Structural and morphological evolution of metal oxide nanoparticles synthesised via sol–gel auto-combustion

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Abstract: Metal oxide nanopowder synthesis for pure ZnO and α-Al₂O₃ was carried out by a simple and fast sol–gel auto-combustion method. Thermogravimetric analysis (TGA) was performed to confirm the phase purity of nanopowder. The transformation of crystalline phases of as-synthesised nanopowders was then investigated through X-ray diffraction (XRD) in terms of their crystallinity and crystallite size. Subsequently, a detailed transmission electron microscopy (TEM) investigation and surface area study revealed the crystallographic alterations and morphological information even at lattice scale. From selected area electron diffraction (SAED) pattern has specified the d-spacing and corresponding planes which co-include with the XRD d-spacing and planes. The existence of distinctive bonds was studied by applying Fourier-transform infra-red (FTIR) spectroscopy. The transformation of fascinating microstructure and phase formations has been presented to explicate the evolution of an amorphous state into different crystalline phases with increased calcining temperature.

Keywords: metal oxide nanoparticles; calcining temperature; morphology.


Biographical notes: Hasnah Mohd Zaid received her BSc and MSc in Physics from Kansas State University (USA) and University of Alabama (USA), respectively. She joined Universiti Teknologi Petronas as a Lecturer in 1999 and completed her PhD at University of Birmingham in the UK in 2006. She is currently an Associate Professor in the Department of Fundamental & Applied Sciences at Universiti Teknologi Petronas. Her research areas include electron beam lithography and application of nanoparticles in enhanced oil recovery.
1 Introduction

Metal oxide nanoparticles show intriguing novel characteristics owing to their small particle size and a large surface to volume ratio compared with their bulk counterparts including structural stability, nonlinear optical behaviour, electric resistivity and chemical properties [1,2]. Among all metal oxides, zinc oxide (ZnO) and aluminium oxide (Al₂O₃) are of great interest as a suitable material for high temperature application. They can be tailored to match specific applications and conditions. In addition, latest research showed that not only primary particle size but also nanoporosity characteristics have an impact on surface chemistry of nanostructured materials [3].

A range of synthesis routes have been documented for the preparation of metal oxide nanoparticles [4,5]. The major routes include sol–gel auto-combustion method [6], microemulsion method [7], salt reduction [8], physical vapour deposition [9], ultrasonic irradiation [10] and solvothermal synthesis [11].

Compared to other methods, the sol–gel auto-combustion method is one of the emerging synthesis approaches as a potential substitute for the synthesis of nanoparticles [12]. The auto-combustion method is self-sustainable; where once the reaction has begun, high temperature is generated owing to exothermic characteristics of the reaction to ensure the formation and crystallisation of metal oxides in a short time period. This method typically hinders the instantaneous generation of particles’ agglomeration [13]. The advantages of sol–gel auto-combustion include good chemical homogeneity, high purity and crystallinity, fine particle size distribution, simple preparation steps, basic equipment, small processing time and low external energy consumption to initiate the process [14,15].
2 Experimental details

2.1 Materials and synthesis method

All chemicals used in this research were of analytical grade. The sol-gel combustion method which combines the chemical sol-gel and combustion process was utilised for the synthesis of metal oxide nanostructures. To produce nanocrystalline powders of zinc oxide \([\text{ZnO}]\), zinc nitrate powder \([\text{Zn(NO}_3\text{)]}_2\cdot6\text{H}_2\text{O}\) (R&M Chemicals ~98% purity) and citric acid \([\text{C}_6\text{H}_8\text{O}_7]\) (Sigma-Aldrich ≥99.5%) were used as a start-up material and the fuel respectively. The stoichiometric fraction of zinc nitrate to citric acid was taken as \(1 : 0.56\). The zinc nitrate powder was dissolved in 100 ml de-ionised water (conductivity of 0.0549 \(\mu\text{S.cm}^{-1}\)) by stirring on a hot plate at 40°C, and citric acid was added to get a clear solution. Then the solution was given several minutes to cool down to ambient temperature. Ammonia solution \([\text{NH}_4\text{OH}]\) (R&M Chemicals ~30%) was added carefully to the solution mixture in small amount to alter the pH value to 7. The solution was then placed on a hot plate for heating with continuous stirring for 1 day at 80°C to convert into a dried-gel. The solution started to bubble with the evaporation of water until it became viscous. Spontaneously gel was ignited by the gradual increase in temperature up to 230°C with the formation of large amount of gas, resulting in lightweight voluminous powder. Finally the powder was accumulated and annealed for 3 h at various temperatures determined by the thermogravimetry of uncalcined samples.

