Chapter 6

Recent Characterisation of Sol-Gel Synthesised TiO_2 Nanoparticles

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Additional information is available at the end of the chapter

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Abstract

High demand and current applications have led to continuous study and subsequent improvement of TiO_2 nanoparticles. The versatility of the sol-gel method allows employing different process parameters to influence the resultant properties of TiO_2 nanoparticles. The evaluation and characterisation process of the synthesised TiO_2 nanoparticles commonly involves a series of methods and techniques. Such characterisation methods include phase, structural, morphology and size analysis. A combination of data from these evaluations provides the relationship between the synthesis parameters and the end properties of TiO_2 nanoparticles. Apart from the research findings on TiO_2 nanoparticles, the characterisation used to obtain these findings is equally important. Thus, this chapter highlights the recent characterisation techniques and practices employed for TiO_2 nanoparticles synthesised by the sol-gel method.

Keywords: TiO_2 nanoparticles, sol-gel, phase analysis, Rietveld refinement, morphology, particle size

1. Introduction

Developments in the polymorphic TiO_2 nanoparticles have extensively drawn major interest of researchers and scholars. The wide exploitation of TiO_2 nanoparticles includes the study and application in photovoltaics [1], photocatalysis [2], batteries [3], filler material in composites [4] and biomedical products [5]. The key issues addressed focused on achieving better characteristics of TiO_2 nanoparticles as well as improved performance of end devices. This

explains the large number of ongoing research studies considering the versatility of TiO_2 nanoparticles in a broad range of applications.

The significant interest on TiO_2 nanoparticles was driven by the unique characteristics of the material, such as low preparation cost, non-toxic, favourable band edge positions and diverse morphologies possibilities [6–8]. Factors determining these end properties are mainly dependent on the synthesis routes used to produce TiO_2 nanoparticles. Since 1971, the sol-gel has been the most significant synthesis method known and applied in producing multi-component oxides such as TiO_2 [9]. Parameters such as the type of precursors [10], the pH of solution [11], preliminary solution treatment [12] and calcination temperatures [13] yielded varying properties of the resultant TiO_2 nanoparticles.

The process of evaluating the performance/defects of TiO_2 nanoparticles involves a series of characterisation methods. To ensure sufficient data, the selection of characterisation methods is highly important. Highly practised characterisations attributed to the evaluation of TiO_2 nanoparticles include:

(i) Structural and phase analysis

(ii) Morphological observations

(iii) Particle size analysis

These analyses allow researchers to determine the effects of the sol-gel parameters for the synthesised TiO_2 nanoparticles. Such information is vital to continuously develop TiO_2 nanoparticles. This explains the reasons why such characterisation methods are highly preferred in the current research works related to TiO_2 nanoparticles.

Currently, there are several available review articles on TiO_2 nanoparticles, which discuss the photocatalytic performances in various applications [14–16]. The preparation and synthesis were critically reviewed as well [17–19]. Other available reviews include the phase and structural transformation of TiO_2 nanoparticles [20, 21]. Technical review on TiO_2 nanoparticles characterisation, however, has received only little attention although it is significantly relevant to the evaluation of TiO_2 nanoparticles.

Thus, this chapter focuses on recent characterisation of TiO_2 nanoparticles synthesised by the sol-gel method. Commonly practised configuration of characterisation corresponding to TiO_2 nanoparticles for over 7 years (2010–2016) is selectively reviewed in this chapter. Few earlier articles were also referred to strengthen the overall understanding on the subject matter.

2. Chemical reaction of the sol-gel method

The sol-gel method is the process of transforming sols (solid particles suspended in liquid) into gels (particulate networks of sols). This involves two main reactions: hydrolysis and condensation, prior to obtaining crystalline TiO_2 nanoparticles by calcination (**Figure 1**). For synthesising TiO_2 nanoparticles, commonly used precursors include $Ti(OBu)_4$ [22], $TiCl_3$ [10],

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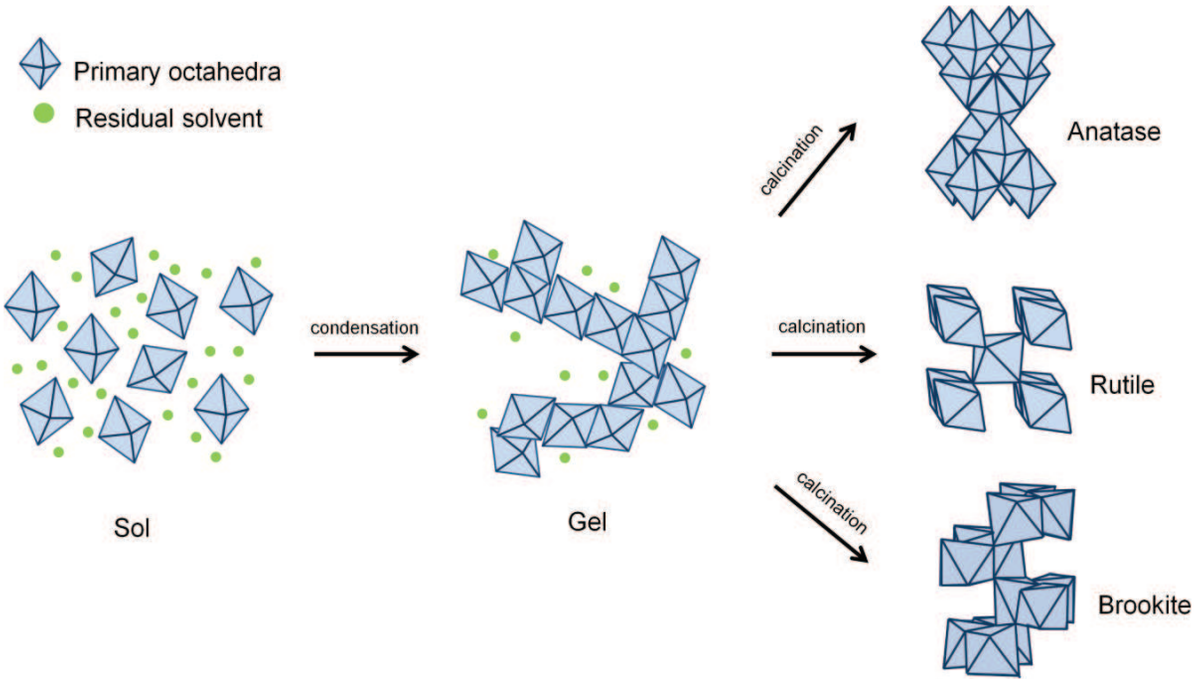

Figure 1. The hydrolysis, condensation and calcination process of the sol-gel method in synthesising the crystalline anatase, rutile and brookite TiO_2 nanoparticles.

