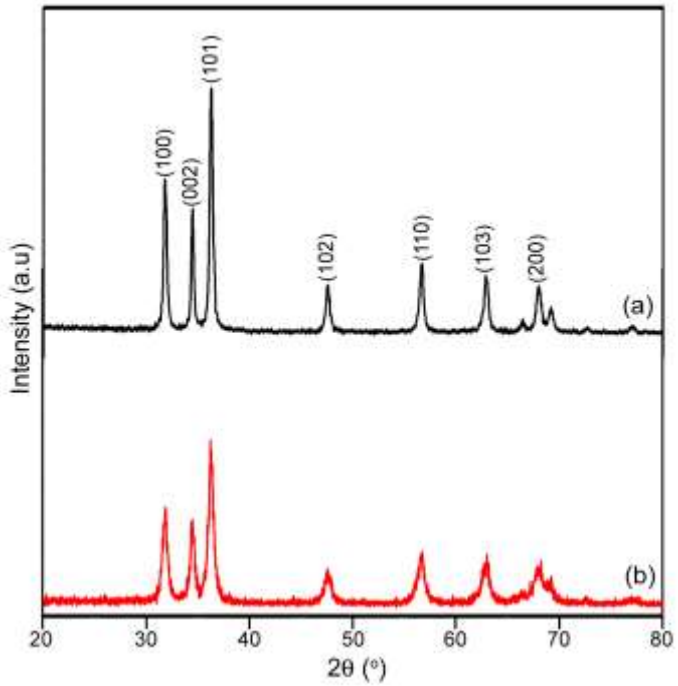

Fig. 2 XRD patterns of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.3. FE-SEM with EDX analysis

The morphologies of the samples were analyzed by FE-SEM. As shown in Fig. 3a, we found that the uncapped ZnO is mainly comprised of little agglomerated spherical particles with sizes in the range of 30–50 nm. However, on capping the FE-SEM exhibits well-separated spherical particles with a particle size confinement (Fig. 3b). EDX analysis has also been employed to explore the chemical composition of the samples. Fig. 4a and 4b show the EDX spectra of ZnO and EDTA capped ZnO nanoparticles, respectively. In both the cases, the signals of oxygen and zinc alone are seen suggesting the purity of the prepared products.

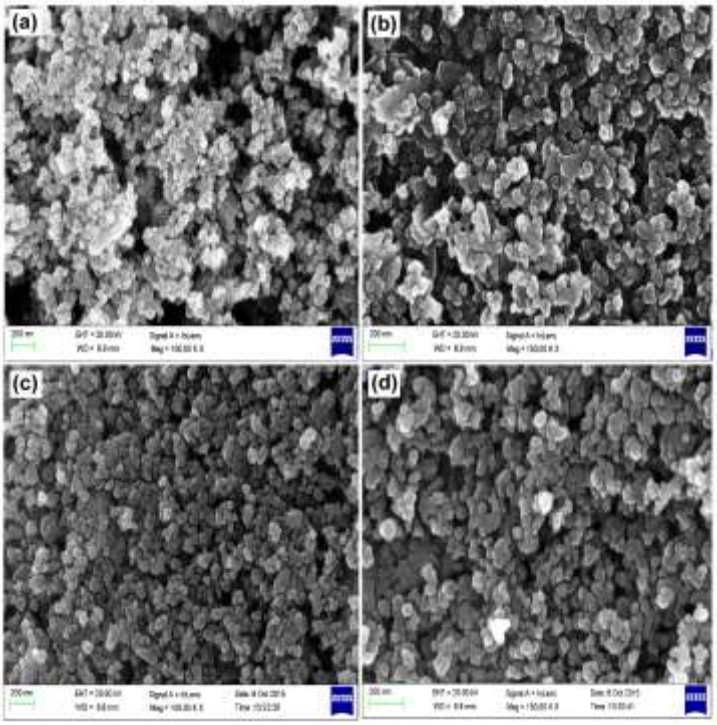

Fig. 3 FE-SEM images of a,b) pure ZnO and c,d) EDTA assisted ZnO nanoparticles (100 and 150 KX)