Similar steps were applied to prepare the aluminium oxide sample \([\text{Al}_2\text{O}_3]\), except that instead of zinc nitrate hexahydrate, aluminium nitrate nanohydrate \([\text{Al(NO}_3\text{)]}_3\cdot9\text{H}_2\text{O}\) (Sigma-Aldrich ≥98%) served as the precursor. In this case, the dried gel was combusted at ~300°C. The complete procedure for the synthesis of metal oxide nanoparticles is depicted in Figure 1.

![Figure 1](image_url)  
**Figure 1** Stepwise procedure for the synthesis of nano-metal oxide powders

2.2 Characterisation techniques

Thermal and structural characterisation of the nanoparticles were performed by using thermogravimetric analysis (TGA) (Seiko SII Exstar 6000), transmission electron microscopy (TEM) (Zeiss Libra 200FE), X-ray diffraction (XRD) (Bruker D8 Advanced), and Fourier-transform infra-red (FTIR) spectroscopy (Perkin Elmer) in the wavelength range of 400–4000 cm\(^{-1}\).
3 Result and discussion

3.1 Thermal analysis

The TGA curve of ZnO nanopowders synthesised by the sol–gel auto-combustion method is presented in Figure 2(a). The TGA analyses revealed that the weight losses of 7% until 160°C can be associated with the evaporation of absorbed water. Another weight loss of 4% was also recorded in the step from 160°C to 600°C, which is associated to the combustion of nitrate and carbonaceous compounds. No additional change in weight noted up to 800°C. This implies that around 88% pure ZnO nanocrystalline completed as the decomposition product at 600°C. In case of aluminium oxide, the TGA traces as shown in Figure 2(b), a weight loss (10%) during the heating step from 30°C to 200°C. This loss of weight can be related to moisture water loss, whereas the weight losses between 200°C to 550°C can be associated with the organic component decomposition generated by the dissociation of precursor react with oxygen to form CO₂ and H₂O. The weight loss at around 550°C is attributed to the pseudomorphic phase transformation of bohemite to \( \gamma \)-Al₂O₃ [16]. This leads to the further phase transformation from \( \gamma \)-Al₂O₃ to \( \delta \)-Al₂O₃ and \( \theta \)-Al₂O₃ between 550°C to 950°C. Whereas, \( \alpha \)-Al₂O₃ phase formation started to occur at the temperature values more than 1100°C which is in accordance with Park et al. [16] and Mirjalili et al. [17]. This is also in consistence with the XRD results which indicate that pure \( \gamma \)-Al₂O₃ phase occurred at 1200°C. These transformations bring the change in degree of crystallinity and crystallite size characteristic to the nanopowders.

3.2 Fourier-transform infra-red (FTIR) analysis

The compositional analyses of the calcined metal oxide nanostructures, treated at various temperatures, were carried out by the FTIR measurement at room temperature in a particular range of 400–4000 cm⁻¹. Figure 3 shows FTIR spectra of ZnO nanoparticles. Metal oxides typically give adsorption bands in fingerprint region i.e., below 1000 cm⁻¹ originating from inter-atomic vibrations. Here a broad band is recognised for each spectrum between 430 cm⁻¹ and 550 cm⁻¹, which is associated with a Zn-O vibration mode. It can also be observed that the characteristic peaks for metal oxide sharpens with the increase in annealing temperature, suggesting that, the increase in calcination temperature improves the crystalline nature of ZnO. The peaks observed at 3433 and 1611 cm⁻¹ are may be owing to O-H stretching and deformation, respectively attributed to the moisture water on the metal surface. Whereas the peak at 1383 cm⁻¹ corresponds to the C=O bonds. The C=O and O-H bending vibrations reduce gradually for sample calcined at higher temperature. A negligible shift to a lower wavenumber has also been observed owing to the rise in the annealing temperature, above 600°C. This shift can be attributed to a transformation in the lattice parameters of the ZnO nanoparticles, illustrates the alteration in morphology of zinc oxide, analogous to TGA observations.

Similarly Figure 4 shows the FTIR spectra of as-synthesised and annealed Al₂O₃ powder material. Amorphous nano alumina powder represents as a broad peak in the range of 550–900 cm⁻¹. This is owing to Al-O stretching mode (750–850 cm⁻¹) and O-Al-O bending mode (600–700 cm⁻¹) [18]. There is another broad peak between 3000 cm⁻¹ and 3700 cm⁻¹ which indicates OH stretching region. The peak at 1622 cm⁻¹ which can be related as the H-O-H scissor mode is corresponding to the peak at
3417 cm$^{-1}$ can be due to water molecules [19]. Calcined sample has multiple peaks in the range of 600–400 cm$^{-1}$, which affirms the crystalline nature [20]. For the samples annealed above 950°C, there is a notable intense sharp peak at 500 cm$^{-1}$ corresponds to O-Al-O bending mode. The FTIR study tends to propose the formation of pure alumina sample appears through the intermediate formation of a hydroxyl species. The formation of alumina can be depicted by the following chemical reaction [21]:

$$
2\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 6\text{HNO}_3 + 3\text{H}_2\text{O} \quad (1)
$$

$$
\text{Al(OH)}_3 \rightarrow \text{AlOOH} \quad (2)
$$

$$
\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad (3)
$$

Figure 2  TGA curve of as prepared (a) ZnO and (b) Al$_2$O$_3$ nanopowders
3.3 X-ray diffraction analysis (XRD)

