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## **COMPARISON BETWEEN ZINC OXIDE SYNTHESIS VIA SOL-GEL TECHNIQUE AND PECHINI METHOD**

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### **ABSTRACT**

Nanotechnology met a lot of applications in several advanced fields. Recently it has gained a lot of research efforts. Zinc oxide nano materials are promising candidates for nano electronic and photonics. ZnO is unique because it exhibits dual semiconducting and piezoelectric properties and can be used in gas sensing and in biomedical science because it is bio-safe. ZnO is a material that has diverse structures, whose configurations are much richer than any known nanomaterials including carbon nanotubes. Zinc oxide powders were synthesized via, sol-gel technique and Pechini method using zinc acetate dihydrate as source of zinc oxide. The obtained zinc oxide powders were dried at 100°C and calcined at different temperatures (500, 700 and 900°C). The samples were characterized by FTIR and their morphology were examined by SEM. The advantages and disadvantages of the two techniques and their expected applications were recorded.

### **KEY WORDS**

Zinc oxide, nanoparticle, sol-gel, Pechini.

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## INTRODUCTION

The unique and fascinating properties of nanostructured materials have triggered tremendous motivation among scientists to explore the possibilities of using them in industrial applications. In particular, the electronic and optical properties of nanostructured materials have been of interest because of their potential applications in the fabrication of microelectronic and optoelectronic devices application. The performances of such nanodevices are expected to be superior as the quantum confinement of charge carriers in small dimensions give rise to spectacular variation in properties [1]. Wurtzite structured ZnO, a key transparent semiconducting oxide, has versatile properties that are important for applications in electrical, optoelectronic [2], photovoltaic devices, and sensors. Quasi-one-dimensional nanostructures of ZnO, such as nanowires, nanobelts, and nanotubes are attracting much interest for their properties and potential applications in nanotechnology [3]. Zinc oxide is a material having a band gap of 3.2 eV. , this band gap value is equivalent to ultraviolet light energy, which means that zinc oxide has ability to absorb UV light [4].

ZnO also has no absorption in the visible range. Therefore nano-particles of zinc oxide exhibit characteristics of transmitting visible light and absorbing UV light. By taking advantage of these characteristics, nano-particle zinc oxide is utilized in various fields such as an UV-absorbing or anti-fading film for fluorescent lamps and a sunscreen material [5].

Zinc Oxide is an important material with wide ranging applications in varistors, gas sensors [6,7], surface acoustic wave devices [8], transparent conducting oxide electrodes [9], solar cells [10], blue/UV light emitting devices [11], catalysis [12], etc. A wide variety of synthetic methods have been employed to prepare ZnO colloids and films, some of which are sol-gel [13-15], Pechini method [16,17], spray pyrolysis[18], metal-organic chemical vapor deposition,[19]and cathodic electro deposition [20], pulsed laser deposition [21] or sputtering [22-24].

In this work zinc oxide colloid was prepared via sol gel technique and Pechini method using zinc acetate as a precursor. The factors affecting preparation were selected to be the same for comparing the two methods. The colloids formed were dried at 100°C and calcined to 600°C 700°C and 900°C. FTIR was used to characterize the formed bulks. The morphological analyses of the formed powders were studied by scanning electron microscope. The factors affecting the formation were studied.

## EXPERIMENTAL SECTION

### 1-Chemicals

The source, origin and specifications of the used chemicals are listed in the following table. They were used in the experimental work without further purification.

Table 1. Chemicals used and their specifications

Name	Formula	M wt. g/mole	Grade %	Source
Zinc acetate dihydrate	$Zn(CH_3COO)_2 \cdot 2H_2O$	219.49	98	May & Baker, England
Ethanol	$C_2H_5OH$	46.07	>99	Merck Germany
Lithium hydroxide monohydrate	$LiOH \cdot H_2O$	41.96	99	BDH, England
Citric acid	$HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$	210.4	99	BDH, England
Ethylene glycol	$HOCH_2-CH_2OH$	62.07 (sp.g. 1.115)	pure	Koch-light, England

## 2- INSTRUMENTATION:

The SEM was fulfilled with Philips XL30 scanning electron microscope. The powder sample was placed on double face carbon adhesive tape fixed in the microscope vacuum chamber. After complete evacuated of the chamber, an electron beam was generated till the sample picture was clear on the computer screen.

