Low-temperature Hydrothermal Synthesis of Titanium Dioxide Nanoparticles for Photocatalytic Applications

M Abdelhamid Shahat1,*, F M El-Hossary2, Ahmed Ghitas1, A M Abd El-Rahman3,2 and A A Ebnalwaled4

1 PV Unit, Solar and Space Research Department, National Research Institute of Astronomy and Geophysics (NRIAG), 11421 Helwan, Cairo, Egypt.
2 Physics Department, Faculty of Science, Sohag University, Sohag, Egypt.
3 King Abdulaziz University, Jeddah, KSA.
4 Electronics & Nano Devices Lab, Physics Department, Faculty of Science, South Valley University, 83523 Qena, Egypt.

* E-mail: m.abdelhamid999@gmail.com

Abstract. Titanium dioxide nanoparticles (TiO2 NPs) were synthesized by a surfactant-templated hydrothermal method at low temperature (75 °C) for photocatalytic applications. Investigation of structural, optical and photocatalytic properties of TiO2 NPs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), FT-IR and UV–vis absorption spectroscopy. The structural analysis confirmed a polycrystalline tetragonal anatase TiO2 phase with nanocrystalline structure and almost regular spherical shape. It has been found that the synthesized TiO2 NPs have an energy bandgap value between 4.42 and 4.46 eV; achieving a photodegradation efficiency of methyl orange dye of 81% to 88 % under UV visible light.

Keywords: Photodegradation, TiO2 NPs, Energy band gap, Hydrothermal Method

1. Introduction

Long-time ago, Organic dyes are considered as one of the most significant environmental and water pollutants. They are mostly non-biodegradable organic compounds (stable to light and oxidation) and have high toxicity to humans even at low concentrations [1]. Consequently, the large-scale disposal of toxic organics during wastewater purification considered a massive environmental challenge. Photocatalytic water treatment has been considered as a reliable technology, which aims to convert organic matter into inorganic compounds [2]. Metal oxides semiconductors (MOS) with good hydrophobicity and high photocatalytic activities have been effectively used in water treatment technology. They work on enhancing the oxidation of unmanageable pollutants suspended in water, through the generation of highly reactive hydroxyl (OH) and oxygen (O2) free radicals [3]. In addition, metal oxides such as TiO2, GO, rGO, CdS and Fe2O3 nanoparticles (NPs) are used as active materials for water purification process due to their ability to remove toxic elements on a large scale. [4–7]. Titanium dioxide nanoparticles (TiO2 NPs) have attractive characteristics, such as high surface areas, synthesis simplicity, affordability, outstanding chemical stability and unique features (optical,
electrical and magnetic). These properties are unique and suited for a wide spectrum of applications, such as PV cells, water splitting, electro-chromic devices, fillers, ceramics, coatings, pigment and photocatalysis [8]. In addition, it can be used in other applications for energy storage, sensors and optics [9–11]. Consequently, TiO$_2$ with its attractive properties and characteristics has found to be linked to fundamental and practical research. As known, TiO$_2$ is synthesized in different nanoforms, such as NPs films, nanorods, nanowires, and nanotubes, in which optimizing their properties can be adjusted by controlling preparation conditions [12]. For example, optimizing crystal size and phase structure lead to control of the TiO$_2$ NPs band gap for a specific kind of applications. Band gap energy (E$_g$) has a value of 3.0 and 3.1 eV for rutile and brookite structure, respectively. However, for anatase structure it was discovered to be more than 3.2 eV and hence UV light (λ < 380 nm) could be excited [13–15].

Bavykin et al. have prepared TiO$_2$ NPs in anatase, rutile and brookite structures using the hydrothermal process by producing and consecutively wrapping titanate nanosheets [16, 17]. Different physics and chemistry procedures were used to prepare TiO$_2$ NPs, for example solvothermal, sol-gel, sonochemical, hydrothermal, CVD, PVD and electro-deposition, etc. [18–24]. Herein, the surfactant-free hydrothermal process is employed as one of the soft solution techniques. It is a low-temperature process, used to synthesis various nanomaterials by creating a chemical reaction in water in a sealed pressure vessel [25]. As previously known, the degradation of the organic compound mechanism using TiO$_2$ is mainly based on the fast generation of electron-hole pairs by the irradiation with UV light. Then, it is followed by oxidation and reduction reactions [26]. TiO$_2$ works well as a heterogeneous photocatalyst in a dye polluted water environment and has the ability to oxidize donor molecules through photo-induced holes and reduce the adsorbed oxygen by electrons [27]. The following simple chemical equations show the oxidation and reduction process:

$$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(h^*_{VB} + e^-_{CB}) \quad (1)$$
$$h^*_{VB} + \text{OH}^- \rightarrow \text{OH}^\cdot \quad (2)$$
$$e^-_{CB} + \text{O}_2 \rightarrow \text{O}_2^\cdot \quad (3)$$
$$\text{H}_2\text{O} + \text{O}_2^\cdot \rightarrow \text{OH}^\cdot + \text{O}_2 \quad (4)$$
$$\text{HOH}^\cdot \rightarrow \text{H}_2 + \text{H}_2\text{O}_2 \quad (5)$$
$$2\text{HOH}^\cdot \rightarrow \text{OH}^\cdot + \text{OH}^- + \text{O}_2 \quad (6)$$
$$\text{OH}^\cdot + \text{O}_2^\cdot + h^*_{VB} + \text{Pollutants} \rightarrow \text{CO}_2^\uparrow + \text{H}_2\text{O} \quad (7)$$

The current research work deals with the synthesis of TiO$_2$ NPs by surfactant-free hydrothermal method at low temperature. In this study, the hydrothermal reaction time is adjusted in order to control the crystal structure and optical properties of TiO$_2$ NPs, which in turn improve their photocatalytic efficiency for the degradation of organic dye in non-toxic forms.

2. Experimental Setup

2.1. Materials and Preparation method of TiO$_2$ NPs

As raw ingredients for the manufacture of TiO$_2$ NPs, TiO$_2$ powder (titanium powder, Ranbaxy, >5μm) were employed. The hydrothermal method of typical TiO$_2$ NPs is shown in Fig. 1. By placing 10 g of powder in a glass vial under a magnetic stirring (900 rpm) in 40 ml of distillated water for a 1h reaction period at room temperature. The mixture was sonicated for roughly 10 min then heat treated in a Teflon stainless steel autoclave at 75°C for 4h. The solution was able to cool down gradually to room temperature (RT) over 24h. The precipitate generated was filtered out, then washed with ethanol and water multiple times and calcinated for 3h at 500 °C. In general, the preceding process was employed to produce TiO$_2$ NPs at various periods of 8 and 12h of reaction.
2.2. Instrumentation and Characterization

The structure and phase purity of the synthesized samples were determined by X-ray powder diffraction (XRD, Philips diffractometer 1710) using Cu-Ka radiation (1.5418 Å). The morphology of the TiO$_2$ NPs was assessed by SEM (JOUL SEM model JSM – 5500 - Japan) with an accelerated voltage of 10 kV. Quantifying particle's shapes and features were characterized by HRTEM (JEOL, JEM- A 2100 – Japan) by applying an accelerating voltage of 200 kV. Furthermore, FT-IR (Jasco Model 4100 Japan) spectrum scanned from 4000 to 400cm$^{-1}$ at RT with resolution of 4cm$^{-1}$ have been evaluated for samples functional groups. In addition, under normal incidence wavelength ranging from 190-1100 nm, the optical characteristics of TiO$_2$ NP have been evaluated by a computerised SPECORD 200 PLUS spectrophotometer with 1nm step.

2.3. Photocatalytic activity

The photocatalytic activities of TiO$_2$ NPs were evaluated by the degradation level of the methyl orange (MO) dye. In order to achieve TiO$_2$ NPs with a catalyst concentration of 0.75 g/L, 75 mg of TiO$_2$ NPs was dissolved in 100ml of MO solution (50mg/L). The photocatalytic experiment was conveyed out in a beaker illuminated with a UV lamp (wavelength 264 nm). Preceding to photoirradiation, the nanoparticle suspension was stirred in a dark environment for 30 min to maintain adsorption/desorption equilibrium between the catalyst and MO dye molecules. The suspensions were collected, then centrifuged (4000 rpm, 15 min) at all irradiation intervals to separate the photocatalyst NPs. The UV-Vis Spectrophotometer (analytic Jena, Specord 200 plus, 190-1100 nm) was used to measure the concentrations of MO; the absorption was monitored at $\lambda_{max} = 464$ nm. An alignment plot was carried out in relation to absorption and concentration, based on Beer-Lambert’s law. Conducting experiments without catalysts was taken into consideration when the dye-catalyst solution was illuminated.

