Effect of solvents on the morphology of TiO2 nanoparticles prepared by microwave method

Reda S. Jalawkhan1, Aseel Adnan Ouda2, Ahmed M. Abdul-lettif1 and Firas K. Mohamad Alosfur3,4*
1Department of Physics, College of Science, University of Kerbala, Kerbala, Iraq
2Ministry of Education, Educational Directorate of Holy Kerbala, Kerbala, Iraq
3Department of Environmental Health, College of Applied Medical Sciences, University of Kerbala, Kerbala, Iraq
4Faculty of Dentistry, University of Alkafeel, Najaf, Iraq
Corresponding author: firas.k.m@uokerbala.edu, frsos2005@yahoo.com

Abstract
In this study, titanium dioxide (TiO2) was synthesized using microwave method as rapid, uncostly and effective method. In order to study the effect of the solvent on the morphology of the prepared samples, two different solvents were used. The first solvent was ethylene glycol (EG, 99.8%) and the other was deionized water (DIW), while titanium isopropoxide Ti[(CH3)2CHO]4 was used as TiO2 precursor. A commercial microwave oven was used with a power of 750 W and 5 minutes was selected as a duration of time preparation. The prepared specimens were annealed at 400 °C for 1 h. Diverse techniques were used in this study, such as X-Ray diffraction (XRD), field emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FESEM-EDX) and Fourier transforms infrared spectroscopy (FTIR) to study the structures and morphology of the prepared TiO2. Surface area was measured using Brunauer EmmettTeller (BET) technique. The XRD results revealed that the prepared samples were a pure TiO2 in anatase face.

Noticeably, FESEM results show that the prepared TiO2 samples were nanorods-like shape with a length varied from 2 µm to 30 µm and a diameter varied from 500 nm to 6 µm when EG was used as a solvent. In contrast, spherical agglomerated nanoparticles with average diameters 20 nm were obtained when DIW was used as a solvent. The BET analysis revealed that the surface area of TiO2 nanorods was 151.413 m²/g, while it was 103.365 m²/g for TiO2 nanoparticles.

Keywords: TiO2; nanorods; microwave; surface area

1- Introduction:
Due to the significant population growth, numerous studies regarding to environmental and energy applications such as photocatalysis, sensing, solar-cells and photo-chromics have been done in the past decades [1]. Semiconductors metal oxides have attracted tremendous interest in recent years because of their unique electrical, mechanical and optical properties when their structural feature size is down to nanoscale. Various metal oxides have been evolved to be utilized in purification and photocatalysts applications but Titanium dioxide (TiO2) has stimulated a great deal of attention in comparison with other metal oxide materials. TiO2 in particular is preferred and employed due to its unique properties such as high photo-stability, non-toxicity, high oxidation, abundance, wide band gaps (3.0 - 3.2 eV) and inexpensive cost [2].

TiO2 has been formed in three crystalline polymorphs anatase and rutile in tetragonal phase while brookite in orthorhombic phase. Each of TiO2 phases is differ in chemical and physical
properties that lead to variant performances in devices fabricated from them. To realize promising TiO$_2$ nanostructures, many synthesis methods have been used to control their physicochemical properties such as polyolsolvothermal method [3], hydrothermal [4], chemical vapor deposition (CVD) [5], microwave [6], electro-spinning methods [7] and so on. TiO$_2$ nanostructures can be fabricated in many shapes such as nanorods [8 and 9], nanotubes [10 and 11], nanowires [12 and 13], nanobelts [14 and 15], nanospheres [16], nanoparticles [17], and etc. The morphologies and the crystal structures of TiO$_2$ depend on the conditions of synthesis, which are responsible for the arrangement and formation.

In this paper, TiO$_2$ nanostructures have been prepared with different purity by using a microwave-assisted method. Titanium isopropoxide (TTIP) was used as the metal precursor and Ethylene Glycol (EG) and deionized water (DIW) as solvent. The obtained samples were characterized by XRD, FESEM and BET techniques.

