

Microwave assisted citrate gel combustion synthesis of ZnO Part-I: assessment of structural features

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Nanocrystalline ZnO containing Ag^+ , Al^{3+} and mixtures of (Ag^+ , Al^{3+}) as dopants has been synthesized through a microwave assisted citrate gel decomposition technique. The study has two parts and in part-I, the process conditions for obtaining nanocrystalline ZnO have been investigated and the influence of pH upon microwave assisted gelation, interaction of microwaves with the precursor gels, evolution of structural features and ZnO particle morphology have been studied. Single phase ZnO has also been prepared to compare the effect of dopants. The analyses of the ZnO powders have been supported by XRD, TEM and SEM. The optimum is a gel precursor containing zinc nitrate and citric acid prepared in the molar ratio of 1 : 2 and pH = 6.5, which results in nanocrystalline ZnO directly under microwave calcination at 950 W within 20 minutes. The TEM analysis confirms the ZnO particles have a size below 50 nm. The addition of dopant ions resulted in the formation of ZnO nano clusters. All these powders have also been studied for their photocatalytic and photoluminescence functional properties and the results are reported in part-II.

Key words : Microwave calcination, Citrate gel, Dopants, Nanocrystalline ZnO.

Introduction

Zinc oxide (ZnO) is a fascinating, n-type II-VI semiconducting material which exhibits a wide direct band gap energy [$E_g = 3.35$ eV] and a large exciton binding energy [60 meV]. Presently, development of ZnO nano structures such as nano scale spherical particles, tubes, rods, arrays, sheets and hollow spherical particles have been given more importance due to their multifunctional characteristics and possible applications in the forefront areas, namely biosensors, smart pigments, H_2 gas storage and CO_2 capturing agents [1-6]. Chemical methods such as hydrothermal, solvothermal and sol gel synthesis techniques have been reported extensively for nano ZnO [5].

Combustion synthesis is another capable technique for obtaining ZnO powders with controlled size and shape [6]. However, in this technique, the various processing parameters such as the oxidizer to fuel ratio, chemical nature of the starting precursor [e.g nitrates, sulphates and acetates], fuel source, pH of the precursor solution and the mode of heating have to be carefully optimized for producing fully-crystalline ZnO nano particles. For example, when glycine was used as the fuel, hexagonal nanocrystalline ZnO was obtained [7]. Whereas when a gel-template fuel such as gelatin was used, the ZnO particles

attained spherical and elliptical shapes [8]. Similarly when the combustion synthesis was conducted using zinc metal, zinc nitrate and glycine mixtures, the ZnO morphology varied from rods to needles and finally to tetra-pods [9].

In this study, combustion synthesis has been conducted under microwaves using citric acid and zinc nitrate as fuel and oxidizer respectively. This study is very much close to the solution-combustion process [SCP] reported by Park and his coworkers [10]. However, in our work zinc nitrate and citric acid reactants were dissolved in aqueous medium and the microwave energy was utilized for the gelation followed by combustion. Microwave processing is well known in ceramic materials research and detailed reviews were published in the early 90's by the pioneer researchers Sutton and Clark [11]. Agrawal and his team have extensively applied this technique for producing varieties of ceramic oxides and sintered ceramics [12]. The main advantage of microwave energy is its rapid heating rates due to the dielectric polarization of the precursor molecules. Thus we employed microwaves for the rapid gelation as well as combustion and calcination reactions. In the first part of the study, the effects of microwave gelation at various pH ranges, the interactions of microwave energy with various zinc nitrate/citric acid molar ratios, and the effect of microwave heating upon crystallinity, structural features, and particle morphology were investigated and the optimum conditions for obtaining fully crystalline ZnO nano particles are reported. The functional properties of doped ZnO are reported as second part of the study in this same journal.