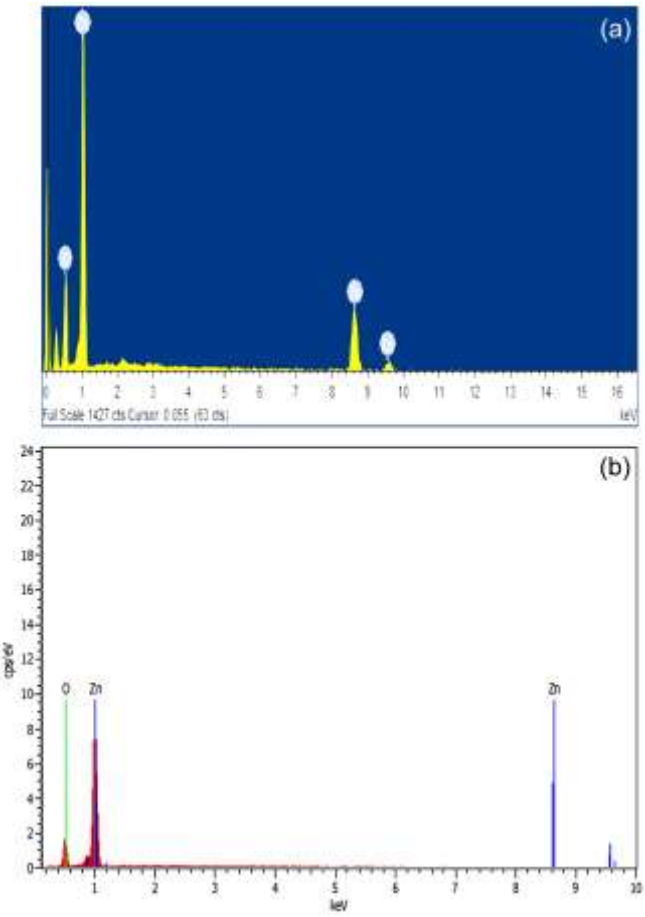

Fig. 4 EDX analysis of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.4. FT-IR analysis

FT-IR spectra of pure and surfactant-assisted ZnO nanoparticles are shown in Fig. 5a and 5b. For the pure ZnO, the functional group located at 428 cm^{-1} is attributed to the stretching vibration of Zn–O group indicating the existence of ZnO. The appearance of absorption bands at 3444 and 1624 cm^{-1} are assigned, respectively to the O–H stretching and bending vibrations of surface absorbed water [11]. The band obtained at 2366 cm^{-1} indicated the presence of CO_2 molecules, which samples might have trapped from the atmosphere during IR characterization [12]. On capping, these bands are shifted to the lower wave number regions (except ZnO stretching). The stretching vibration of ZnO was shifted to higher wave number region with broadening. The broad and well distinguished peaks of ZnO after capping suggest that the particles are of well separated. Furthermore, few additional absorption bands are appeared at 920, 1388 and 2926 cm^{-1} in the capped ZnO. The bands at 920 and 1388 cm^{-1} are due to the presence of inorganic ionic compounds [13] in the EDTA whereas, the band at 2926 cm^{-1} attributed to C–H stretching [14].

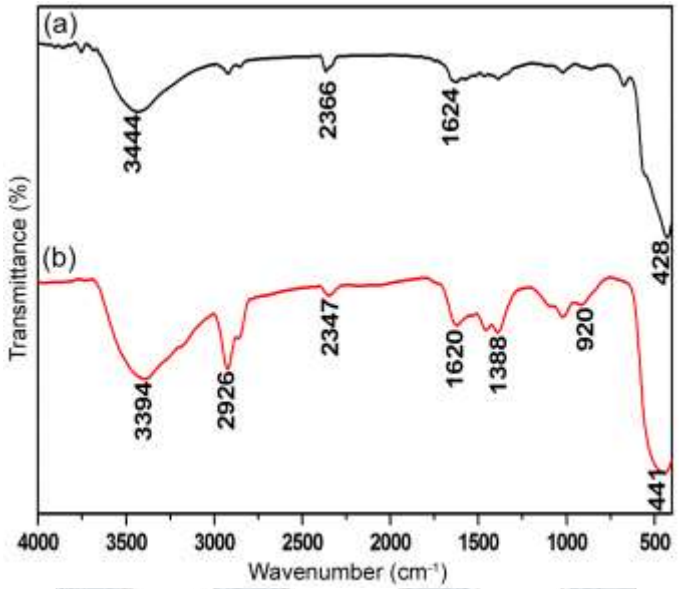

Fig. 5 FT-IR spectra of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.5. Optical study

3.5.1. UV-visible analysis

The UV-visible absorption spectra of the pure ZnO and ZnO:EDTA nanoparticle samples are shown in the Fig. 6a and 6b. A careful perusal of this image shows that the wavelength absorption peak of the ZnO is at around 372 nm, and shifts to the lower wavelength (367 nm) for EDTA capped ZnO as a result of quantum confinement effect. The band gap values of the products are determined from the simple formula $E = hc/\lambda$. The obtained band gap values are 3.34 and 3.39 eV, respectively for ZnO and capped ZnO.