$TiCl_4$ [23], $TiBr_4$ [24] and $Ti[OCH(CH_3)_2]_4$ (TTIP) [25]. These precursors were then hydrolysed by adding water (hydrolysis), resulting in the formation of complex three-dimensional network (condensation) as shown in the following equations:

Hydrolysis:

$$Ti(OR)_4 + 4H_2O \rightarrow 2Ti(OH)_4 + 4ROH \quad (1)$$

Condensation:

$$Ti(OH)_4 + Ti(OH)_4 \rightarrow 2TiO_2 + 4H_2O \text{ (oxolation)} \quad (2)$$

$$Ti(OH)_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4ROH \text{ (alcoxolation)} \quad (3)$$

where R in the equation represents ethyl, i-propyl, n-butyl and so on [26, 27]. The titanium precursor is often diluted before adding water. This reduces the rapid reaction rate of the hydrolysis process.

Size and morphology of the end TiO_2 nanoparticles are highly influenced by the precursor–water ratio [28]. Lower ratio of water–precursor resulted in monodisperse particle of 0.5–1 mm in diameter [11]. For higher ratio values, unstable colloidal and predicates would form and aggregate. Peptisation is commonly carried out for these aggregates to achieve the final size, which is usually less than 100 nm [29]. Higher pH of solution contributed to increased

particle size of TiO_2 nanoparticles [30]. The calcination process should be carefully determined as the phase transformation of TiO_2 is highly influenced by the employed temperature [31]. The end structures of crystalline TiO_2 polymorphs (anatase, rutile or brookite) are thus formed from the colloidal suspension, depending on the above parameters.

3. Phase and structural characterisation

The phase and structural analyses are significant characterisation techniques that are usually associated with the main discussion in analysing the current sol-gel-synthesised TiO_2 nanoparticles. The means of X-ray diffraction (XRD) are utilised to qualitatively identify the phases obtained by referring to the XRD databases [32]. Additionally, the data then can be subjected to the Rietveld refinement to yield significant fitting parameters for quantitative evaluations.

Due to nanosized TiO_2 nanoparticles (<100 nm), deviations on the diffraction signal can be avoided to achieve a reliable XRD analysis. Physically, the fine powder form of the TiO_2 nanoparticles provides relatively easy sample handling and preparation, ensuring smooth and flat surface. This is important as sample displacement is the main factor contributing to errors in the determination of structural parameters. The dominant TiO_2 diffraction peaks were found to lie between the angle of $2\theta = 25–30°$. Thus, Bragg angle range of $2\theta = 20–80°$ was practically applied in analysing TiO_2 nanoparticles [33, 34]. Due to the increase in crystallinity, TiO_2 nanoparticles subjected to calcination were commonly associated to higher peak intensities compared with the untreated TiO_2 nanoparticles [35]. The lattice plane corresponding to the particular peak reflects the preferable growth orientation of TiO_2 nanoparticles crystal [32, 36, 37]. Additionally, by employing the Debye-Scherrer equation, the crystallite sizes of the synthesised TiO_2 nanoparticles can be calculated directly.

Examples of phase determination (by search and match) can be observed from the work by Banerjee et al. [38] in examining the addition of Pd and Ga on synthesised TiO_2 nanoparticles. In addition to the observation on the intensities reduction (**Figure 2a**), the observed peak broadening (**Figure 2b**) and deconvolution of peaks (**Figure 2c–e**) in the XRD pattern is also another indication that can be discussed in parallel to the phase identification. These phenomena, however, are often related to structural alteration due to the presence of non-uniform strain, posed by the substitutional and interstitial dopants [39, 40]. Similarly, the work by Chen et al. [33] also utilise the phase analysis in investigating the Fe^{3+}-doped TiO_2 nanoparticles. With reference matched only to the JCPDS File No. 21-1272, the formation of pure anatase phase was reported. Additionally, as secondary phases were absent in the observed XRD pattern, it can be concluded that the added Fe^{3+} from the ferric nitrate had been completely incorporated into the TiO_2 nanoparticles. Relating to the current sol-gel practices, such phase identification is essential as most sol-gel synthesis approaches involve a wide diversity in chemical variations. Apart from that, other effects of Fe^{3+} addition, such as reduction of the peak intensities, were also compared in explaining the crystallinity of TiO_2 nanoparticles.

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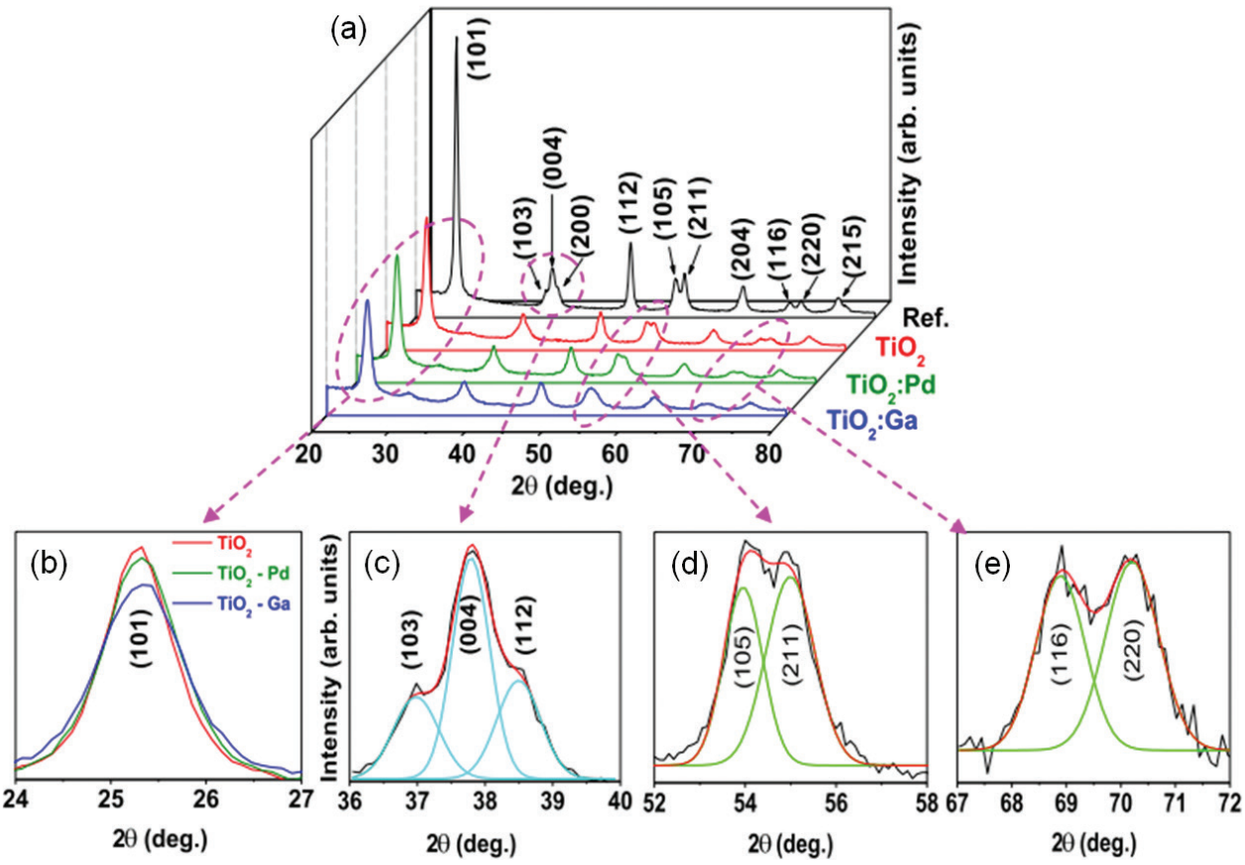