3. Results and Discussion

3.1. Phase formation and structural study

The phase identification and crystallinity of TiO$_2$ NPs samples were performed by X-ray diffraction. Fig. 2 shows the XRD patterns of the TiO$_2$ NPs hydrothermally prepared at various
reaction times. Phase purity and crystallite size of the investigated samples were produced. The XRD spectrum of TiO$_2$ NPs exhibits tetragonal structure with clear peaks corresponding to the lattice planes of (101), (103), (200), (105), (213), (116), and (107). Table 1 presents $d_{hkl}$ for the obtained TiO$_2$ NPs at different reaction times, which is in a good agreement with the standard XRD card [28].

![XRD spectra of TiO$_2$ NPs obtained at different reaction times.](image)

**Figure 2.** XRD spectra of TiO$_2$ NPs obtained at different reaction times.

**Table 1.** Comparison between $d_{hkl}$ for the obtained TiO$_2$ NPs and $d_{hkl}$ for the standard tetragonal TiO$_2$ crystals.

| hkl  | $d_{hkl}$ (Å) Calculated | $d_{hkl}$ (Å) for standard Tetragonal TiO$_2$ |
|------|--------------------------|---------------------------------------------|
|      | 4h | 8h | 12h |                                 |
| (101)| 3.52 | 3.52 | 3.52 | 3.52 |
| (103)| 2.39 | 2.38 | 2.38 | 2.37 |
| (200)| 1.90 | 1.89 | 1.89 | 1.88 |
| (105)| 1.70 | 1.70 | 1.70 | 1.70 |
| (213)| 1.48 | 1.48 | 1.48 | 1.48 |
| (116)| 1.36 | 1.36 | 1.36 | 1.36 |
| (107)| 1.26 | 1.27 | 1.26 | 1.26 |

Williamson-Hall analysis was applied to determine crystallite size ($D$) and microstrain ($\varepsilon$) of the investigated samples [29]. XRD peak broadening is concerned in these calculations. As illustrated from eq. (8), the total line broadening reflects two physical factors that consider the crystallite size ($D$) and strain ($\varepsilon$) effects:

$$\beta = \beta_D + \beta_e$$  \hspace{1cm} (8)

The Williamson-Hall equation is written as follows:

$$\Gamma \cos \theta = \frac{0.94 \lambda}{D} + 4 \varepsilon \sin \theta$$  \hspace{1cm} (9)
The broadening factors of the TiO$_2$ NPs samples are directly calculated from drawing $\Gamma\cos\theta$ versus $\sin\theta$ as shown in Fig.3. Table (2) shows the crystallite size 31.48, 18.33 and 11.87 nm and their corresponding microstrain values 30, 33 and 34 x10$^{-4}$ for TiO$_2$ NPs samples prepared for different reaction times of 4, 8 and 12h, respectively. The positive sign of the microstrain for TiO$_2$ indicates lattice expansion.

![Williamson-Hall plot for TiO$_2$ NPs synthesized at different reaction times.](image)

**Table 2.** Structural parameters of the obtained TiO$_2$ NPs at different reaction times.

| Reaction time | Lattice-Parameters | Williamon-Hall |
|---------------|--------------------|----------------|
|               | $a$ (Å) | $c$ (Å) | D size (nm) | Microstrain X ($10^{-4}$) |
| 4 h           | 3.77   | 9.48   | 31.47       | 30 |
| 8 h           | 3.77   | 9.48   | 18.33       | 33 |
| 12 h          | 3.78   | 9.48   | 11.86       | 34 |

3.2. *Fourier transform infrared (FT-IR) spectroscopy*

FT-IR is conducted as a spectroscopic technique to examine a wide range of organic materials. FT-IR spectra of the KBr sample pellets is analyzed in order to characterize the bond structure of TiO$_2$ NPs. All FT-IR spectra of TiO$_2$ NPs prepared at various reaction times (4, 8 and 12h) indicate three absorption bands as shown in Fig. 4. The FT-IR spectra of various TiO$_2$ NPs show the main absorption peaks with changes in the intensity of the absorption peak and peak width indicating the high influence of processing times on chemical bonds during the formation of TiO$_2$ NPs. The first peak appeared between 3700 and 3000 cm$^{-1}$ confirms stretching hydroxyl (O-H), and represents water in moisture form. The second peak observed between 1700 and 1627 cm$^{-1}$ is attributed to the
The third FT-IR spectrum peak that detected between 800 and 450 cm\(^{-1}\) corresponds to Ti-O stretching bands [30]. It has been previously stated that, preparing samples at relatively long hydrothermal reaction time led to detect strong absorption between 800 and 450 cm\(^{-1}\). This was found to be attributed to the strong vibrations in the stretching Ti-O-Ti bonds [31, 32].