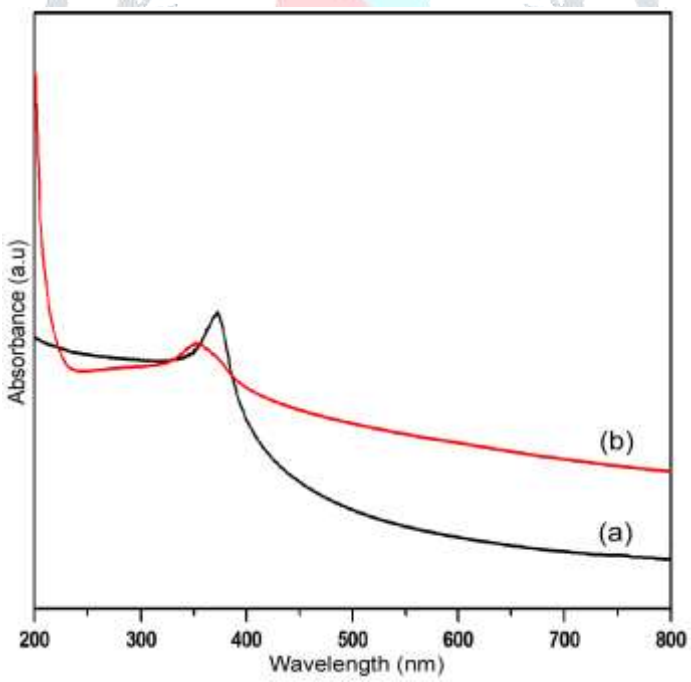

Fig. 6 UV-visible absorption spectra of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.5.2. PL analysis

The room temperature photoluminescence emission spectra of the pure and EDTA assisted ZnO nanoparticles are shown in the Fig. 7a and 7b. From the figure, the PL spectrum of pure ZnO shows a less intense UV emission (388 nm) and three shallow visible emissions (450, 470 and 500 nm). The less intense UV emission is originated from near-band-edge emission of ZnO. The rest of the visible emission are ascribed to defects related emissions. Further, on EDTA capping, the emission band in the UV region was diminished but intense visible emissions are predicted confirming the generation of more defects on capping.

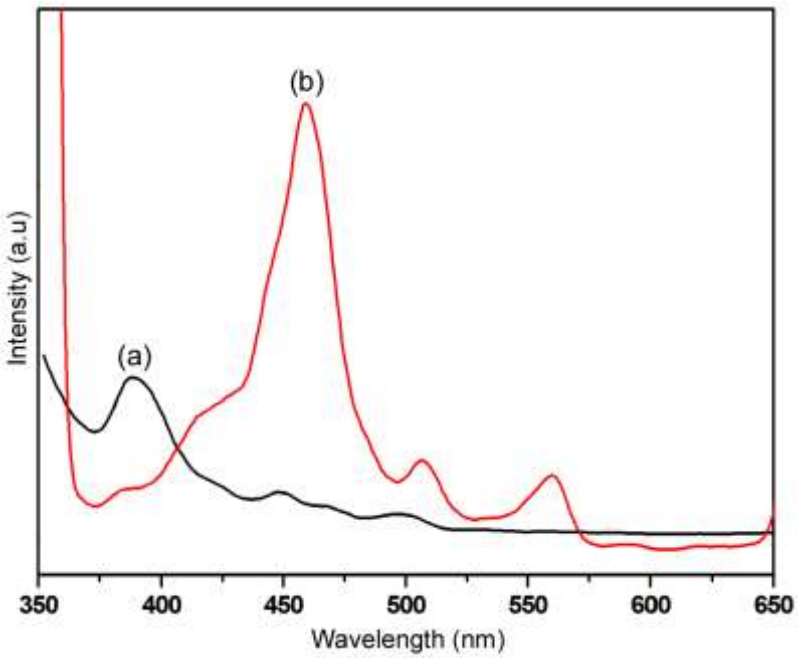

Fig. 7 PL spectra of a) pure ZnO and b) EDTA assisted ZnO nanoparticles

3.6. Surface topographic analysis

Fig. 8 shows a topographical image of surfactant capped ZnO nanostructure recorded in contact mode. The analysis revealed that the prepared sample exhibited very smooth surface and good crystal structures. The size of the surfactant capped ZnO was in the range of 5–45 nm.