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Experimental

Materials: Analytical grade zinc nitrate tetrahydrate (Central Drug House (p) LTD, Purity 99%), anhydrous citric acid (Merck private limited, Purity 99%), ammonia solution 25% GR (Merck private limited, Purity 99%), aluminium nitrate nonahydrate (Merck Limited, Purity 99%) and silver nitrate (Merck Limited, Purity 99%) were procured as reactants and all the reagents were used in the as-received condition. Double distilled water was used as the medium.

Microwave-assisted citrate gel decomposition synthesis

In a typical experiment, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and citric acid reactants in the mole ratios 1 : 1, 1 : 2 and 1 : 3 were taken and dissolved in an excess quantity of water. For example, in the 1 : 1 composition, 16.06 g zinc nitrate and 12.93 g citric acid were dissolved in 250 ml of distilled water. A basis of 5 g was fixed for the synthesis. The initial pH of the precursor solution was found to be acidic which was increased to 6.5 by the addition of 10% NH_4OH solution. The reactant solutions were mechanically stirred for 2 h and then inserted into a conventional microwave oven (Electrolux, 950 W, 2.45 GHz). The solution was treated under microwaves at an input power level of 300 W. The solution became a viscous liquid in 10 minutes and finally turned to a transparent gel in 30 minutes. Subsequently the gel after complete drying was transferred into an alumina crucible (120 ml capacity) and subjected to microwaves at a power of 500 W. The precursor gel mixture started absorbing the microwaves instantaneously and within 120 seconds of exposure time, a rapid combustion occurred and the reaction mixture started to decompose releasing brown nitrogen oxides fumes. Upon continuous exposure, the precursor mixture partially melted and foamed up. Within an exposure of 15 minutes, the reaction mixture produced a porous, black colored residue. At this stage the reaction was stopped. The rise in reactant temperature was not measured but once the reaction was stopped the temperature inside the alumina crucible was measured and found to be 320 °C.

The black powder was collected after cooling and ground simply by a mortar-pestle. After grinding, it was transferred again into an alumina crucible and subjected to microwave-assisted calcination. The calcination was carried out at 950 W for 30 minutes. The temperature inside the crucible was measured using an external thermocouple and it was observed as 485 ± 20 °C. The whole synthesis procedure was repeated for other citric acid/zinc nitrate reactant mixtures prepared with 1 : 2 and 1 : 3 molar ratios and at pHs varied from 6.5 to 9.9. To understand the complete thermal decomposition of the gels, the dried precursor gel was subjected to thermo gravimetric analysis [TGA] using a TG/DT-50H (SHIMADZU, Japan) at a constant heat flow of $10^\circ \text{Kmin}^{-1}$ in an air atmosphere up to 600 °C. From the TG analysis, it was established that a temperature of at least 500 °C was required to obtain

fully-crystalline ZnO. In our experiments, this condition was established by directly heating the gel under microwaves at 950 W.

Synthesis of doped zinc oxide

Microwave-assisted citrate gel decomposition was extended to prepare aluminium and silver doped ZnO. For synthesizing silver ion doped ZnO, 2 wt% silver nitrate salt was dissolved in the zinc nitrate solution. Similarly nitrate salts of aluminium (2 wt%) and zinc were dissolved to make aluminium-doped ZnO. In the case of mixed dopants, 2 wt% aluminium and 1 wt% silver nitrate salts were dissolved in the zinc nitrate precursor solution. The precursor pH was controlled at 6.5 and the citric acid fuel-to-nitrate ratio was fixed at 1 : 2. All the other synthesis conditions such as microwave exposure schedule, time, and the calcination conditions were kept constant.

Characterization

The crystalline nature and phase evolution of the as-prepared and calcined ZnO powders were studied by powder X-ray diffraction using a Philips, X'pert Pro with a monochromator on the diffraction beam side ($\text{Cu K}\alpha$ radiation, $\lambda = 0.154 \text{ nm}$). The crystallite size of the powder was calculated using Scherrer's equation [13]. The ZnO powder morphology was probed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM studies were carried out by a JEOL 5600 SL-SEM, operated at 15 KV. TEM was performed with a JEOL JEM 2000X, using carbon coated copper grids. Selected area electron diffraction (SAED) patterns using TEM were also taken to identify the crystalline nature of the samples.