![Figure 4. FT-IR spectra for TiO\(_2\) NPs prepared at different reaction times.](image)

3.3. Morphology

SEM and HR-TEM are used as microstructural characterization techniques in order to reinforce the phase identification analysis. Further, based on image analysis, particle shape and crystallite size of the TiO\(_2\) NPs can be obtained. In HR-TEM analysis, the interference between the transmitted and the scattered beams leads to obtain a high-quality interference image. As shown from Fig. 5, the TiO\(_2\) NPs are characterized with a semi-spherical particle form but with some variations in their particle size (≥ 50 nm) as the reaction time increases. It was observed that the sample, prepared at a 4 h reaction time, revealed TiO\(_2\) NPs with a relatively smaller size than in samples prepared at 8 and 12 h. Similar results were obtained at relatively higher hydrothermal reaction temperatures [33 – 37]. Jun Ho Kim et al. succeeded in preparing TiO\(_2\) NPs with uniform spherical shape by hydrothermal Teflon autoclave at 180 °C for 5 h, they found a relative increase in particle size owing to the sintering effect at different calcination temperatures (105- 700 °C) [33]. Sawanta S. Mali et al. prepared anatase TiO\(_2\) with spherical shape nanoparticles using a hydrothermal reaction method at 160 °C for 4, 6 and 8 h [34]. Other research groups synthesized TiO\(_2\) NPs with typical structural and morphological properties using the same method but with higher reaction temperatures and longer processing times; they increased the reaction temperature and time up to 240 °C and 36 h, respectively [35 – 37]. The formation mechanism of nanoparticles is agreed well with the previous nanoparticles growth mechanism. The hydrothermal growth mechanism for the TiO\(_2\) NPs is summarized into four main stages, namely: (1) The dissolution process, in which the bonds of TiO\(_2\) are broken in aqueous solution; (2) a thin-layer growth in a form of nanosheets; (3) nanoscale exfoliation process and finally (4) growing nanosheets with an increasing tendency of curling; leading to nanospheres' formation [38 – 41].
3.4. Optical properties

One can obtain the desired absorption (maximum absorption) at a specific wavelength when light with different wavelengths interact with any material. UV-visible spectrophotometer is used to identify the absorption spectrum of TiO$_2$ NPs which are suspended in distilled water at room temperature. Fig. 6a shows the absorbance spectra of TiO$_2$ NPs over a spectral range between 200 nm and 800 nm. The absorption edge of all TiO$_2$ NPs samples is found to be equal and has a value of around 269 nm. This value is much lower compared to that of the bulk TiO$_2$ (374.9 nm). Almost the same behaviour has been observed by Hariharan et al. [42]. However, TiO$_2$ NPs doped by other materials of graphene/Fe$^{3+}$ and CdS found a relative higher absorption edge at 413 nm and at < 380 nm, respectively [43, 44]. Fig. 6b illustrates the transmission characteristics of TiO$_2$ NPs prepared at various reaction times. The TiO$_2$ NPs have a relatively higher transmission along the visible wavelengths.

Figure 6a,b. UV-VIS absorption and transmission spectra for TiO$_2$ NPs prepared at different reaction time.
Tauc relationship is considered as a universal method used to determine the optical band gap for direct transition semiconductor materials [45 – 47]. Fig. 7a-c shows plots of \((\alpha h\nu)^2\) vs \(h\nu\). The values of the optical band gap \(E_g\) were calculated for TiO\(_2\) NPs samples prepared at different reaction times. Based on that, a limited change is obtained in the \(E_g\) values of TiO\(_2\) NPs, indicating values of (4.46, 4.43 and 4.42 eV) for samples prepared at hydrothermal treatment times of 4, 8 and 12 h, respectively. Previously, the energy gap values of TiO\(_2\) nanomaterials showed a high dependence on the preparation method as it achieved 3.85-4.32 eV in direct \(E_g\) values [48], and varied from 2.78 to 3.31 eV with the DC plasma sputtering method [49].