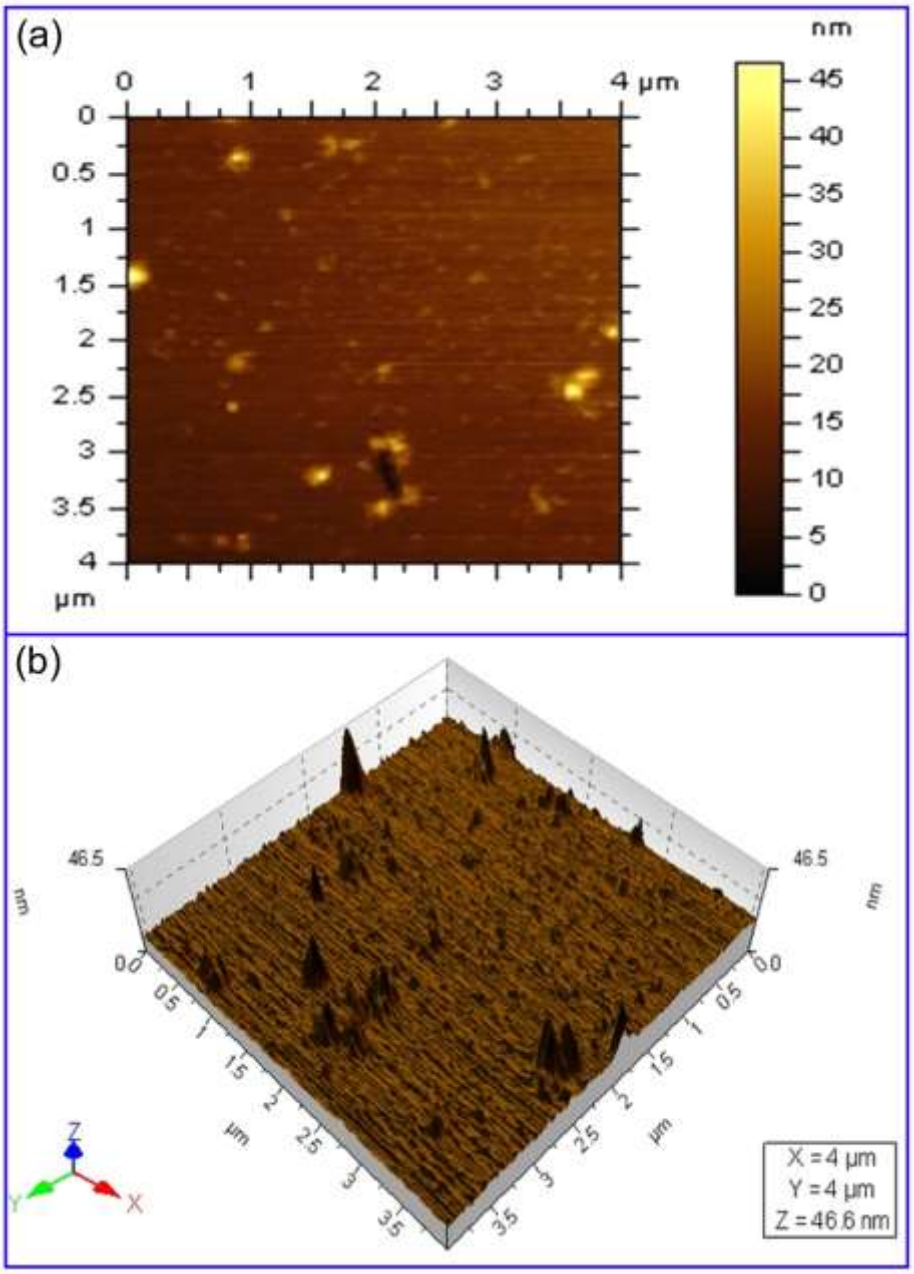

Fig. 8 AFM images of EDTA assisted ZnO nanoparticles: a) 2D image and b) 3D image

4. CONCLUSION

We synthesized free-standing and EDTA encapsulated ZnO nanoparticles by chemical precipitation method. Thermal analysis confirms that the crystalline phase of ZnO formed at the annealing temperature of 450 °C. The results of XRD indicate that without capping, the ZnO nanoparticles crystallized in a single wurtzite phase with a particle size of about 30 nm, while upon EDTA capping the size of ZnO reduced to 20 nm. FE-SEM studies showed that after capping ZnO nanoparticles posses better morphology than the uncapped one and also EDTA encapsulation on ZnO decreases the size of the particles. The FT-IR analysis has confirmed the formation of ZnO by the appearance of stretching vibration of ZnO. The absorption maximum of ZnO showed a blue shift on capping as a result of strong quantum confinement. Furthermore, the PL emission spectra demonstrate enhanced defects related visible emissions on capping. The surface topographical (AFM) analysis of capped ZnO revealed that the prepared sample exhibited very smooth surface and good crystals structures with sizes in the range 5–45 nm. Therefore, it is concluded that the surfactant EDTA-mediated ZnO synthesis is a promising approach to harvesting well crystalline, smaller sized and optically stabilized ZnO nanoparticles.

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