The infrared spectra of the products were carried out with Mattson Infinity Series FTIR, in the wave number range from 400-4000  $cm^{-1}$  using the KBr disc technique.

A 198 mg of very fine grinding and dried KBr mixed with 2 mg of a sample for 30 seconds in special vibrator. The mixture was placed in a special die compressed with hydraulic press for 15 min, under 5000 PSI in a vacuum press to form a transparent disc.

**3-The preparation of zinc oxide colloidal via sol-gel** was essentially the same as that of Spanhel [13]. The procedure consists of the following steps:

A 0.1M ethanolic solution of zinc acetate was prepared by dissolving 0.05 mol of zinc acetate in 0.5 L of ethanol in a 1-L round-bottom flask. The flask was fitted with condenser and calcium chloride moisture trap and refluxed while stirring (with a magnetic stirring bar) for 180 min at 80°C. The condensate was collected continuously at the end of this procedure; 0.2 L of reaction product (precursor) and 0.3L of condensate (which was discarded) were obtained. The 0.2L of precursor was diluted back to the original volume of 0.5 L with absolute ethanol. Then, 0.07 mol of lithium hydroxide powder ( $LiOH \cdot H_2O$ ) was added to this precursor to give a final lithium concentration of 0.14 M. The mixture was then hydrolyzed in an ultrasonic bath to accelerate the reaction. This hydrolysis reaction was continued at room temperature until lithium hydroxide powders no longer visibly present (about 1hr).

The ZnO colloidal suspension was filtered to remove any undissolved lithium hydroxide that might remain. This colloid was then concentrated by evaporation from 0.1 M to 0.5 M (with respect to zinc concentration) by heating at 80°C with stirring, the product is a colorless liquid, and if it remains in open atmosphere more than 3 days, the white bulk of ZnO will appear. The zinc oxide bulk dried at 100°C for 24 hr.

The produced samples were fired to 500°C and 700°C. The morphology of the formed samples was analyzed by SEM and the all formed samples characterized by FTIR.

#### 4-The preparation of zinc oxide powders using Pechini method same as prepared by Lima et al [15].

The process consists of following steps:

A 0.2 M citric acid was prepared in 1-L flat bottom round flask (dissolved in deionized water). The flask was fitted with reflux condenser while stirring (with a magnetic stirring bar) for 30 min at 80°C, then 0.01M zinc acetate dihydrate  $Zn(CH_3COO)_2 \cdot 2H_2O$  was added until completely dissolved about 30 min.

After complete dissolution of the reactants, ethylene glycol was added to the mixture with molar ratio 1:1 with citric acid while stirring and heating at 80°C for 3 hrs under reflux condenser. The viscosity of the solution increased by time due to the formation of polyester which dried at 100°C and calcined at 500, 700 and 900°C. The morphology of the formed samples was analyzed by SEM and the all formed samples characterized by FTIR.

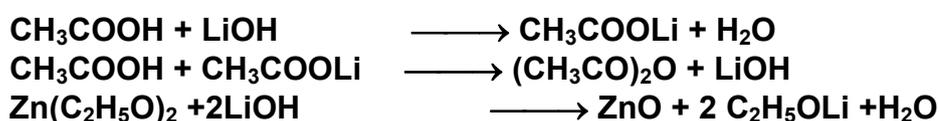
## RESULTS AND DISCUSSION

### Preparation of zinc oxide

The reaction mixture in the case of sol-gel technique was composed of zinc acetate dihydrate solution in ethanol which was hydrolyzed in basic medium under the influence of lithium hydroxide. The reaction was expected to proceed as the following proposed rout represented by equation



After three hrs of reaction, the formed solution was left to concentration to 25% of its original value. The precursor likely contains a zinc ethoxide, which hydrolysed by lithium hydroxide to form ZnO colloidal under ultrasonic waves for 1 hr (optimum time for complete hydrolysis).