![Figure 7a, b, c. The relation between \((\alpha h\nu)^2\) and \(h\nu\), (a, b, c) for the obtained TiO\(_2\) at different reaction times.](image)

3.5. Water Treatment

Many organic compounds can be efficiently decomposed into the existence of photocatalytic metal oxide NPs. The degradation process of these organic compounds is realized by establishing a photooxidation reaction with the formation of surface hydroxyls (OH\(^-\)) on the TiO\(_2\) NPs. Electron–hole (e/h) pairs are generated in TiO\(_2\) NPs during their irradiation with the UV light. To ensure the production of electron-hole pairs, the incident light should have energy higher or equal to the bandgap energy of the photocatalytic nanoparticles according to the photochemical reaction in eq.1 [50]. Photocatalytic materials with lower bandgap assure a fast generation of e/h pairs. This is accompanied by a low recombination possibility for the photogenerated charges carries produced in the water
solution. The generated e/h pairs migrate to the interface and react with $O_{2}^•$, $OH^−$ that existed in $TiO_2$; leading to radicals formation consisting of hydroxyl cations ($•OH$) and anions ($O_2^−$).

\[
(TiO_2) \cdots OH^− + h^+ \rightarrow •OH
\]  

(10)

The hydroxyl radicals are the most effective oxidizing species which attack toxic organic pollutants and then produce nontoxic compounds (volatile $CO_2$ and water) [27]. Fig. 8a-c shows the UV-vis absorption spectra for MO dye solution after different time intervals treated with 75 mg of $TiO_2$ NPs at various reaction times of 4, 8 and 12h. The maximum absorption peaks are detected around 464 nm for all prepared solutions. The absorption peak intensity of $TiO_2$ NPs in the water-dye solution is observed to be gradually decreased with the increase of UV exposure time. Correspondingly, the MO dye decomposition is gradually decreased. Fig. 9 shows typical colors of MO dye solution mixed with $TiO_2$ NPs synthesized at a reaction time of 12h. As observed, orange to light yellow color degradation has detected with the gradual increase in UV exposure time. In Comparing the absorption spectra for MO dye solution treated with $TiO_2$ NPs, the highest photocatalytic activity is achieved with using $TiO_2$ NPs prepared at a reaction time of 12h. One can observe that the absorption peak for water treatment solution by $TiO_2$ NPs prepared at 12h has disappeared faster than for other solutions mixed with different $TiO_2$ NPs; leading to faster stopping for the dye decomposition. This is mostly attributed to structural changes of $TiO_2$ NPs, which is in particular found in the crystallinity improvement of $TiO_2$ NPs with the increase of hydrothermal reaction time [37].

![Figure 8a,b,c. Absorbance changes of MO after different irradiation times in the presence of TiO2 photocatalyst under UV light illumination, (a, b, c) for the obtained TiO2 at different reaction times.](image-url)
The photodegradation efficiency of the photocatalytic materials was calculated according to the simple formula of $C / C_0$, where $C_0$ is the photocatalytic initial concentration after equilibrium adsorption and $C$ its concentration during the reaction time. Fig. 10a indicates a photocatalytic degradation for the MO dye in the presence of TiO$_2$ NPs. The results show a complete decomposition for the MO dye after 270 min under irradiation by UV-visible light. The anatase TiO$_2$ NPs with low energy band gaps, exhibit high photocatalytic activity owing to a rapid generation of e/h pairs [46]. This is owing to that the metal ions act as electron trap centers in the bandgap which leading to exceed carrier's lifetime and reduce carrier's recombination loss. These processes keep a high concentration of e/h pairs that directly exhibit high photocatalytic activity [46, 51]. The results that are presented in Fig. 10b explore that the organic materials cannot be decomposed without the photocatalyst or UV irradiation. The degradation efficiency was found to be gradually increased (81, 86 and 88%) after 270 min under UV irradiation with the increase of the hydrothermal reaction time of TiO$_2$ NPs (4, 8 and 12 h). The little change in the degradation efficiency is mostly ascribed to the gradual decrease in the values of the optical band gap (4.46, 4.43 and 4.42 eV). The photocatalytic efficiency of TiO$_2$ compared to that of ZnO, and GO in removing of methyl orange (MO) dye has been previously studied [52]. Other results indicated the best efficiency for TiO$_2$ in removing MO dyes with lower initial concentrations [53]. Further, the anatase TiO$_2$ as photocatalyst has been effectively used in the removal of MO and BPB dyes, with a degradation efficiency of 85.51% within 240 min [53].
Figure 10a,b: a) Kinetic of the degradation of MO in the presence of UV, b) Degradation efficiency ($\eta$), as a function of the irradiation time for the obtained TiO$_2$ NPs prepared with different reaction times