Results and Discussions

The citrate gel decomposition process is better known as a thermally-induced anionic oxidation-reduction reaction [14]. When citric acid is mixed with precursor salt in an aqueous solution in specific ratios or concentrations, chelates are formed between metal ions facilitating atomic scale distribution of ions in a polymer network. Heating of this resin causes the breakdown of the polymer and a solid amorphous precursor material is finally obtained. On subsequent heating between 500 to 900 °C, the cations are oxidized to form the respective metal oxides.

In the microwave-assisted solution-combustion route, the gelation behaviour was first attempted at various pH values. A homogenous gelation was found only at pH = 6.5 due to high deprotonation of citric acid with a maximum coordination of Zn^{2+} . In all the other pH ranges, only a thick white precipitate was formed indirectly showing the instability of the Zn^{2+} complex with citric acid. When the pH is regulated by adding a dilute NH_3 solution, ammonium carboxylate bonds are generated which acts as a cross linking or a bridging agent produces a viscous gel. During microwave heating, the precursor gel

spontaneously attracts microwaves and interacts efficiently resulting in a rapid increase in the reaction temperature. The high microwave interaction with the reaction mixture is mainly by the high polarity of the solvent water, high dielectric constant of the ammonia solution ($\epsilon \approx 22$) and presence of microwave-active functional groups in the citric acid fuel. At low input power, say up to 200 W, we observed that the reactant mixture absorbs microwaves but generates only a low temperature ($\sim 70^\circ\text{C}$). No gelation is noticed at this condition, except a very slow evaporation of solvent water. However, when the microwave power is increased to 300 W, there is an accelerated microwave-matter interaction. With this condition, the heat generation is at faster rate and a temperature of $> 110^\circ\text{C}$ is noticed within 20 minutes of exposure time. Such rapid heating generates a transparent viscous gel. The gelation is seen only when the Zn^{2+} /citric acid complex is prepared at pH 6.5 with molar ratios 1 : 1 and 1 : 2. Beyond pH 6.5 and a zinc/citrate ratio above 1 : 2, the stability of the complex collapsed. Such instability is caused by the high polarity of the whole reaction mixture due to the presence of excess ammonia. The microwaves interact very rapidly to this highly polar medium, de-stabilize the zinc-citrate complex and finally produce a white precipitate. Also, in this case, the water medium evaporates at a faster rate further increasing the precipitation tendency. Therefore, we fixed the molar ratio of 1 : 2 and pH 6.5 to achieve a homogenous gelation for the preparation of nano-ZnO under microwave assisted combustion. Infact a homogeneous gelation is usually preferred for fine-particle formation. In the case of conventional combustion, the conversion of a precursor solution to a homogeneous gelation will take several hours [6, 14]. The microwave energy is found to be more advantageous in this regard since the gelation occurs within 20 minutes of microwave exposure. Gaseous products such as N_2 , CO , CO_2 and NO_x were also released during microwave-assisted gelation. The release of NH_3 and N_2 gases can be understood from the thermogravimetric patterns.

The TGA curves obtained from the thermal decomposition analysis of microwave-derived gel, prepared at pH 6.5 with a Zn^{2+} /citric acid ratio 1 : 2 are presented in Fig. 1. Three major decompositions were observed and in the first step a drastic weight loss occurred up to 240°C . At this temperature melting of the citric acid fuel followed by the decomposition are usually expected. Precisely, at 157°C the citric acid melting is seen but it decomposes strongly between the temperatures 215 to 220°C . The weight loss is also associated partly with the dehydration of the free water molecules present in the gel network. The total weight loss of 49.47% is seen in the first stage. The second step took place between 240 to 370°C and in this temperature range, the decomposition of metal complexes to metal hydroxides, decomposition of free nitrates, formation of byproducts such as ammonium citrate were expected to occur. Nitrates thermally decompose below 350°C with the evolution of nitrogen oxides [NO_2 , NO and N_2O_5] [15].