The structure was determined and the investigation of the factor affecting processing by Sameh A. was shown [25].

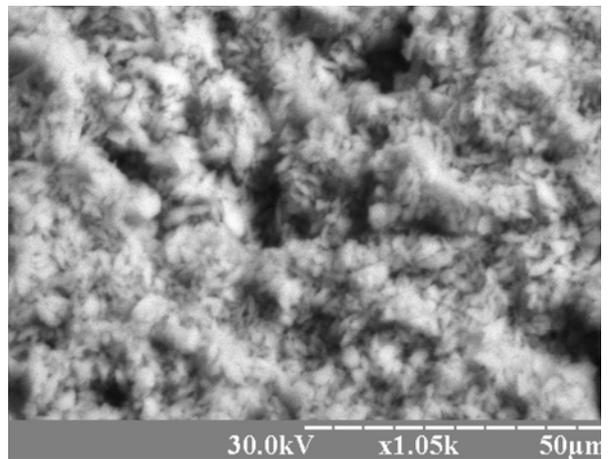
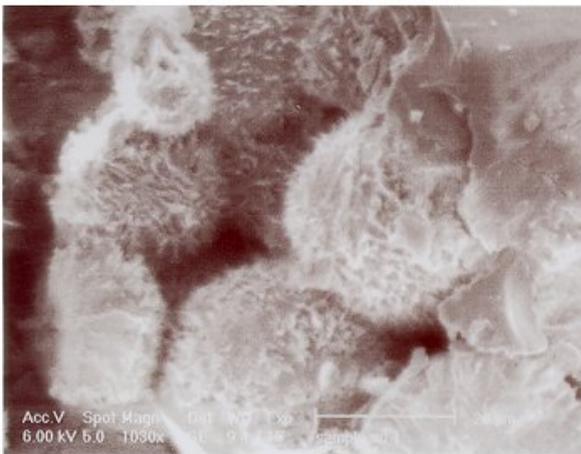
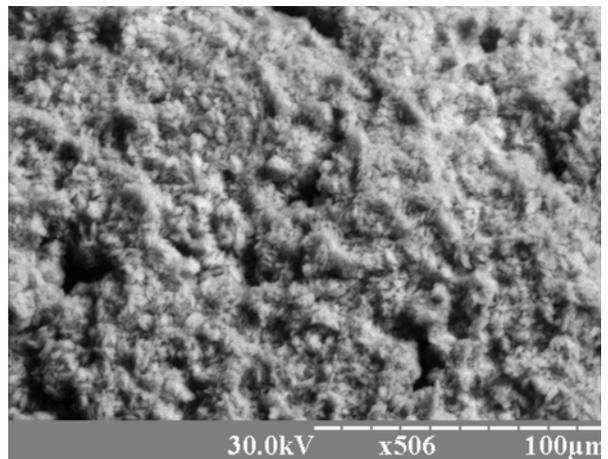
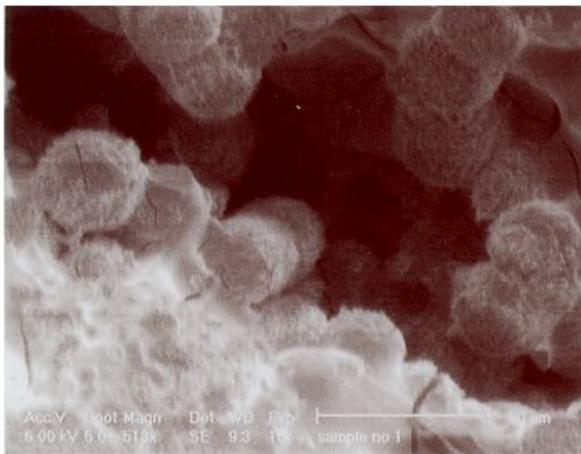
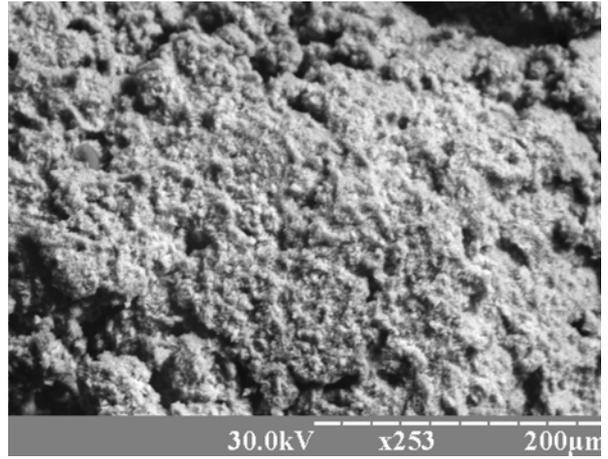
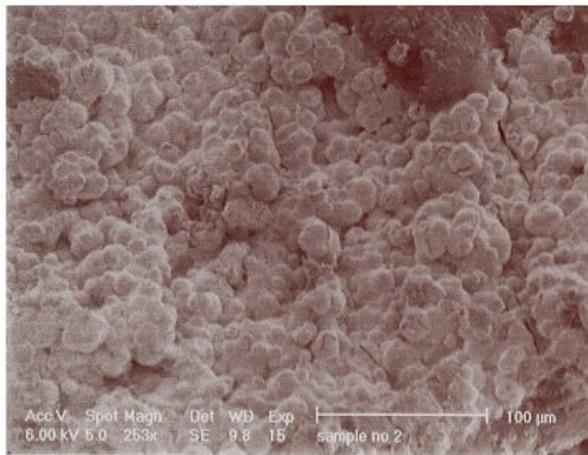
While in the preparation of zinc oxide powder by Pechini method the results show that the formation of a metal citrate salt as follows: where citric acid acts as a chelating agent to zinc ion.