2 - Experimental procedures

2.1 Materials and Synthesis

All the materials utilized in the synthesis process were used without any purification. Titanium (IV) isopropoxide (TTIP, 98% Acros Organics) Ti(OCH(CH$_3$)$_2$)$_4$ was used as a TiO$_2$ precursor material. Two solvents were used to prepare the samples, Ethylene glycol (EG, J.T. Baker 99.8% Anhydrous solvent) C$_2$H$_4$(OH)$_2$ and highly pure deionized water (DIW). Two samples were synthesized using different solvents ethylene glycol (EG) and deionized water (DIW). In the synthesis procedure, (10 ml) of TTIP was added dropwise into (100 ml) of EG or DIW in a glass vessel under vigorous magnetic stirring at 600 rpm for 10 min. The microwave-assisted syntheses were conducted using a commercial microwave oven with a 2.45 GHz microwave frequency and a power of 750 W for 5 min. The resulted precipitation was collected and washed with DIW and absolute ethanol several times. Then the product was dried in an oven at a temperature of 60 ºC overnight. Finally, the powder was calcined at a temperature of 400 ºC in the air for 1h.

2.2 Characterizations

The crystal structure, phase identification and crystallite size of the prepared powder samples were studied using X-ray diffractometer model (Panalytical X’pert) with CuKα radiation of λ = 1.5405 Å. Field Emission Scanning Electronic Microscopy (FESEM) model (SIGMA VP) is used to depict the surface morphology characteristics such as particle size and shape of TiO$_2$ nanoparticles. The specific surface areas of TiO$_2$ nanoparticles were measured using BET method by (micromeritics TriStar II plus) device.

3 - Results and Discussions

3.1 X-ray Diffraction analysis

Figure (1) shows the X-ray diffractograms of the synthesized TiO$_2$ nanoparticles samples. From the X-ray patterns, the peaks have affirmed the formation of nanomaterials with high crystallization. It can be deduced that the TiO$_2$ nanoparticles synthesized in this study exist in anatase TiO$_2$ phase (according to JCPDS file No. 021-1272). The diffraction peaks of the prepared samples reveal a sharp domain (101) peak at about 2θ = 25.28º ascribed to a tetragonal structure of TiO$_2$ anatase phase with lattice constants a = b = 0.37852 nm, c = 0.65139 nm and angles α = β = γ = 90. The X-ray patterns also showed that there are no peaks of other materials, indicating that the samples were prepared with a high degree of the purity.
Figure (1): The XRD patterns of TiO$_2$ nanoparticles.

Table (1) summarizes the XRD results of TiO$_2$ nanopowders prepared at selected microwave power. The average crystallite size of TiO$_2$ nanoparticles has been determined from the broadening of anatase TiO$_2$ peaks at different 2θ in the pattern using Debye-Scherrer equation. The results reveal that the average crystallite size of the synthesized samples at different solvents (DIW and EG) was 5.28 nm and 6.47 nm, respectively.

Table (1) the XRD results for TiO$_2$ nanopowders

| Sample | 2θ (°) standard | d(Spacing(Å) standard | d(Spacing(Å) DIW) | 2θ (°) DIW | d(Spacing(Å) EG) | 2θ (°) EG | d(Spacing(Å) EG) |
|--------|----------------|-----------------------|------------------|--------|----------------|--------|----------------|
| 101    | 25.28          | 3.52000               | 25.32            | 3.51470| 25.32          | 3.51470|
| 004    | 37.85          | 2.37800               | 37.86            | 2.37444| 37.87          | 2.37384|
| 200    | 48.05          | 1.89200               | 47.88            | 1.89832| 48.10          | 1.89015|
| 105    | 53.89          | 1.69900               | 53.92            | 1.69906| 53.92          | 1.69906|
| 211    | 55.06          | 1.66650               | 55.10            | 1.66543| 55.10          | 1.66543|
| 204    | 62.69          | 1.48080               | 62.80            | 1.47847| 62.80          | 1.47847|
| 116    | 68.76          | 1.36410               | 69.06            | 1.35894| 68.84          | 1.36274|
| 220    | 70.31          | 1.33780               | 70.24            | 1.33897| 70.24          | 1.33897|
| 215    | 75.03          | 1.26490               | 75.03            | 1.26492| 75.10          | 1.26391|
| 224    | 82.66          | 1.16640               | 82.58            | 1.16735| 82.58          | 1.16735|
| 321    | 95.14          | 1.04360               | 94.92            | 1.04545| 94.92          | 1.04545|