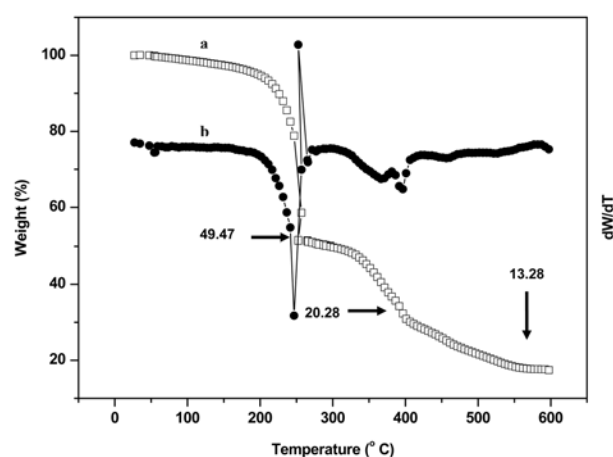


Fig. 1. TG analysis of precursor gel (a) Weight loss pattern (b) Derivative Plot.

In the second stage the total weight loss is calculated as 20.28 wt%. The total weight loss in both these steps comes to nearly 70 wt%. This shows that the reactant zinc nitrate + citric acid required a minimum of 400°C for the complete decomposition and formation of nano crystalline ZnO.

The TG pattern confirms that there is no major weight loss above 550°C . Although the citric acid undergoes almost complete gasification below 400°C , the thermal analysis data in air shows the combustion of a small amount of carbonaceous material at 471°C . The third stage above 400°C is associated with the loss of free carbon as CO_2 and dehydroxylation of zinc hydroxide into ZnO. As evidenced from the thermogram, an intermediate decomposition between 250°C to 300°C is crucial, because at this range the nitrate and citrate gel networks collapse and primary zinc hydroxide nuclei formation starts in the precursor gel mass. The nuclei size formed should be controlled because it gets converted to crystalline ZnO upon further calcination. TG analysis, confirmed that the precursor gel became fully-crystalline ZnO powders only above 400°C . As observed in the TG results, the dehydration as well as the evolution of gaseous products was taking place when the precursor gel was exposed to microwaves at 500 W for 30 minutes. However, the gel only gets converted to a dried black foam at this stage and it became a white powder only after the calcination at 950°C . The powder crystallinity is confirmed from the X-ray diffraction analysis which is presented in Fig. 2.

The powder X-ray diffraction analysis of the porous black residue showed three broad peaks correspond to the hydroxylated zinc and partially-formed ZnO nuclei [Fig. 2 (insert)]. At microwave input energy of 500 W the reaction temperature was only $< 320^\circ\text{C}$. ZnO nuclei are formed by the molecular level interactions of microwaves with the precursor matter. Apart from the molecular heating effect, the energy released by the citric acid fuel during combustion was also another possible reason for the formation of ZnO nuclei. A theoretical energy of 10.2 kJ/g is expected when the citric acid fuel is decomposed. The

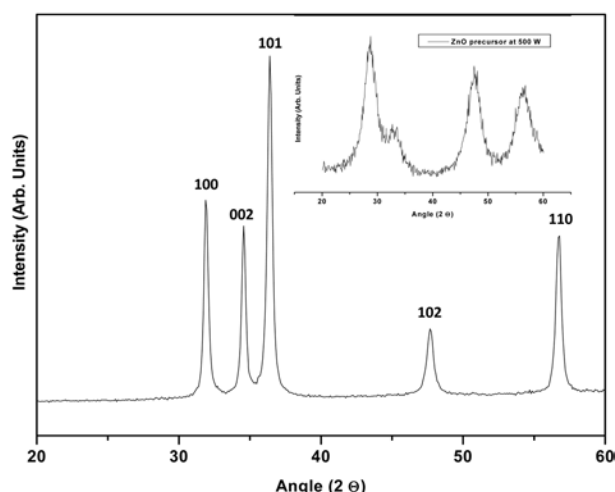


Fig. 2. X-ray analysis of microwave-assisted calcined nanopowder at 950 W [insert- microwave exposed ZnO precursor at 500 W].