On the other hand citric acid combined with ethylene glycol to form a polyester under the reaction conditions for 3 hrs. If there is no stirring ZnO precipitate as large scales in the flask while the reflux prevent loss of alcohol which react with the citric acid and enhance the reaction. The formed ZnO in each method was filtered and tested.

### **Morphology analysis: -**

The morphology analysis of the formed zinc oxide prepared via sol-gel technique dried at 100°C. Fig. 1a shows agglomerated spherical particles with average diameter 15 µm. while the prepared samples by Pechini method dried at 100 °C ( Fig. 1b) shows separate fine particles with average size range less than the zinc oxide which was prepared via sol-gel. The morphology analysis of sample prepared via sol-gel technique and calcined at 500°C Fig. 2a shows that the particles has a relatively different crystalline shape oriented to the fibrous configuration while the SEM of the samples calcined to 700°C Fig. 2b shows a fused grain indicating partial fusion of grains showing the start of sintering. The zinc oxide prepared by Pechini don't shows a fused particles at 700°C Fig. 3 like which was prepared via sol-gel or at 900°C Fig. 4a, the fused grains appears at 900°C for 6 hrs, its seemed closed to each other and start to sintering Fig. 4b with average grain size about 500 nm same size of analysis results which was achieved by Lima et al [15]. While Pedro et al [26] were achieved zinc oxide of 28 nm. For more magnification the grain size of the sample which was prepared via Pechini method about 40 nm Fig. 3b.



