

SHAPE-CONTROLLED SYNTHESIS OF TITANIA
WITH 4-PENTYL-4-BIPHENYLCARBONITRILE AS A STRUCTURE
ALIGNING AGENT UNDER THE INFLUENCE OF MAGNETIC FIELD

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requirements for the award of the degree of
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I dedicate my thesis for my beloved

♥ *DAD, HJ. ABU BAKAR*

♥ *MOM, HJH. MASHITOH*

♥ *HUSBAND, MOHD FARID*

♥ *SON, IZZ ADAM IRFAN*

♥ *SIBLINGS*

♥ *FRIENDS*

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ABSTRACT

The synthesis of shape-controlled materials remains a big challenge today. The aim of this research is to explore the effects of magnetic field and line in the synthesis of shape-controlled titanium dioxide. 4-Pentyl-4-biphenylcarbonitrile (5CB), a liquid crystal, has been used as an alignment agent. In this research, the synthesis of shape-controlled titanium dioxide with liquid crystal as a structure-aligning agent is demonstrated using sol-gel method under a magnetic field. The mixture of 4-pentyl-4-biphenylcarbonitrile (5CB), tetra-*n*-butyl orthotitanate (TBOT), 2-propanol and water underwent slow hydrolysis under magnetic field (up to 0.3 T). The obtained titanium dioxide samples were characterized by scanning electron microscopy (SEM), diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and photoluminescence spectroscopy. Interesting results were observed when an external magnetic field was applied in the hydrolysis of TBOT in the presence of 5CB liquid crystal. The titanium dioxide is 'needle' like in shape when the reaction mixture containing tetra-*n*-butyl orthotitanate (TBOT), 2-propanol and water was placed under external magnetic field. The titanium dioxide is spherical in shape when the reaction mixture was not under the influence of magnetic field. The DR UV-Vis spectra showed that the absorption peak of shape-controlled titanium dioxide synthesized under magnetic field decreased compared to the sample synthesized without magnetic field due to the chromophore-chromophore interaction. Furthermore, photoluminescence spectra showed a decreased in the intensity of shape-controlled titanium dioxide and an increased in the intensity of photoluminescence peak of liquid crystal, suggesting the occurrence of electron transfer from titanium dioxide to liquid crystal during ultraviolet irradiation. Based on these results, strong interaction has occurred between 5CB and titanium dioxide. This interaction was required to control the shape of titanium dioxide with liquid crystal under magnetic field during the hydrolysis process. Based on this synthetic approach, this research has generated new perspectives for the application of magnetic field in shape-controlled synthesis of titanium dioxide with liquid crystal as a structure-aligning agent.

ABSTRAK

Sintesis bahan bentuk terkawal menjadi satu cabaran yang besar pada masa kini. Kajian ini bertujuan untuk mengkaji kesan medan dan garisan magnet terhadap penghasilan titanium dioksida bentuk terkawal. 4-Pentil-4-bifenilkarbonitril (5CB) adalah sejenis cecair kristal yang telah digunakan sebagai agen penjajaran. Kajian ini menunjukkan bahawa titanium dioksida bentuk terkawal dapat dihasilkan dengan menggunakan cecair kristal sebagai agen penjajaran di bawah aruhan medan magnet dengan menggunakan kaedah sol-gel. Campuran 4-pentil-4-bifenilkarbonitril (5CB), tetra-*n*-butil ortotitanat (TBOT), 2-propanol dan air telah melalui proses hidrolisis secara perlahan di bawah aruhan medan magnet (sehingga 0.3 T). Sampel titanium dioksida yang diperolehi dicirikan dengan menggunakan mikroskopi pengimbas elektron (SEM), spektroskopi pantulan serakan ultralembayung-cahaya nampak (DR UV-Vis), spektroskopi infra-merah transformasi Fourier (FTIR) dan spektroskopi fotopendarcahaya (PL). Keputusan yang menarik dapat dicerap apabila medan magnet digunakan dalam proses hidrolisis TBOT dalam kehadiran cecair kristal 5CB. Titanium dioksida yang terbentuk adalah seperti jarum apabila campuran tindak balas yang mengandungi TBOT, cecair kristal 5CB, 2-propanol dan air diletakkan di bawah aruhan medan magnet. Titanium dioksida berbentuk sfera apabila campuran tindak balas diletakkan tanpa pengaruh medan magnet. Spektra DR UV-Vis menunjukkan bahawa puncak penyerapan titanium dioksida bentuk terkawal yang dihasilkan di bawah aruhan medan magnet menurun dibandingkan dengan sampel yang dihasilkan tanpa medan magnet disebabkan oleh interaksi kromofor. Tambahan pula, spektra fotopendarcahaya menunjukkan penurunan keamatan bagi titanium dioksida dan peningkatan puncak keamatan fotopendarcahaya bagi cecair kristal, mencadangkan bahawa pemindahan elektron terjadi daripada titanium dioksida ke cecair kristal semasa penyinaran ultra lembayung. Keputusan ini, menunjukkan bahawa berlakunya interaksi yang kuat antara cecair kristal 5CB dan titanium dioksida. Interaksi ini diperlukan untuk mengawal bentuk titanium dioksida dengan 5CB di bawah aruhan medan magnet semasa proses hidrolisis. Berdasarkan pendekatan sintetik ini, kajian telah menjana perspektif baharu dalam penggunaan aruhan medan magnet bagi sintesis titanium dioksida bentuk terkawal menggunakan cecair kristal sebagai agen penjajaran struktur.