primary nuclei, formed at 500 W, are converted to fully-crystalline ZnO at high microwave input power. Fig. 2 (main part) corresponds to the X-ray pattern of the sample calcined under microwaves at 950 W. It clearly shows intense diffraction peaks corresponding to the fully-crystalline ZnO phase at different crystallographic planes with a dominant (101) orientation. All the entire diffraction peaks are similar to those of a bulk wurtzite ZnO, which has a hexagonal structure [lattice parameter $a = 3.22 \text{ \AA}$, $c = 5.2 \text{ \AA}$, space group $P6_3mc$], and its diffraction data is in good agreement with the JCPDS file (75-1526). The primary crystallite size $D = 36 \text{ nm}$ was determined from the (101) peak.

The SEM images of ZnO powders prepared by both microwave and conventional citrate gel decompositions are shown in Fig. 3(a&b). The conventionally processed ZnO shows the formation of hexagonal plate particles with a size as large as $2 \text{ }\mu\text{m}$ at 650°C (Fig. 3(a)). The growth of hexagonal plates may be due to the surface tension of the citric acid-chelated precursor gels [16]. The distributions of nano size particulate agglomerates or clusters are seen only in some selected areas. Such a variation indicates

that the conventional gelation resulted in a high degree of non homogeneity due to differential rates of evaporation of solvent water from the gel network. Whereas the ZnO powders prepared under microwave-assisted processing shows extremely fine, homogeneous ZnO clusters of size $< 500 \text{ nm}$. The clusters have many nano size ZnO crystals (Fig. 3(b)) which is further clear from the TEM analysis shown in Fig. 4.

The TEM and SAED analysis in Fig. 4 reveals polycrystalline, hexagonal ZnO comprised of agglomerated nano particles with a particle size below 50 nm . This value was close to the crystallite size measured from the XRD data. Moreover, the particle size of microwave-derived ZnO is smaller than the conventional citrate gel derived ZnO [17].

Characterizations of doped ZnO

Earlier reports have shown that the Al and Ag doping favors band gap reduction and hence the optical transmission in the visible and near-infrared (IR) regions. This is expected because of the change of valence band by Ag-O linkage due to the substitution of Ag^+ into Zn^{2+}

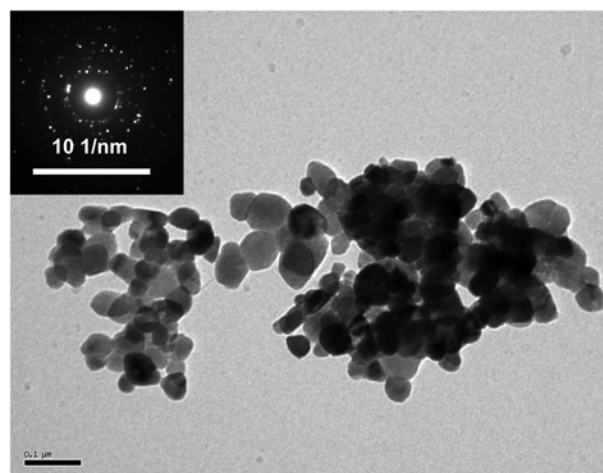


Fig. 4. TEM of nano crystalline ZnO powder through microwave-assisted calcinations with precursor ratio 1 : 2 M at pH 6.5 (Insert- SAED corresponding to polycrystalline ZnO nano powder).