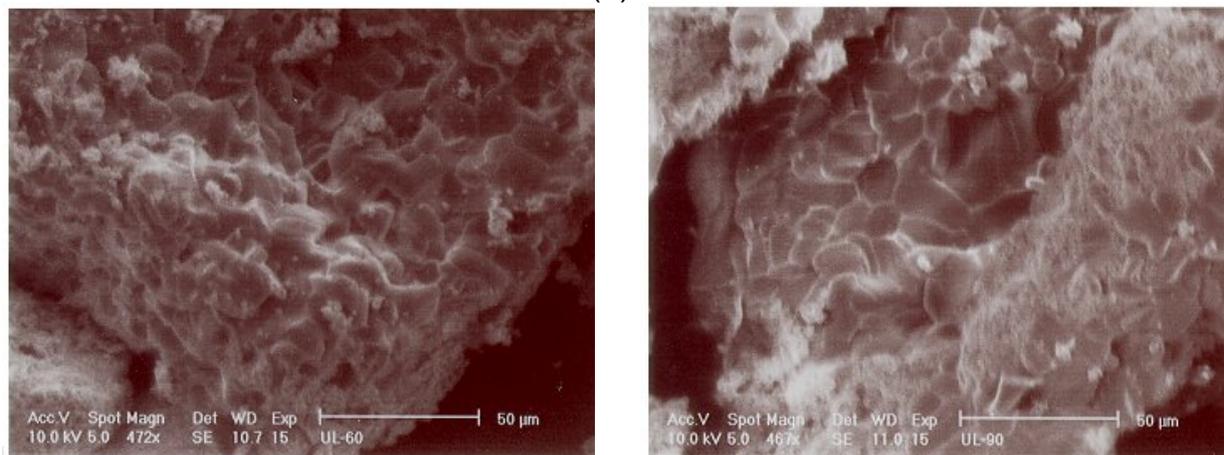
(a)

(b)

Fig. 1. SEM of the zinc oxide powder dried at 100°C  
a) via Pechini method b) by sol-gel technique



(a)



(b)

Fig. 2. The SEM of zinc oxide prepared by sol-gel technique calcined at (a) 500°C and (b) 700°C