Figure 2. Comparison of XRD patterns for (a) pure TiO_2 nanoparticles and TiO_2 nanoparticles doped with Pd and Ga, (b–e) overlapped XRD curves representing peak broadening and deconvolution with respect to the crystallographic orientation. Reprinted with permission from Ref. [38]. Copyright 2016, Elsevier.

Furthermore, comparison by the phase analysis is highly preferable in investigating large variation of sol-gel techniques. As an example, from the spectra comparison, synthesis with different precipitation conditions clearly portrayed a significant influence on the resultant structural analysis of the TiO_2 nanoparticles (**Figure 3a–b**). It is shown that the storage condition favours earlier rutile transformation as compared to the centrifuge condition [41]. Other example includes the studies on the use of weak/strong acids in favouring different mixtures of TiO_2 polymorphs. Interestingly, pure anatase phase was reported to be more favourable with the usage of milder acid [42]. In another case, different mixtures of anatase and rutile phases were also obtained in the XRD spectra. However, these preferences were mainly associated to the different ranges of applied calcination temperature [43]. In most cases, higher calcination temperature tended to produce rutile, mainly due to its stability compared with anatase and brookite [43, 44]. Apart from that, Potlog et al. [45] reported that the reverse transformation of rutile to anatase is possible by utilising the H_2 environment. Such behaviour can be distinguished clearly from the XRD curves after annealing, which indicates the absence of the rutile (110) peak when compared to before annealing in the H_2 environment.

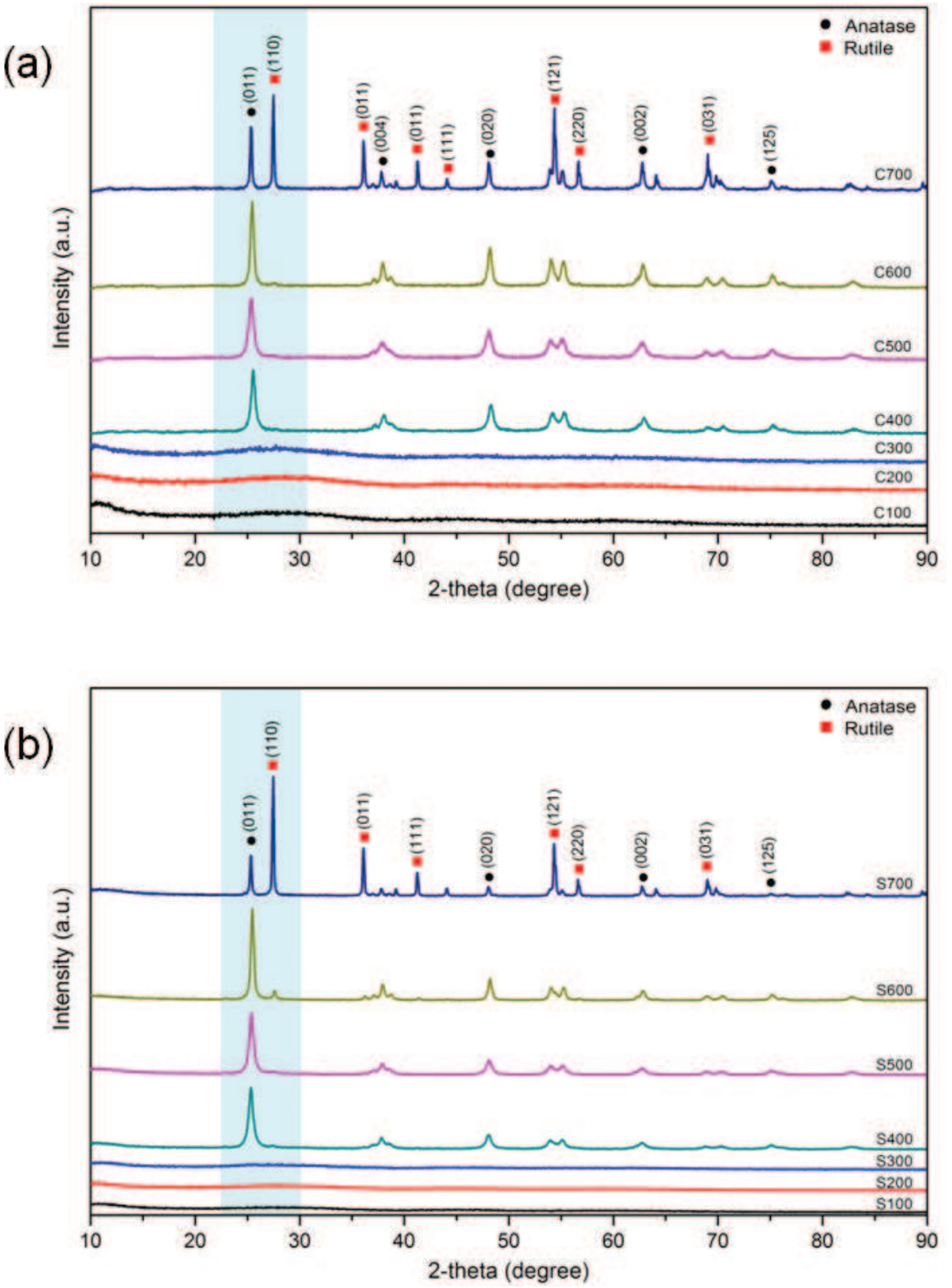

Figure 3. X-ray diffraction patterns of TiO_2 nanoparticles at various calcination temperatures synthesised through (a) centrifuge and (b) storage precipitation conditions (the shaded area represents changes on the anatase and rutile peak). Reprinted with permission from Ref. [41]. Copyright 2015, Elsevier.