3.2 Field Emission Scanning Electron Microscopy (FESEM)
The samples morphology was investigated using field emission scanning electron microscopy (FESEM). Figure (2 - a) shows a spherical and irregular shaped particles with uniformly distribution for DIW sample with an average size of 20nm diameter. Figure (2 - b) shows hexahedral pillar and nanorod shaped particles with a length varied from 2 µm to 30 µm and a diameter varied from 500 nm to 6 µm, while the aspect ratio (length/diameter) is 4.6. All the obtained rods consisted of homogeneous small neuromas nanoparticles with a uniform size around 50 nm.
Figure (2): The shape of nanoparticles size

3.3 Specific surface area (BET)

Brunauer–Emmett–Teller (BET) characterization is used to study the specific surface areas. Figure (3) shows the N$_2$ adsorption-desorption isotherms of the synthesized TiO$_2$ nanocrystals. The relative isotherms of the samples were of Type IV, characteristics of mesoporous materials. Particles showed a relative high surface area. The specific surface areas of DIW and EG were $103.365$ m$^2$/g and $151.413$ m$^2$/g respectively. Figure (4) shows the calculated pore size distribution curves, according to the (BJH) approach. Pore volume of DIW and EG are $0.131$ cm$^3$/g and $0.246$ cm$^3$/g respectively.
Figure (3): The TiO$_2$ isotherms Nitrogen adsorption-desorption.

Figure (4): The calculated pore size distribution curves.

The data of crystallite size, morphology, particle BET size, BET surface area, pore size and pore volume obtained in this study are summarized in Table (2).
Table (2) Summary of physical properties of the synthesized TiO$_2$ structures

| Sample | Crystallite size (nm) | Morphology          | Particle BET size (nm) | BET surface area ($\text{m}^2\text{g}^{-1}$) | Pore size (nm) | Pore volume ($\text{cm}^3\text{g}^{-1}$) |
|--------|----------------------|---------------------|------------------------|--------------------------------------------|----------------|----------------------------------------|
| DIW    | 5.28                 | Spherical           | 58.046                 | 103.365                                    | 4.805          | 0.131                                  |
| EG     | 6.47                 | hexahedral pillar   | 39.626                 | 151.413                                    | 5.728          | 0.246                                  |

4-Conclusions

The study shows that the technique of the microwave is simple, rapid and convenient for synthesizing TiO$_2$ nanoparticles. Microwave heating provides many possible advantages over traditional heating to the induction or enhancement of chemical reactions over regular heating. Two different solvents were used, ethylene glycol and deionized water (DIW). XRD results showed that TiO$_2$ nanoparticles were in an anatase phase with a very high crystallinity. The FESEM results show that the prepared TiO$_2$ samples are in an average size of 20 nm, when DIW was used as a solvent. The length varied from 2 µm to 30 µm, and the diameter varied from 500 nm to 6 µm for EG. The BET analysis revealed that the surface areas of TiO$_2$ were 103.365 m$^2$/g and 151.413 m$^2$/g, when DIW and EG are used respectively.