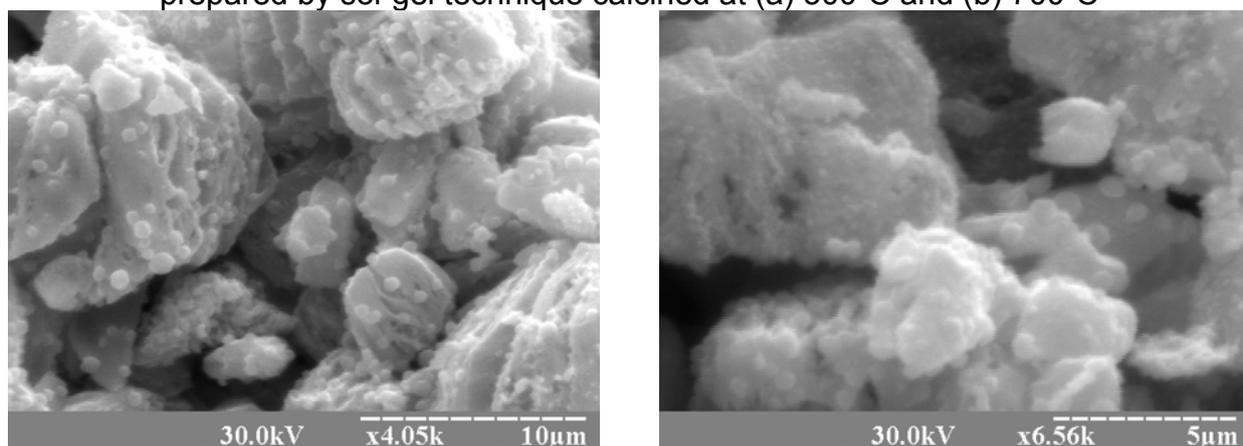


Fig. 3. The SEM of zinc oxide prepared by Pechini calcined at 700°C

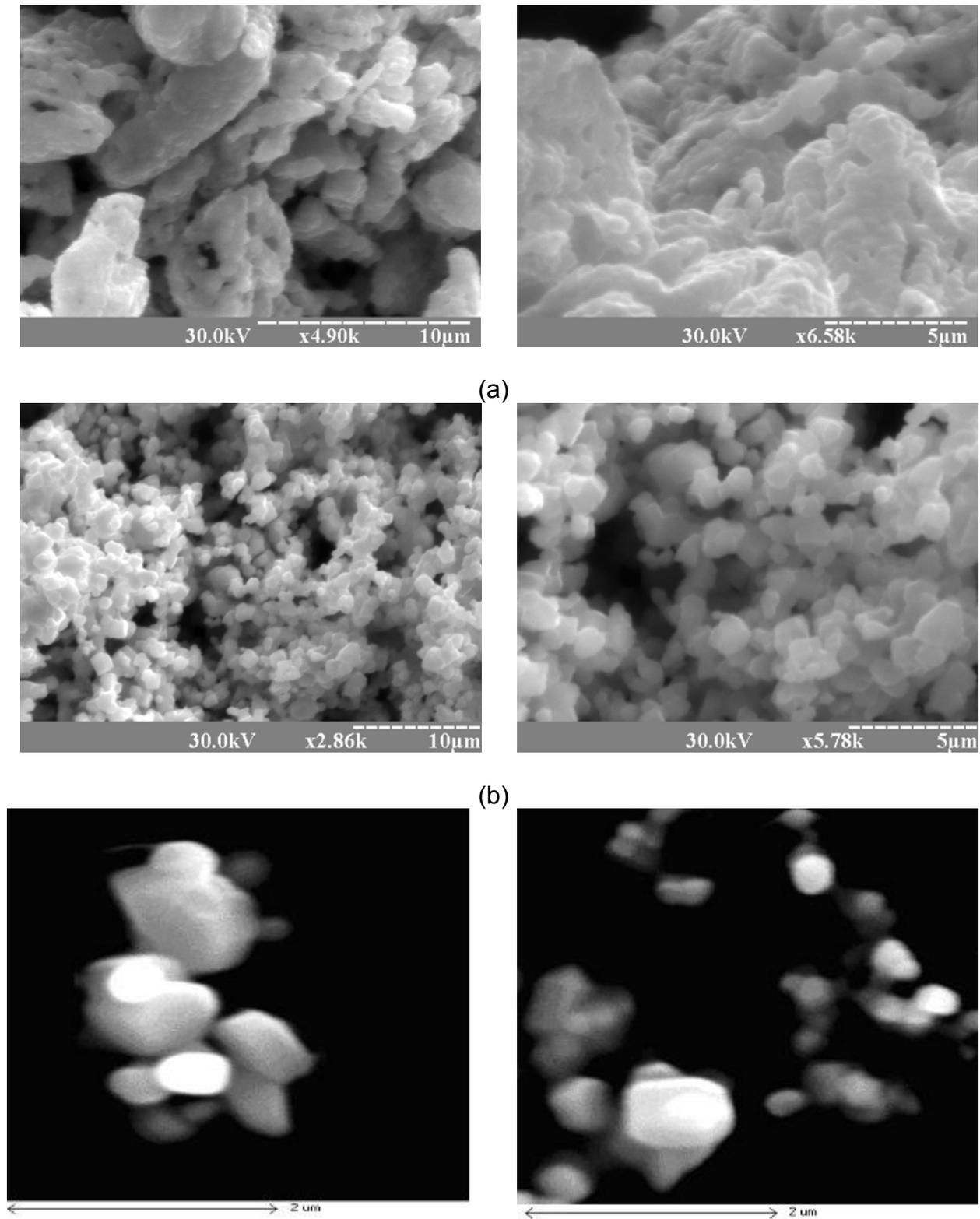


Fig. 4. The SEM of zinc oxide prepared by Pechini calcined at (a) 900°C and (b) 900°C for 6 hrs

**Infrared analysis: -**

Fig.5 shows the IR spectrum of the samples prepared at room temperature and dried at 100°C by sol-gel technique. The carboxylate anion has two strongly coupled carbon to oxygen bonds with bond strengths intermediate between single and double (C-O and C=O) due to resonance. So the carboxylate ion gives rise to two bands: a strong asymmetrical stretching band near 1650-1550  $\text{cm}^{-1}$  and weaker stretching band near 1400  $\text{cm}^{-1}$  [27]. The two peaks at 1400 and 1600  $\text{cm}^{-1}$  in Fig. 5 b are due to acetate group of acetate salts (zinc acetate, lithium acetate), while the sharp peak at 3500 and 3300  $\text{cm}^{-1}$  Fig. 5a due to citric salt (of the sample prepared by Pechini). Fig.6 shows the IR spectra of the samples calcined at 900°C and pure zinc oxide. Comparing the two spectrums, it is clear that zinc oxide is the remaining substance in the sample with its characteristics IR peak at 500  $\text{cm}^{-1}$ . In Fig. 6 b the peaks at 1600  $\text{cm}^{-1}$  due to residual carbon and 3412  $\text{cm}^{-1}$  due to the adsorbed moisture (OH group), while still there is a residue of Carbon due to citric acid salt (3500 and 3300  $\text{cm}^{-1}$ ) Fig.6a.