4. Rietveld refinement

In Rietveld analysis, the experimental XRD pattern is fitted onto a reference data, yielding a resulted/simulated XRD model. Differences between the experimental and simulated XRD produce the fitting parameters through the Rietveld algorithm. Such parameters (goodness of fit (GOF), R_{exp} and R_{wp}) reflect the reliability of the corresponding XRD pattern. To relate, the analysis was significantly practised to further characterise TiO_2 nanoparticles, indicating the reliability of the XRD analysis and the synthesis process as a whole.

The refinement process utilises the pattern and data obtained from XRD. Thus, factors that affect the XRD analysis are also responsible in determining the accuracy of the Reitveld refinement. In the phase quantification analysis, the evaluations are attributed to the intensities of the diffraction peaks, yielding the phase percentages of TiO_2 anatase, rutile or brookite. Additionally, the increment on the full width at half maximum (FWHM) of TiO_2 polymorph peaks reduces the resultant crystallite sizes of these phases [46].

During refinement, various parameters (peak shape, lattice parameter and atomic position) were adjusted to achieve the best-fit model, commonly discussed as the visual fit process. These optimised models were generated from the differences between the observed and computed intensities to yield fitting parameters such as the weighted R profile (R_{wp}), R expected (R_{exp}) and the goodness of fit (GOF) [47]. The values vary accordingly to the different sol-gel approach employed in synthesising TiO_2 nanoparticles. For instance, typical GOF values obtained for the anatase TiO_2 synthesised by various heat treatments were in the range of 1.0–2.0 [41, 48].

As an example, the fitted model obtained by Yahaya et al. [41] was used in determining the structural parameters of TiO_2 nanoparticles synthesised by centrifuge and storage precipitation (**Figure 4a**). Most Reitveld discussions focused on this crucial plot (as it is the sole figure directly representing the visual fit) by observing the displacement of the peaks between the calculated and observed pattern. Then, from such displacement, the fitting parameters were generated (**Figure 4b–c**). From these quality indicators ($R_{wp,}$ R_{exp} and GOF), the centrifuge condition was quantitatively determined as the synthesis route to ensure better reliability in the XRD analysis. In most refinement works, these parameters are the commonly reported results, which, however, are significant towards the phase and structural analysis/discussion of the synthesised TiO_2 nanoparticles [49].

In different cases, the usefulness of the Rietveld analysis was capitalised in investigating chemical reactions of TiO_2 composite coatings [50]. The approach was to compare the refined pattern of pure rutile and anatase TiO_2 with the refined pattern of the hydroxyapatite (HAP)/TiO_2 composite coatings. Two main points were used to prove that the chemical reactions did not occur. The first was by obtaining similar structural parameters of TiO_2 and HAP in the composites compared with the parameters of the corresponding phases individually. The second was by obtaining comparable occupancy factor value (acquired from the refinement) of the HAP for all HAP/TiO_2 composite samples (similar values indicate retaining of its structure by HAP, which reflect the absence of any reactions) [51]. In complex TiO_2 sol-gel synthesis,

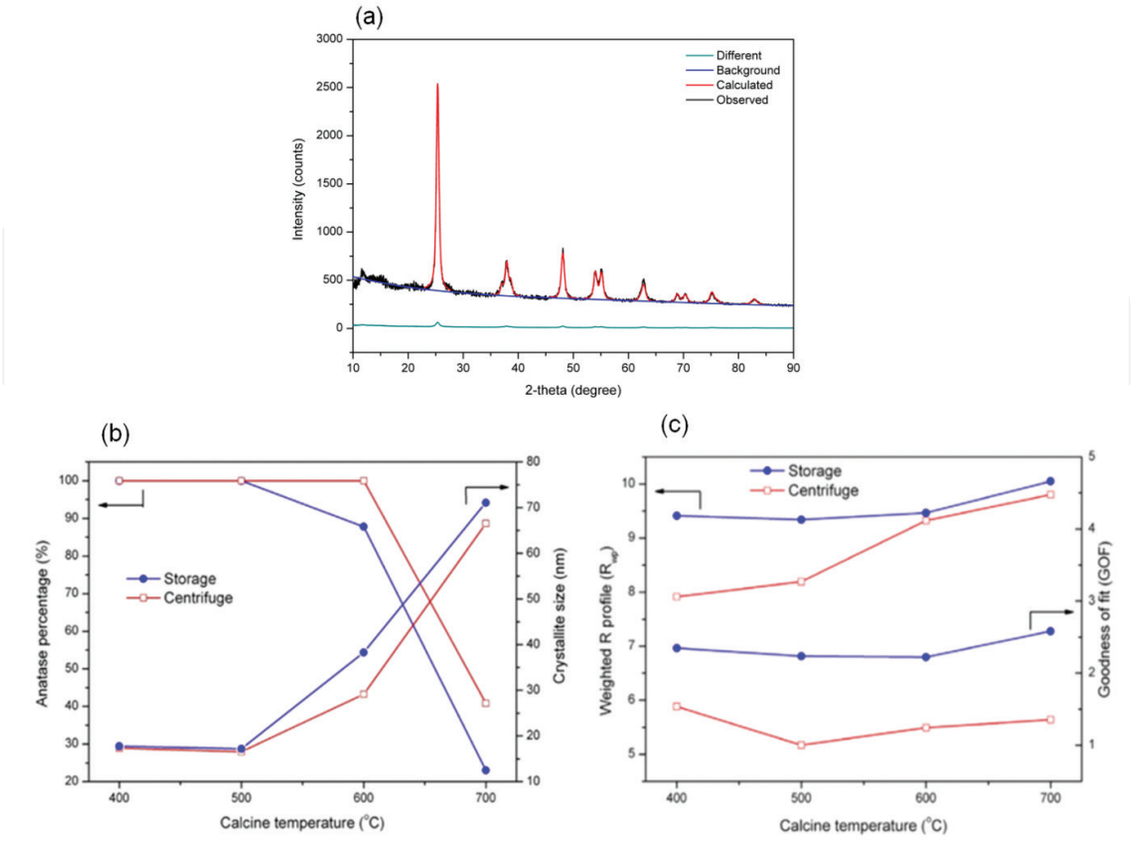

Figure 4. Example of the fitted profile for (a) the TiO_2 nanoparticles synthesised by centrifuging and 500°C calcination temperature and the Rietveld analysis for the synthesised TiO_2 nanoparticles, (b) Anatase percentage and crystallite size and (c) Weighted R profile. Reprinted with permission from Ref. [41]. Copyright 2015, Elsevier.

this approach (occupancy value determination) is highly essential in phase investigation/studies, as it provides quantitative comparison—an added bonus apart from the conventional phase analysis from the XRD.