4. Conclusion

The current work was accomplished with one of the most strategic metal oxide materials science research goals of finding an economic and efficient photodegradation system for water treatment applications. Photocatalyst TiO$_2$ NPs were synthesized by utilizing a free surfactant hydrothermal method at low temperature (75 $^\circ$C) for various treatment times. The structural results confirm obtaining tetragonal TiO$_2$ NPs with the anatase phase. The crystallinity and surface morphology of the synthesized NPs are found to be influenced by changing the hydrothermal reaction time. The TiO$_2$ NPs have a spherical particle shape with a small crystallite size (31.4 -11.8 nm). Different reaction time process reveals that the bandgap decreased from 4.46 to 4.42 eV, which in turn leads to an increase in the degradation efficiency from 81 to 88% after 270 min under UV light irradiation which ensures good applications of TiO$_2$ NPs in water treatment.

References
[1] McCallum J E B, Madison S A, Alkan S, Depinto RL, Rojas Wahl RU 2000 Environ Sci Technol 34 (24) 5157–64
[2] Hadjeltaief H B, Zina M B, Galvez M E, Da-Costa P 2016 J Photochem Photobiol A Chem 315 25–33
[3] Chen D, Du Y, Zhu H, Deng Y 2014 Appl Clay Sci 87 285–91
[4] El-Hossary FM, Ghitas A, El-Rahman AMA, Shahat MA, Fawey MH 2021 Vacuum 110158
[5] El-Hossary FM, Ghitas A, Abd El-Rahman AM, Ebnalwaled AA, Shahat MA, Fawey MH 2021 J Mater Sci Mater Electron 1–14
[6] El-Hossary F M, Ghitas A, Abd El-Rahman AM, Ebnalwaled AA, Shahat MA, Fawey MH 2020 IOP Conference Series: Materials Science and Engineering 956 (1)
[7] El-Hossary FM, Ghitas A, Abd El-Rahman AM, Ebnalwaled AA, Fawey MH, Shahat MA 2020 IOP Conference Series: Materials Science and Engineering 762 012001
[8] Lamba R, Umar A, Mehta SK, Kansal SK 2015 J Alloys Compd 653 327–33
[9] Osman DAM, Mustafa MA. 2015 J Nanosci Nanoeng 1 (4) 248–51
[10] Benazir A, Gomathi K, Aram S 2017 J Environ Nanotechnol 6 (1) 39–43
[11] Panda KK, Golari D, Venugopal A, Achary VMM, Phaomei G, Parinandi NL, et al 2017 root bioassay system. Antioxidants 6 (2) 35
[12] Behnajady MA, Modirshahla N, Fathi H 2006 J Hazard Mater 136 (3) 816–21
[13] Chen X, Mao SS. 2007 Chem Rev 107 (7) 2891–959
[14] Kuo H-L, Kuo C-Y, Liu C-H, Chao J-H, Lin C-H. 2007 Catal Letters 113 (1–2) 7–12
[15] Reyes-Coronado D, Rodríguez-Gattorno G, Espinosa-Pesqueira ME, Cab C, De Coss R d, Oskam G. 2008 Nanotechnology 19 (14) 145605
[16] Bavurk D V, Parmon VN, Lapkin AA, Walsh FC 2004 J Mater Chem 14 (22) 3370–7
[17] Peng T, Ray S, Veeravalli SS, LaiMAN JA, Arefi-Khonsari F 2018 Mater Res Bull 105 104–13
[18] Manjunath K, Yadav LSR, Jayalakshmi T, Reddy V, Rajanaika H, Nagaraju G 2018 J Mater Res Technol 7 (1) 7–13
[19] Lin H, de Oliveira PW, Grobelsek I, Haettich A, Veith M 2020 Zeitschrift für Anorg und Allg Chemie 636 (11) 1947–54
[20] Manjunath K, Souza VS, Nagarshthappa T, Nagaraju G, Scholten JD, Dupont J 2016 Mater Res Express 3 (11) 115902