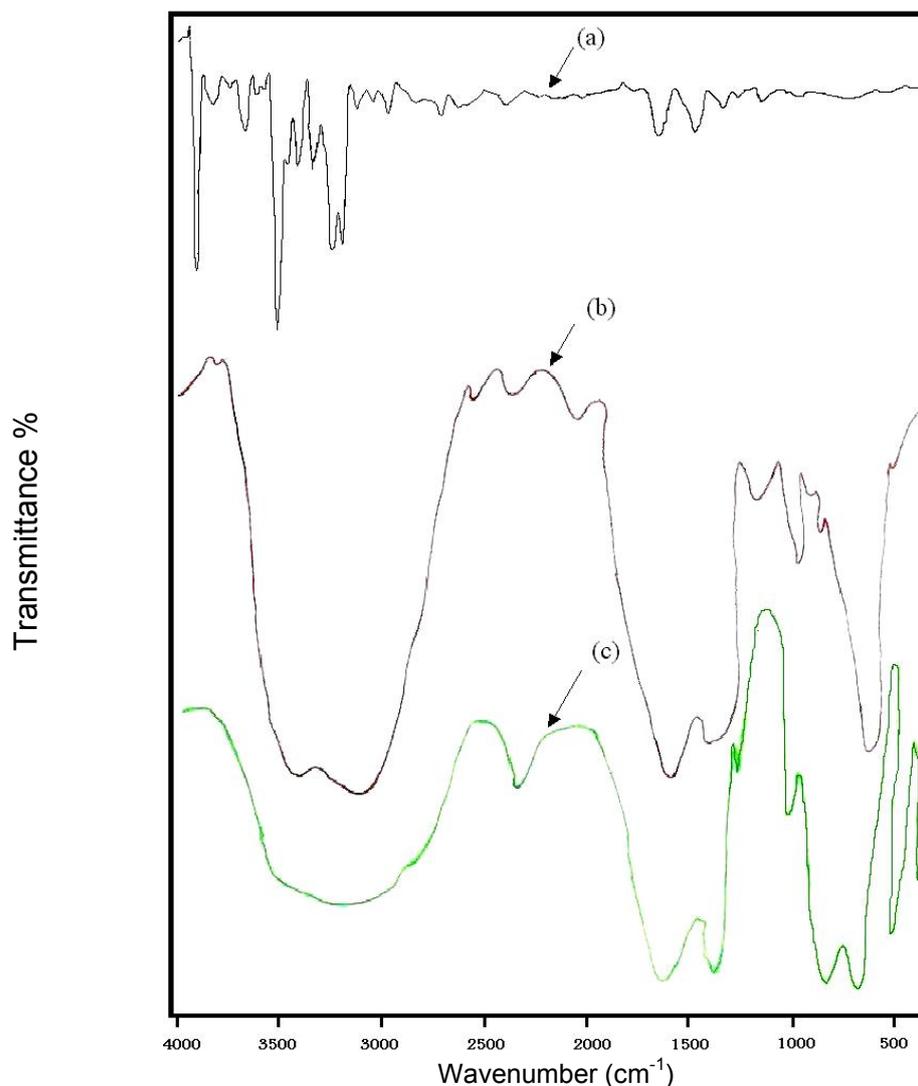


Fig.5. The IR spectrum of the samples prepared at room temperature and dried at 100°C  
(a) by Pechini (b) via sol-gel and (c) pure zinc acetate dihydrate