5. Microstructural and elemental characterisation

Morphologies observation is an important qualitative characterisation in analysing TiO_2 nanoparticles. Observation on the microstructural behaviour of nanoparticles was done based on the micrograph obtained from electron microscopy, commonly the FESEM [52] and HRTEM [53]. Selection of the characterisation method usually depends on the samples' suitability and resolution of the techniques. Methods such as the FESEM and HRTEM offer higher versatility, as both can be further exploited to compensate additional analysis such as the elemental analysis.

5.1. Field emission scanning electron microscope

In FESEM imaging, the secondary electron (SE) mode is more preferable compared with the backscattered electron (BSE) mode. SE mode allows more detailed surface images of TiO_2 nanoparticles, which is more significant compared with the BSE mode [52]. This is significant

in allowing better interpretation on micrographs as TiO_2 nanoparticles are commonly subjected to agglomerations.

The observation of the TiO_2 nanoparticles' morphology commonly requires magnification up to 30,000 times [54]. However, higher magnification up to 200,000 times has also been reported in characterising the surface morphology of TiO_2 nanoparticles [52, 55]. These mainly depend on the condition of TiO_2 nanoparticles prior to characterisation. In addition, dry TiO_2 nanoparticles resulting from calcination allow higher magnification observation compared with uncalcined nanoparticles. Coatings with conductive metals such as gold are required prior to the imaging process. In terms of image acquisition, less crystalline TiO_2 nanoparticles were commonly subjected to higher charging effects during imaging, causing whitish disturbance, which can be wrongly interpreted to the actual TiO_2 nanoparticles.

Good examples of how SE images are much preferable for TiO_2 nanoparticles can be demonstrated by the significant differences on the morphology of the rutile and anatase phases which was attained by different route of sol-gel synthesis [41]. With magnification of up to 30,000 times, the shapes and sizes of both centrifuge and storage TiO_2 nanoparticles were clearly distinguishable from the micrographs (**Figure 5a–f**). Additionally, the capability to go as high as such magnification was also contributed by high calcination temperature (450–700°C) [52]. Apart from providing easier observation and interpretation on TiO_2 nanoparticles, the ability to go for high magnification allows accurate size determination of the particles (size determination from SEM micrograph currently gained significant interest in TiO_2 nanoparticles characterisation). A similar approach was also demonstrated by Khatun et al. [55] in observing agglomerated TiO_2 nanoparticles. Images obtained with magnification up to 200,000 times clearly distinguished the morphological behaviour of the TiO_2 nanoparticles. Due to that, the fusing of individual TiO_2 nanoparticles into larger agglomerates was proven in the work. The initial decarburisation process at 450°C for 6 h allowed such SEM observation. Furthermore, most relatively high heat-treating processes (mainly above 400°C) allowed good observation on the sol-gel synthesised TiO_2 nanoparticles during SEM imaging [35, 56].

5.2. High-resolution transmission electron microscope

The main difference of the HRTEM technique from that of the FESEM is how images are generated by the transmission of electron through TiO_2 nanoparticles. Thus, a very thin sample is required for observation through HRTEM.

In the initial preparation, TiO_2 nanoparticles were suspended in a solution and then deposited onto a silicon oxide film supported by a Cu mesh. This allowed observing individual and non-agglomerate particles of TiO_2. Apart from morphological and surface behaviour characterisations, higher resolution of HRTEM provided observation and measurement on the lattice fringes of TiO_2 nanoparticles as well. This was used for the validation of the structural analysis from XRD and to observe the possible growth plane of TiO_2 nanoparticles [34]. The common magnification range used to observe TiO_2 nanoparticles ranged from 195,000 times for shape and distribution observation to 610,000 times for lattice fringes analysis [57].

Observation on the shape of TiO_2 nanoparticles synthesised by the centrifuge precipitation sol-gel method was obtained by Yahaya et al. [41] by utilising a magnification of 610,000 times.