The XRD has been in use in two major areas, for fingerprint characterisation of crystalline materials and the determination of their structure. Figure 5 depicts the XRD patterns of the products obtained at 300°C and 800°C. The diffraction peaks at 300°C is mostly (99.3%) indexed to wurtzite ZnO (hexagonal phase, P63mc space group, ICDD 002-7791) with minor wulfingite Zn(OH)₂ (orthorhombic phase, P212121 space group, ICDD 001-7724). This result, in accordance with TEM images, suggest that the Zn(OH)₂ have low crystallinity and are difficult to detect by XRD. Therefore Zn(OH)₂ must form at a lower growth temperature (<300°C), which begins to evolve into crystalline ZnO at a temperature of 300°C and above. The increase in calcination temperature from 300°C to 800°C provides the increment of peak height and a decrease in full width at half
maximum (FWHM), resulting in a stronger and sharper diffraction peaks. This indicates that the crystal quality has been enhanced; whereas the size of particles becomes bigger. The orthorhombic (wulfingite) crystal structure is transformed to hexagonal structure (wurtzite) as per the following reaction [22]:

\[
\begin{align*}
\text{Zn(OH)}_2 & \rightarrow [\text{Zn}^{2+} + 2\text{O}^2^- + \text{H}^+]_{\text{solid}} \rightarrow [\text{Zn}^{2+} + \text{O}^2^-] + [\text{O}^2^- + 2\text{H}^+] \\
\rightarrow [\text{ZnO}]_{\text{solid}} + \text{H}_2\text{O}_{\text{gas}}
\end{align*}
\]

(4)

Figure 5 X-ray diffraction patterns of ZnO nanopowders calcined at temperature 300°C and 800°C (see online version for colours)

Considering, XRD patterns for Al₂O₃ nanoparticles annealed at different temperatures are shown in Figure 6. It can be seen that the diffraction pattern for material annealed at temperature below 750°C is highly attenuated owing to the presence of amorphous state. Thermal treatment at 850°C for three hours leads to the formation of γ-Al₂O₃ (cubic phase, Fm3m space group, ICDD 001-3124), corresponding to the (002) and (022) diffractions. However, further increment of the temperature of heat treatment up to 1050°C results in the formation of δ-Al₂O₃ (orthorhombic phase, Pna2₁ space group, ICDD 003-9290), having relatively better degree of crystallinity. Peaks due to γ-Al₂O₃ diminish when temperature is higher to 1200°C, forming the highly crystalline Α-Al₂O₃ (hexagonal phase, R3c space group, ICDD 004-0015). This is in accordance with the results of Zuo and Jagodzinski [23] using the traditional methods of synthesis. The series of transformation can be observed as:

\[
\text{am-AlO(OH)} \rightarrow \gamma\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \theta\text{-Al}_2\text{O}_3 \rightarrow \kappa\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3
\]

(5)

Particle size, heating rate, and atmosphere are the few influential factors that may control the sequence of phase transformations of Al₂O₃ due to the impact on the kinetics of transformation [24].

3.4 Crystallite size determination

Modified Scherrer formula [25] is used to calculate the particle size based on the fact that we must obtain the average value of L through all the peaks by using least squares
method to mathematically decrease the source of errors. The results are tabulated in Table 1.

**Figure 6** The XRD pattern of alumina powder annealed at different temperatures (see online version for colours)

<table>
<thead>
<tr>
<th>Nano samples</th>
<th>Crystallite size L (nm)</th>
<th>Lattice parameter</th>
<th>Crystal structure</th>
<th>Space group</th>
<th>Crystallinity (%) [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO (300°C)</td>
<td>350</td>
<td>a = 4.93</td>
<td>Orthorhombic</td>
<td>P212121</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 5.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 8.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO (800°C)</td>
<td>171</td>
<td>a = 3.24</td>
<td>Hexagonal</td>
<td>P63mc</td>
<td>98.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 3.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 5.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ (850°C)</td>
<td>943</td>
<td>a = 3.93</td>
<td>Cubic</td>
<td>Fm3m</td>
<td>72.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 3.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 3.93</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Al₂O₃ (1050°C)</td>
<td>551</td>
<td>a = 4.93</td>
<td>Orthorhombic</td>
<td>Pna21</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 5.17</td>
<td></td>
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<td></td>
<td></td>
<td>c = 8.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ (1200°C)</td>
<td>84</td>
<td>a = 4.75</td>
<td>Hexagonal</td>
<td>R3c</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 4.75</td>
<td></td>
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<td></td>
<td></td>
<td>c = 12.99</td>
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</tbody>
</table>