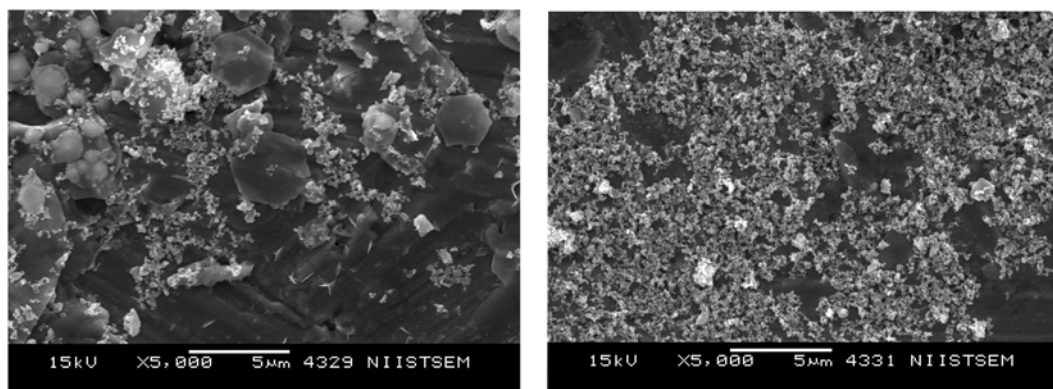


Fig. 3. Morphological variation of ZnO (a) derived through conventional citrate gel decomposition ($650^\circ\text{C}/2 \text{ hrs}$) (b) microwave-assisted citrate gel decomposition.

site [18, 19, 20]. Silver ion doping is widely reported in ZnO. In most of the studies, the doping is employed at a high content of silver, say 2–4 wt%.

The crystalline nature of the doped ZnO corresponding to Ag and the mixture of Ag^+ + Al^{3+} dopants are presented in Fig. 5. One of the main observations is that the peaks are identical with the undoped counterparts and all the peaks can be indexed to a pure hexagonal phase, wurtzite ZnO. However a marginal reduction in the crystallite size of 24 nm is observed in doped ZnO. Since the percentage of doping is very little there is no extra diffraction lines observed for Al^{3+} and Ag^{+1} oxides. Therefore it can be assumed that all the dopant ions [Al^{3+} and Ag^{+1}] are possibly substituted in Zn^{2+} sites.

The morphologies corresponding to doped and undoped ZnO are presented in Fig. 6(a-d). The TEM images clearly indicate the reduction in particle size due to dopants. The doped ZnO powders are nano crystalline with an average particle size less than 30 nm. This is in good agreement with the crystallinity features and crystallite size values calculated from the XRD analysis. However, the doped ZnO showed a high tendency for agglomeration. In doped ZnO powders, the basic hexagonal plate morphology is changed to an irregular morphology. Even though the amount of doping is significantly small, the microwave interaction with the doped precursor solution seems to be aggressive; possibly due to the increased bulk electronic conductivity of the soluble Ag^+ and Al^{3+} ions. Similar to the undoped samples, the doped ones also possessed ring and spot patterns in SAED indicating the polycrystalline nature.

Conclusions

Microwave-assisted citrate gel decomposition technique was applied to synthesize ZnO with and without dopants. In the first part of the study, the dependence of powder processing conditions such as initial precursor solution pH and oxidizer-to-fuel ratio were investigated with respect to the powder properties such as crystalline nature, particle size and morphology. The zinc nitrate and citric acid precursor solution prepared at pH 6.5 with Zn^{2+} /citric acid ratio 1 : 2 was found to be optimum for achieving

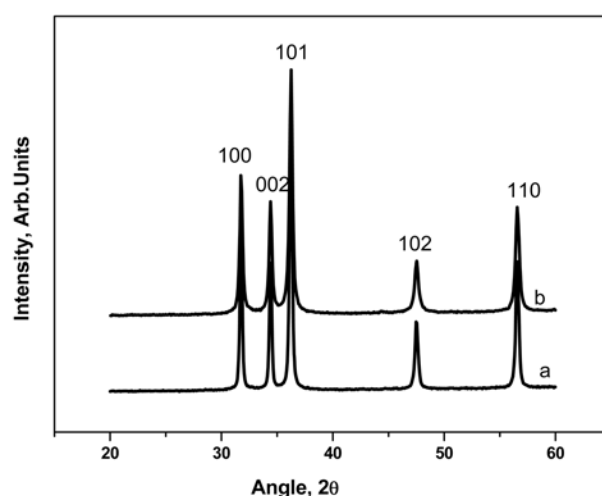


Fig. 5. XRD patterns of samples dried at 650 °C (a) ZnO (b) ZnO doped with 1% AgNO_3 and 2% $\text{Al}(\text{NO}_3)_3$.