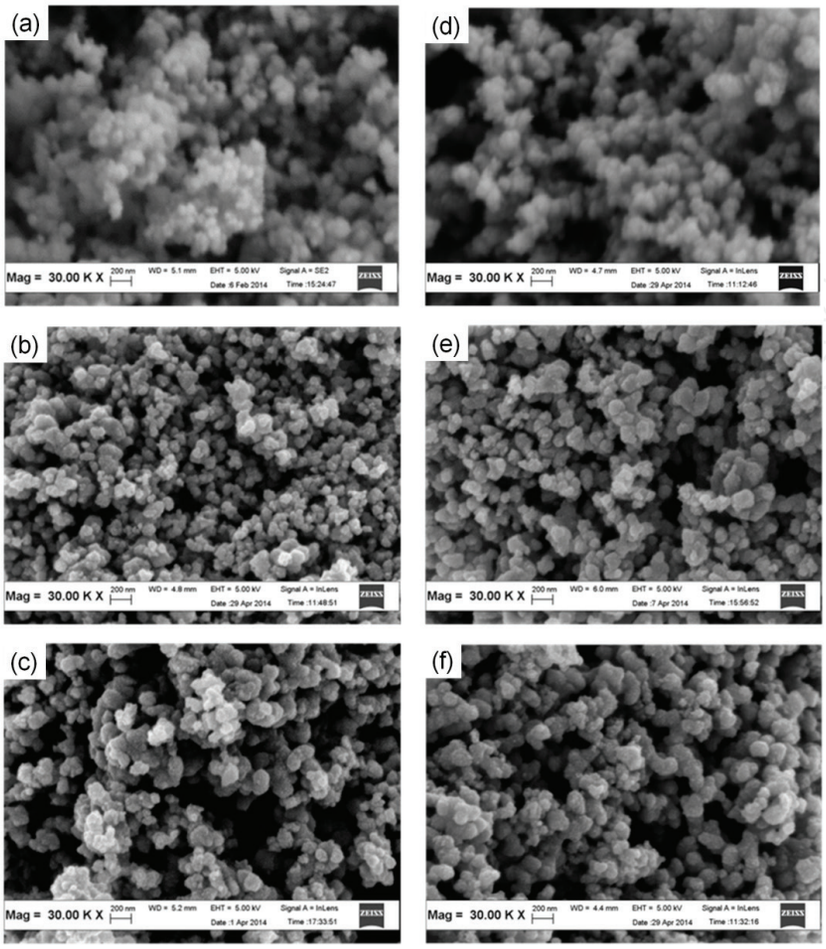

Figure 5. SEM images of the TiO_2 nanoparticles synthesised by the sol-gel method for (a) as synthesised centrifuge, (b) centrifuge calcined at 500°C, (c) centrifuge calcined at 600°C, (d) as synthesised storage (e) storage calcined at 500°C, and (f) storage calcined at 500°C. Reprinted with permission from Ref. [41]. Copyright 2015, Elsevier.

The preferable circular shapes of the TiO_2 nanoparticles favour by such synthesis method were obviously revealed with such high magnification (**Figure 6a, b**). Similar magnification was also employed by Shen et al. [34] in observing the rectangular shape of the microwave-assisted sol-gel-synthesised TiO_2 nanoparticles. Making such observation is the main benefit of employing HRTEM when compared with SEM. However, HRTEM is mainly employed for sol-gel-synthesised TiO_2 nanoparticles, which also depend on the lattice fringes measurement and observation [43]. Additionally, high-resolution images (**Figure 6c**) of the TiO_2 nanoparticles indicated favourable crystal growth along the (011), evaluated by the lattice fringes (**Figure 6d**).

Apart from morphological analysis, common practices involving HRTEM micrograph include the validation of structural analysis from XRD [32]. For instance, in this work, the measured lattice distance was comparable with the d-spacing value, thus supporting the initial XRD evaluation by the author. As an example, lattice fringes of anatase (0.347 nm) were evaluated from the HRTEM images (**Figure 6d**), indicating a good correlation to the values attained from the structural analysis [41]. Other than single-phase studies, such approaches were also widely applied in investigating mixtures of TiO_2 polymorphs [58]. This kind of evaluation was indeed to further prove the co-existence of the phases in the TiO_2 mixtures [59]. It

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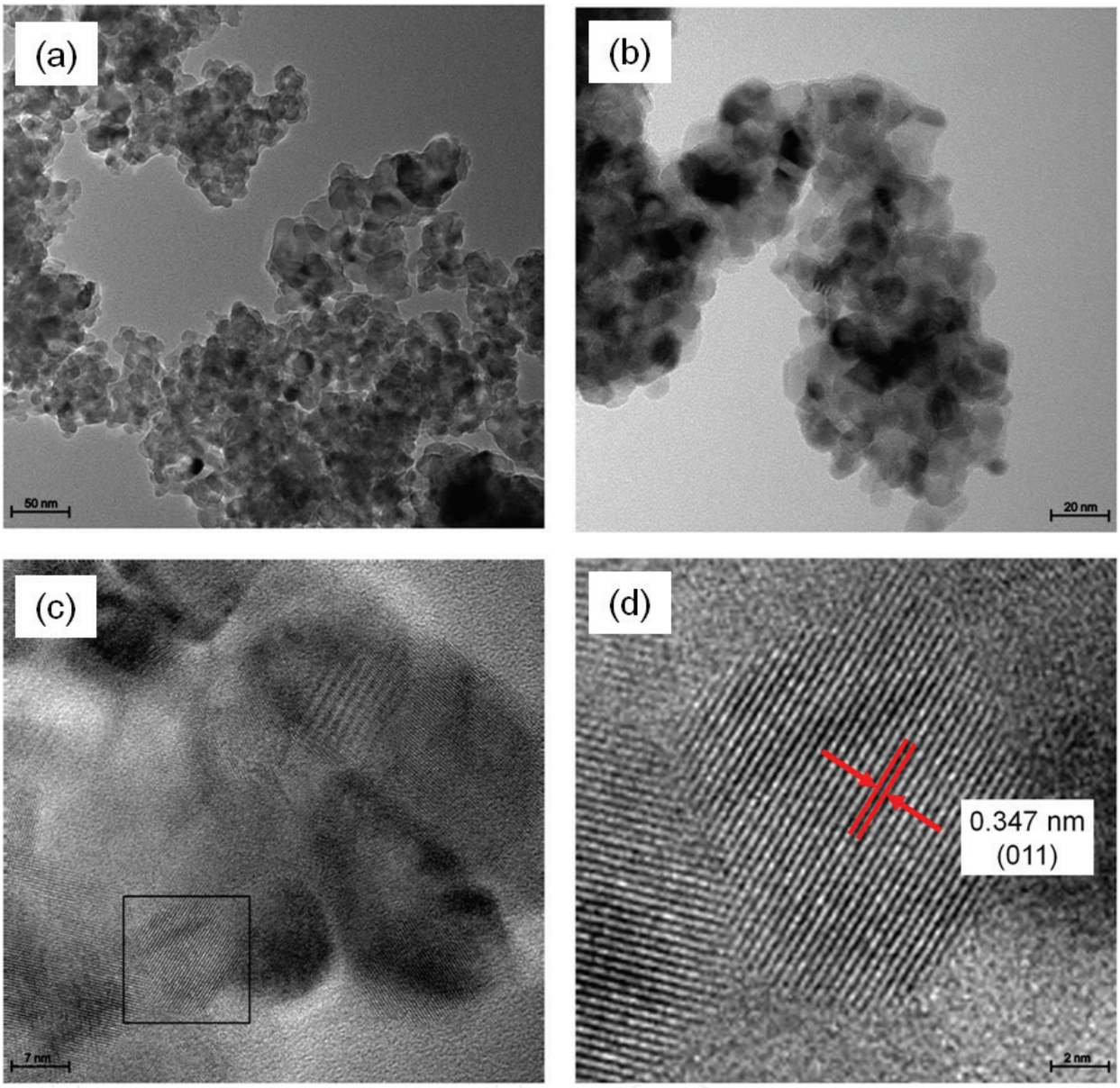

Figure 6. TEM and HRTEM images of TiO_2 nanoparticles synthesised by centrifuge sol-gel method at magnification of (a) 97 kx, (b) 195 kx, (c) 610 kx and (d) magnified image of selected square in (c). Reprinted with permission from Ref. [41]. Copyright 2015, Elsevier.

was clear that HRTEM provides a direct relation between the qualitative analysis (from the images) and the quantitative analysis (structural parameters) from the XRD. In the context of sol-gel synthesis, this clearly opened up more plausible explanation when investigating and characterising TiO_2 nanoparticles.