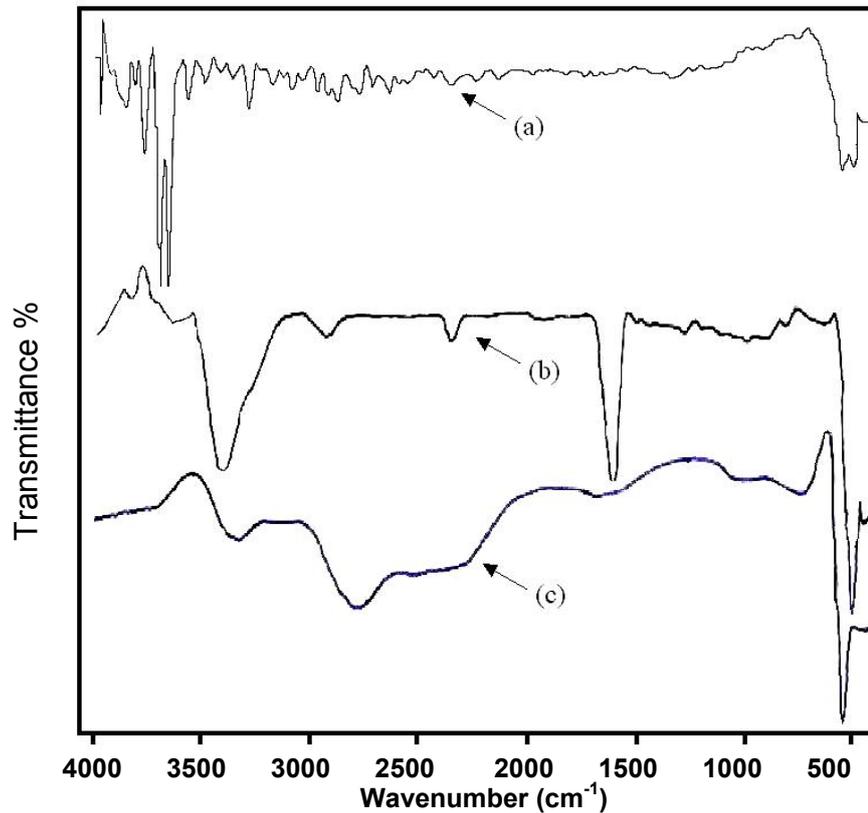


Fig.6. The IR spectrum of the samples calcined at 900°C (a) by Pechini (b) by sol-gel, (c) pure zinc oxide

## CONCLUSION

The two techniques gave a method for making multicomponent powders containing oxides or alkoxide or carboxylates.....etc together under reaction conditions of each method.

The colloidal ZnO prepared via sol-gel can be used in thin film and coating formation at low temperature, which has a wide range of application in the preparation of electronic [6-10] and, optical application. Zinc oxide powder prepared via Pechini method can be used in layer formation in battery [9], catalysis [12], varistors and gas sensors [6, 7]...etc.

The high purity, composition control, low temperature of preparation, chemical homogeneity and special product such as films are the advantages of sol-gel technique, and its disadvantages due to its high cost of raw material. While the inexpensive raw material and the availability to form a lower particle size are the advantages of Pechini method, and its disadvantages due long process time. The comparison between the selected two techniques for processing of zinc oxide can be summarized in table 2.

Table 2. Comparison between Sol-gel and Pechini in the preparation of ZnO.

The comparison point	Method of processing	
	Sol-Gel	Pechini
Raw material	Expensive raw material	Not expensive
Availability	Easy technique	Long processing time.
Purity	Higher purity	Residual hydrocarbon
Zinc oxide colloidal	suitable technique to produced a zinc oxide colloidal	Only zinc oxide bulk (no colloidal formed)
Thin film formation	Successful (by dip or spin coating ) with no need to advance processing like CVD or plasma vapor deposition	Can't be used in thin film formation by dip or spin coating (the powder produced can be used to form thin film CVD or plasma vapor deposition ..etc)
Fused grains	Obtained at low temperature 700°C	Obtained at higher temperature 900°C for 6 hrs
Grain size	In micro size	Less than micro size

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