[21] Manjunath K, Souza VS, Nagaraju G, Santos JML, Dupont J, Ramakrishnappa T 2016 New J Chem 40 (12) 10172–80
[22] Nagaraju G, Ravishankar TN, Manjunatha K, Sarkar S, Nagabhushana H, Goncalves R, et al 2013 Mater Lett 109 27–30
[23] Nagaraju G, Manjunath K, Sarkar S, Gunter E, Teixeira SR, Dupont J 2015 Int J Hydrogen Energy 40 (36) 12209–16
[24] Krishnappa M, Souza VS, Ganganagappa N, Scholten JD, Teixeira SR, Dupont J, et al 2015 Chem Eur J 21 (49) 17624–30
[25] Adschiri T, Hakuta Y, Sue K, Arai K 2001 J Nanoparticle Res 3 (2–3) 227–35
[26] Hariharan D, Sriniwasan K, Nehru LC 2017 J Nanomedicine Res 5 (6) 138–42
[27] Ramakrishnan VM, Natarajan M, Santhanam A, Asokan V, Velauthapillai D 2018 Mater Res Bull 97 351–60
[28] Hanawalt JD, Rinn HW, Frevel LK. Chemical analysis by X-ray diffraction 1938 Ind Eng Chem Anal Ed 10 (9) 457–512
[29] Hamann TW, Martinson ABF, Elam JW, Pellin MJ, Hupf JT. 2008 Adv Mater 20 (8) 1560–4
[30] Dobrucka R 2017 Iran J Pharm Res IJPR 16 (2) 756
[31] Guo Y, He D, Xia S, Xie X, Gao X, Zhang Q 2012 J Nanomater 2012
[32] Kumar PSM, Francis AP, Devasena T 2014 J Environ Nanotechnol 3 (4) 78–85
[33] Kim JH, Noh BH, Lee G-D, Hong S-S 2005 Korean J Chem Eng 22 (3) 370–4
[34] Mali SS, Betty CA, Bhosale PN, Patil PS 2011 CrystEngComm 13 (21):6349–51
[35] Collazzo GC, Jahn SL, Carreño NL V, Foletto EL 2011 J Chem Eng 28 (2) 265–72
[36] Vijayalakshmi R, Rajendran V 2012 Arch Appl Sci Res 4 (2) 1183–90
[37] Kavitha M, Gopinathan C, Pandi P 2013 Int J Adv Res Technol 2 (4) 102–8
[38] Shahrezai M, Habibzadeh S, Babaluoo AA, Hosseinkhani H, Haghhighi M, Hasanzadeh A, et al 2017 J Exp Nanosci 12 (1) 45–61
[39] Cui L, Hui KN, Hsi KS, Lee SK, Zhou W, Wan ZP, et al 2012 Mater Lett 75 175–8
[40] Chao C, Ren Z, Yin S, Xu G, Gong S, Yang X, et al 2014 Adv Powder Technol 25 (2) 745–51
[41] Wang L-Q, Song S-H, Hodgson S, Baker A, Yu J 2006 J Eur Ceram Soc 26 (8) 1405–9
[42] Hariharan D, Christy AJ, Mayandi J, Nehru LC 2018 Mater Lett 222 45–9
[43] Li W, Liu X, Li H 2015 J Mater Chem A 3 (29) 15214–24
[44] Xie Z, Liu X, Liu W, Liu C, Li Z, Zhang Z 2014 Sci Technol Adv Mater 15 (5) 55006
[45] Pankove JI 1975 Courier Corporation
[46] Ahmadi M, Ghasemi MR, Rafsanjani HH 2011 J Mater Sci Eng 5 (1) 87
[47] El-Hossary FM, Ghitas A, Abd El-Rahman AM, Ebnalwaled AA, Shahat MA 2020 IOP Conference Series: Materials Science and Engineering 956 012003
[48] Rahman K H, Biswas S, & Kar A K 2018 AIP Conference Proceedings 1 (1953) 030022
[49] Abd El-Rahman A M, & Mohamed S H 2018 AIP Conference Proceedings 1 (1953) 030022
[50] Kontos A I, Arabatzis I M, Tsoukeris DS, Kontos AG, Bernard MC, Petrakis DE, et al 2015 Catal Today 101 (3–4) 275–81
[51] Ni M, Leung MKH, Leung DYC, Sumathy K 2007 Renew Sustain Energy Rev 11 (3) 401–25
[52] Ralila R, Avery C, Chakrabarti S, Biswas P 2017 Appl Nanosci 7 (5) 253–9
[53] Dhamalakshmi J, Padiyan DP 2017 Mater Res Express 4 (9) 95020