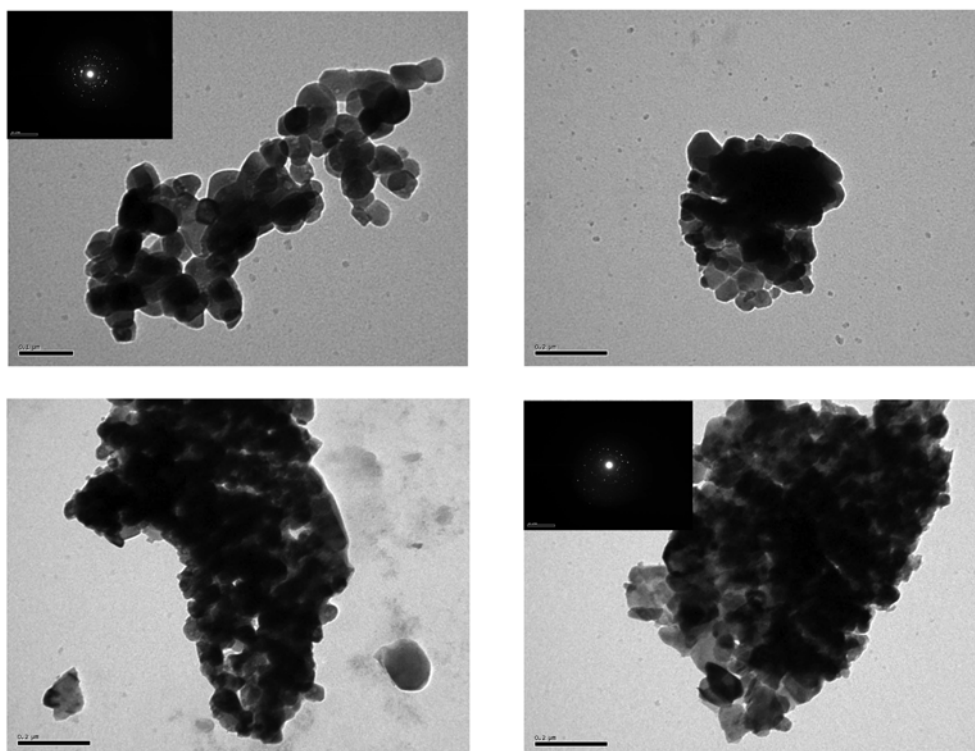


Fig. 6. TEM of microwave-assisted citrate gel derived undoped ZnO and doped ZnO nano powder (at 650 °C/2hrs) (a) undoped ZnO (insert: SAED of undoped ZnO nano powder) (b) 2% Al doped ZnO (c) 2% Ag doped ZnO (d) 2% Al and 1% Ag doped ZnO.

homogeneous gelation under microwave heating. The process yielded fully-crystalline ZnO nano powders with a mean particle size below 50 nm. When the microwave input energy is moderate, say 500 W, the precursor mixture showed the presence of active ZnO nuclei within 20 minutes and upon microwave calcination at 950 W, the precursor mixture became fully-crystalline ZnO. While doping, ZnO possessed no significant change in the crystal symmetry. However, the clustering of nano particles was considerably increased with an increase in dopant addition. The TEM studies confirmed the particle size of the doped ZnO as below 50 nm and the SAED patterns revealed the polycrystalline nature of the samples. The functional properties of such doped ZnO are assessed in Part II of this study.

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