5.3. Elemental analysis

Parallel to FESEM and HRTEM, the electron dispersive X-ray (EDX) paired to the equipment can simultaneously provide the elemental analysis based on the emitted characteristic X-rays. Area scan EDX is commonly practised in providing the overall elemental analysis of TiO_2

nanoparticles due to the involvement of only single phase [41]. The elemental analysis generally follows subsequently after FESEM or HRTEM characterisation by employing the micrograph selected by the two techniques.

In sample preparation, suitable coating elements should be carefully selected to avoid coatings being detected by EDX to avoid misleading analysis. The EDX analysis provides elemental data strictly on atomic behaviour as opposed to molecular information [60]. The information from area under the EDX spectrum, the accelerating voltage and sensitivity factor were mathematically translated into the elemental information consisting of the atomic percent (at. %) and the weight percent (wt. %) values.

For instance, the elemental analyses conducted on the SEM micrograph were used to confirm the existence of titanium and oxygen in the synthesised TiO_2 nanoparticles (**Figure 7a–f**) [41]. In general, such presence of the particular Ti and O element from the EDX spectrum also highly support other characterisation especially the phase and structural analysis [61]. Additionally, the EDX analysis is useful in explaining the effects of certain parameters on

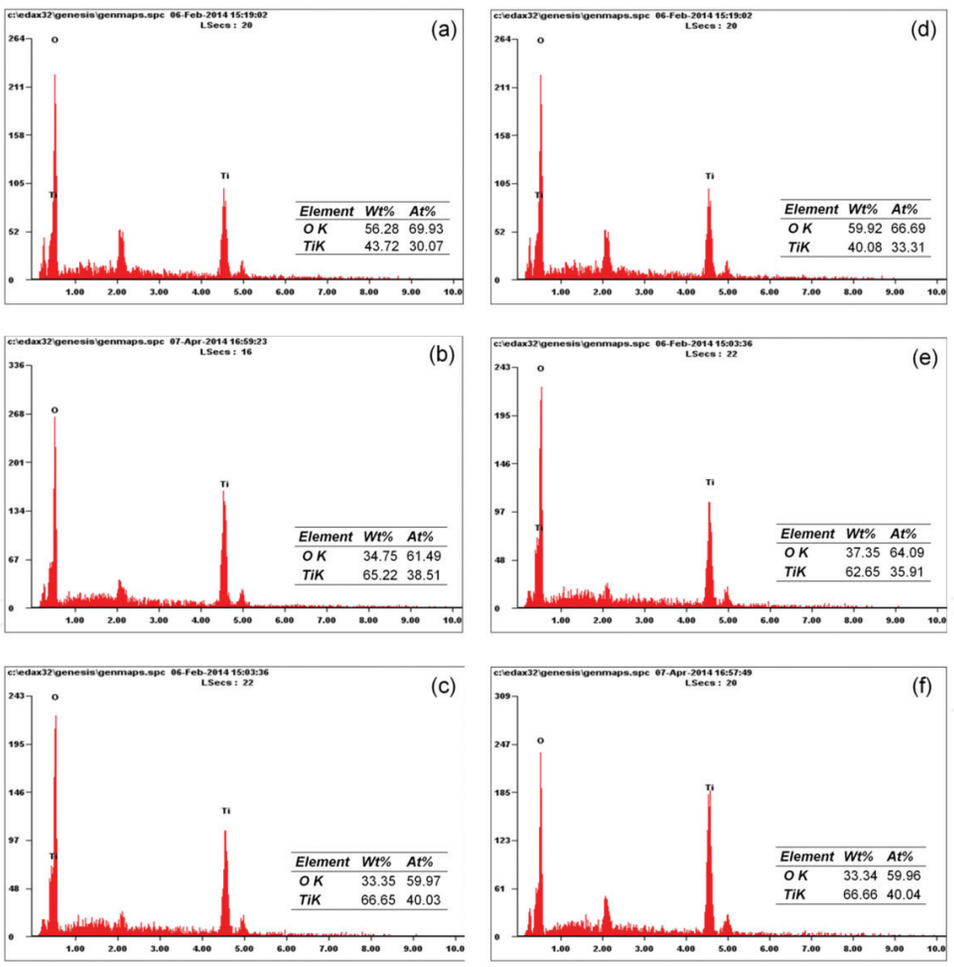

Figure 7. EDX spectrum of the TiO_2 nanoparticles, obtained by centrifuge and calcination at (a) 0°C, (b) 500°C and (c) 600°C, by storage and calcination at (d) 0°C, (e) 500°C and (f) 600°C temperature under ambient atmosphere. Reprinted with permission from Ref. [41]. Copyright 2015, Elsevier.

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the corresponding elements such as heat treatment [41]. As an example, the variations on the elemental composition from the EDX spectra obtained in this work explained the influence of calcination temperatures on the resultant TiO_2 nanoparticles. It was clearly observed that higher calcination temperature depleted the oxygen content in the EDX spectra. As current TiO_2 nanoparticles synthesis by the sol-gel involves various changes in chemical parameters, the EDX acts as an important tool to validate the presence/absence of any additional elements from such a complexity. This can be viewed from the work by Martins et al. [62], where the EDX analysis was used to investigate TiO_2 nanoparticles synthesised with the addition of activated carbon. The presence of oxygen, titanium and carbon on the EDX patterns in such cases confirmed the elements presence on the material surface, which in turn indicates the occurrence of carbon reaction during the synthesis process.

6. Particle size analysis

Size determination of TiO_2 nanoparticles was highly practised in conjunction to other characterisation methods. This analysis is significantly crucial as the size factor greatly influences the end properties of TiO_2 nanoparticles. There are few available techniques that allow such analysis to be conducted on the synthesised TiO_2 nanoparticles. However, each selected application is mainly dependent on the research requirement and suitability.

Size determination through FESEM and HRTEM is commonly practised and utilised. The drawback is the need to carry out the initial morphology observation before the actual size determination. A more straightforward approach can be espoused through the use of the particle size analyzer. For example, the use of laser diffraction provides a fast and reproducible particle size analysis [63]. To aid the analysis, current practices are commonly incorporated in the preliminary dispersion process, which helps eliminate agglomeration issues of TiO_2 nanoparticles [64]. Other methods include the electrospray scanning mobility particle sizer (ES-SMPS) and the dynamic light scattering (DLS). As the DLS is suitable for evaluating hydrodynamic radius of particles, ES-SMPS was proven to yield reliable size distribution of nanoparticles larger than 5 nm [65].