References

[1] Pang, Chi Lun, Robert Lindsay and Geoff Thornton. "Chemical reactions on rutile TiO$_2$ (110)." Chemical Society Reviews 37.10 (2008): 2328-2353.
[2] Yi Ma, Xiuli Wang, Yushuai Jia, Xiaobo Chen, Hongxian Han, Can Li "Titanium dioxide-based nanomaterials for photocatalytic fuel generations." Chemical reviews 114.19 (2014): 9987-10043.
[3] F. K. M. Alosfur, A. A. Ouda, N. J. Ridha, S. H. Abud, Structure and optical properties of TiO$_2$ nanorods prepared using polyolsolvothermal method, in AIP conference proceedings (AIP Publishing, College Park, 2019), p. 030025
[4] F. K. M. Alosfur, A. A. Ouda, N. J. Ridha, S. H. Abud, High photocatalytic activity of TiO$_2$ nanorods prepared by simple method. Mater. Res. Exp. 6, 065028 (2019)
[5] Pradhan S. K., Reucroft P. J., Yang F. Q., Dozier A. "Growth of TiO$_2$ nanorods by metalorganic chemical vapor deposition." Journal of Crystal Growth 256.1-2 (2003): 83-88.
[6] Suwarnkar M. B, Dhabbe R. S., Kadam A. N., Garadkar K. M. "Enhanced photocatalytic activity of Ag doped TiO$_2$ nanoparticles synthesized by a microwave assisted method." Ceramics International 40.4 (2014): 5489-5496.
[7] B. Ding, C. K. Kim, H. Y. Kim, M. K. Seo, S. J. Park, "Titanium dioxide nanofibers prepared by using electrospinning method." Fibers and polymers 5.2 (2004): 105-109.
[8] Zhang, Peilin, Shu Yin, and Tsugio Sato. "The influence of synthesis method on the properties of iron contained N doped TiO$_2$ photocatalysts." Applied Catalysis B: Environmental 103.3-4 (2011): 462-469.
[9] K. Santhi, M. Navaneethan, S. Harish, S. Ponnusamy, C. Muthamizhchelvan. "Synthesis and characterization of TiO$_2$ nanorods by hydrothermal method with different pH conditions and their photocatalytic activity." Applied Surface Science 500 (2020): 144058.
[10] Hui Feng, ThanhThuy Tran, T, Lan Chen, Lijuan Yuan, Qingyun Cai "Visible light-induced efficiently oxidative decomposition of p-Nitrophenol by CdTe/TiO$_2$ nanotube arrays." Chemical engineering journal 215 (2013): 591-599.
[11] J. Jitputti, S. Pavasupree, Y. Suzuki, S. Yoshikawa "Synthesis of TiO$_2$ nanotubes and its photocatalytic activity for H$_2$ evolution." Japanese Journal of Applied Physics 47.1S (2008): 751.
[12] Feng, Xuhui, Xiaopeng Huang, and Xinwei Wang. "Thermal conductivity and secondary porosity of single anatase TiO$_2$ nanowire." Nanotechnology 23.18 (2012): 185701.
[13] Z. G. Shang, Z. Q. Liu, P. J. Shang, J. K. Shang "Synthesis of single-crystal TiO$_2$ nanowire using titanium monoxide powder by thermal evaporation." Journal of Materials Science & Technology 28.5 (2012): 385-390.
[14] Wu N.Q., Wang J., Tafen D. N., Wang H., Zheng J. G., Lewis J. P., Liu X. G., Leonard S., Manivannan A. "Shape-enhanced photocatalytic activity of single-crystalline anatase TiO$_2$ (101) nanobelts." Journal of the American Chemical Society 132.19 (2010): 6679-6685.
[15] Zhao Z., Tian J., Sang Y., Cabot A., Liu H. "Structure, synthesis, and applications of TiO$_2$ nanobelts." Advanced materials 27.16 (2015): 2557-2582.
[16] Ming Z., Qigao S., Yuqi W., Qingrong C., Guiting L., Zhiquan P. "Self-template synthesis of double-shell TiO$_2$-ZIF-8 hollow nanospheres via sonocrystallization with enhanced photocatalytic activities in hydrogen generation." Applied Catalysis B: Environmental 241 (2019): 149-158.
[17] Jing T., Franz R., Yimei Z., Theo S., Louis E., Michael L. "An organometallic synthesis of TiO$_2$ nanoparticles." Nano letters 5.3 (2005): 543-548.