### 3.5 Transmission electron microscopy (TEM)

In particle size measurement, electron microscopy is the only method in which the individual particles are directly observed and measured [27]. Therefore, TEM is used to
yield the information including particle size, size distribution and morphology of the nanoparticles. TEM images can also be used to observe the quality of dispersion, whether it is good or agglomeration exists in the system. Microscopy in combination with diffraction studies provides a very useful mean to the characterisation of nanoparticles [21]. Figure 7 shows the TEM images and selected area electron diffraction (SAED) patterns of ZnO nanoparticles calcined at 300°C and 800°C.

Figure 7(a) and (b) reveals that the product mainly consists of hexagonal particles. The corresponding SAED pattern shown in Figure 7(c) confirms that the synthesised products at 300°C has preferentially oriented growth along (110), (112) and (201) planes which correspond to hexagonal crystal structure of ZnO. These planes exhibit very low relative intensities which indicate the presence of ZnO phase with poorly polycrystalline in nature. The planes (111) and (200) are also present, in accordance to orthorhombic crystal structure of Zn(OH)₂, proves the presence of a mixture of two phase, simultaneously. As seen from Figure 7(d), after calcination, the nanostructure is converted into pure ZnO phase with hexagonal (wurtzite) crystal structure grew along the <002> direction. The SAED also shows the complexity in crystalline structure for variable calcination. It indicates that the synthesised ZnO nanoparticles are not single crystals, but rather the agglomerates of many single crystals. The crystallinity of the synthesised nanoparticles was also supported by the observed lattice fringes of 0.32 nm, which is equal to the lattice constant of the ZnO indicating that the synthesised nanostructures have a wurtzite phase and are preferentially grown.

**Figure 7** TEM images of ZnO nanoparticles (a, b) calcined at 300°C and 800°C, respectively, and their corresponding SAED images (c, d) with inset images of lattice scale fringes (see online version for colours)
On the basis of the number of particles of ZnO shown in the TEM image (Figure 7), the average particle size is found to be about 78 nm and 115 nm at 300°C and 800°C respectively presented by a histogram in Figure 8.

**Figure 8** Histograms showing particle size distribution of zinc oxide nanoparticles at (a) 300°C and (b) 800°C (see online version for colours)

**Figure 9** (a) TEM images of the as-prepared Al₂O₃ nanopowders annealed at 1050°C, (b) corresponding SAED pattern and (c) shows the histogram of particle size distribution (see online version for colours)
As shown in Figure 9(a), TEM micrograph of as-synthesised Al₂O₃ nanoparticles, corresponding to annealing temperature of 1050°C. The images show certain degrees of agglomeration and polydispersity. In TEM image, several randomly oriented crystallites could also be observed. The co-existence of extensive plain area in the image was also evident the amorphosity of the annealed sample. The ring pattern of SAED shown in Figure 9(b) exhibits the presence of β phase of alumina showing the crystal growth along the (002) and (100) planes which correspond to orthorhombic crystal structure of Al₂O₃. The lattice fringe image shows the uniform spacing of the clear lattice plane to be 0.36 nm which in accordance to the (002) lattice plane of the β-phase of alumina. The size distribution data was plotted in the form of a histogram (Figure 9(c)), to determine the average particle size as 146.2 nm. It is noticed that the average particle size is greater than the crystallite size, which could be the result of poor dispersibility of nano sample for TEM, leading to particles’ agglomeration.

4 Conclusion

The ZnO and Al₂O₃ nanoparticles were successfully synthesised by fast and efficient sol–gel auto-combustion method. Stable, highly crystalline hexagonal wurtzite ZnO formed at 800°C with average crystallite size of 47.3 nm using XRD data which is in good agreement with TEM results of 115.1 nm. Whereas the average crystallite size of Al₂O₃ nanoparticles annealed at 1200°C was determined to be 25 nm providing the hexagonal α-phase. It can also be concluded that the crystallite size determined by XRD results is closely associated to the phase transformation, i.e., increase in crystallite size in accordance to the phase transition variation and consequently, with the increase in temperature. Furthermore, the FTIR spectrum showed a broad absorption band attributed to the typical metal oxide bond vibration which further confirms the formation of nanoparticles.

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References

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