A good example of the reliability of the technique can be observed from the investigation on the particle size by Abbas et al. [66], which employed the ES-SMPS method. In the report, high reproducibility of the particle size measurement had been obtained with negligible variations for all TiO_2 nanoparticles. The importance of the consistency is mainly to provide an accurate interpretation on the research parameters. For instance, in this work, the size distribution plotted from the reliable data of ES-SMPS evaluation reflects solely on the influence of the storage condition towards the resultant particle size (**Figure 8a, b**). However, recent work in size determination of TiO_2 nanoparticles mostly presents the measurement obtained from SEM/HRTEM micrographs [57, 67]. Although the processes are more convenient due to the readily available images from SEM/HRTEM, the average size obtained was limited to the particles' presence in the micrograph. Unlike from the particle size analyzer, larger samples quantity can be analysed, thus practically representing better average size value of TiO_2 nanoparticles.

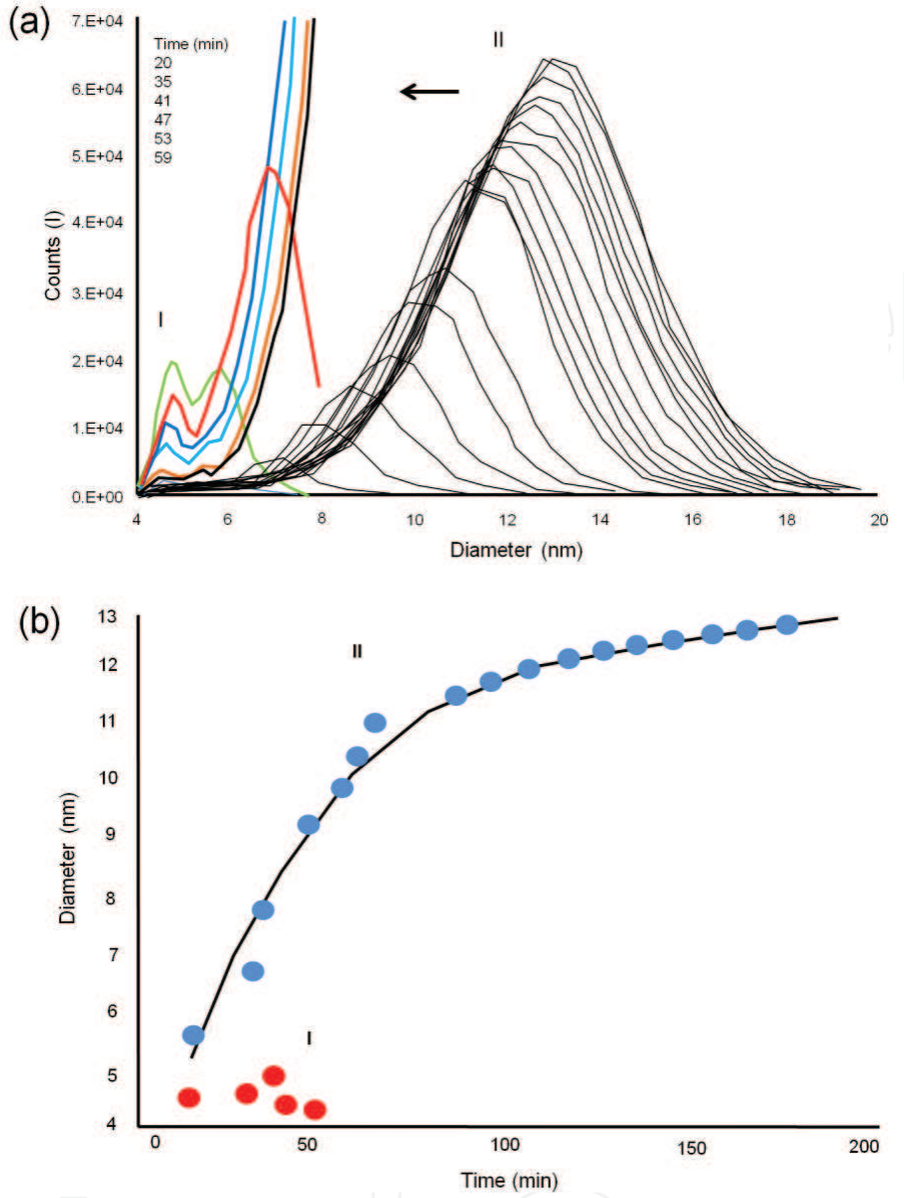

Figure 8. Particle size distribution obtained by the ES-SMPS method for (a) growth over the period of 200 min (II). The data for short times are enlarged by a factor of 10 (I), (b) the changes in the average diameter of the particles during growth. Reprinted with permission from Ref. [66]. Copyright 2011, Elsevier.

Considering the one-step approach rather than measurement from the image (two steps: imaging from SEM/HRTEM then measurement), the particle size analyzer is most suitable for research work focusing on particle size, in addition to higher reliability and accuracy.

7. Conclusion and perspective

Driven by the potential of TiO_2 nanoparticles, continuous development involving numerous research works is expected to rapidly increase in the future. The versatility provided by the

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sol-gel method makes these efforts to synthesise TiO_2 nanoparticles better and more relevant, considering the demands in the current applications. Parallel to the research and development process, characterisation of the synthesised TiO_2 nanoparticles is unavoidable. Despite the large availability of experimental alternatives, characterisation methods such as phase, structural, morphologies and size analysis were highly popular among researchers in different TiO_2-related fields. It is apparent that the characterisation techniques will be constantly used in research studies of TiO_2 nanoparticles.

For future work, it is suggested that the studies on the synthesised TiO_2 nanoparticles should be augmented towards structural modelling and simulation. With recent literatures focusing on the use of dopants, such theoretical works are essential in structurally visualising the doping mechanism. This is practically more significant in terms of discussing the performance and properties of the synthesised TiO_2 nanoparticles. Due to advances in computers and software technologies, the properties of the modelled TiO_2 nanoparticles can be completely simulated. Thus, another interesting approach would be to provide a comparison between the generated properties with the results from the experimental work. Additionally, simulation works can eventually show the potential of a particular formulation, thus providing an insight for researchers before venturing into the actual synthesis of TiO_2 nanoparticles.

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