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LIST OF ABBREVIATIONS

%		Percent
°C		Degree celcius
5CB	-	4-pentyl-4-biphenylcarbonitrile
CTAB	-	Cetyltrimethylammonium bromide
DR UV-Vis	-	Diffuse reflectance ultraviolet visible
EMF	-	External magnetic field
FTIR	-	Fourier transform infrared spectroscopy
g	-	Gram
LC	-	Liquid crystal
nm	-	Nanometer
PL	-	Photoluminiscence
SEM	-	Scanning electron microscopy
T	-	Tesla
TBOT	-	Tetra- <i>n</i> -butyl orthotitanate
TGA	-	Thermal gravimetric analysis
TiO ₂	-	Titanium dioxide
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The developments of shape-controlled metal oxides have been a great interest in recent years due to their unique properties and technological applications. These metal oxides play a very important role in many scientific and technological areas. Their physicochemical properties and useful applications have been extensively studied by solid-state chemists (Seshadri, 2001; Burda *et al.*, 2005). Metal oxides including transition metals are able to form a large diversity of oxide compounds, giving the inspiration for designing new materials (Antonini *et al.*, 1987). In addition, metal oxides having multivalent oxidation states have attracted much attention among specialists because they often exhibit superior catalytic reaction performance.

From previous researches, many efforts have been done in order to synthesize shape-controlled metal oxides. For example, shape-controlled vanadium oxides have focused on the development of synthetic approaches towards nanotubes, nanobelts, nanofibers, nanowires and nanorods (Shah *et al.*, 2008). Furthermore, the synthesis of erbium-compound materials with controllable shape such as spheres, wrinkle-surfaced spheres and flowers has also been reported (Nguyen *et al.*, 2010). The synthesis of Mn_3O_4 with dot, rod and wire shapes has also been reported (Li *et al.*, 2010).

Solvothermal and hydrothermal are the most common and popular techniques used to synthesize shape-controlled metal oxide (Shah *et al.*, 2008; Tenne, 2004; Wang *et al.*, 2005). Hydrothermal and solvothermal synthesis are referred to the synthesis by chemical reactions of substances in a sealed heated solution above ambient temperature and pressure. The only difference between these two techniques is the precursor solution of solvothermal technique is usually non-aqueous. There are some disadvantages in these techniques although they are widely used to synthesize shape-controlled metal oxide materials. The disadvantages are the need of expensive autoclaves, the safety issues during reaction process and impossibility of observing the reaction process since the reaction is done in a black box. Therefore, in this research, a new technique has been applied by using magnetic field to synthesize well-aligned metal oxide material.

Magnetic field is a mathematical description of the magnetic influence towards magnetic materials and it is produced by moving electric charges and the intrinsic magnetic moments of elementary particles associated with a fundamental quantum property, their spin. In everyday life, magnetic fields are most often encountered as an invisible force created by permanent magnets which pulls on iron objects and attracts or repels other magnets. The permanent magnets are objects that produce their own persistent magnetic fields. They are made of ferromagnetic materials, such as iron and nickel, that have been magnetized, and they have both a north and a south pole. Figure 1.1 shows the iron (Fe) powders line up along the magnetic lines of a bar magnet from north to a south pole.

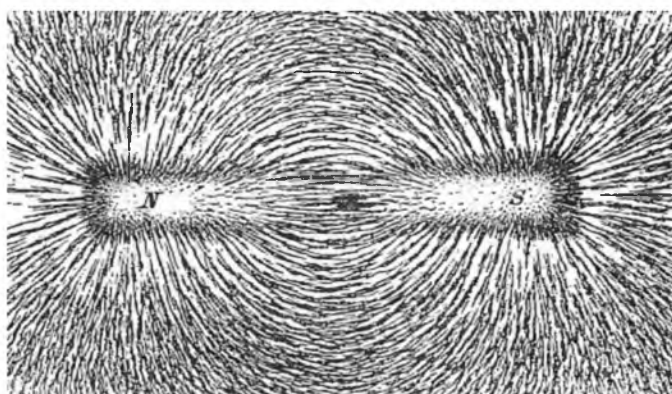


Figure 1.1: Iron powders line up along the magnetic field lines of a bar magnet from north to a south pole (Purcell, 2011).

Most materials respond to magnetic field by producing their own magnetism. The magnetism is one of the main physical properties of materials and every material possesses its own magnetism. It can be classified into three groups which are ferromagnetism, paramagnetism and diamagnetism. For example iron and nickel are the substances that possess ferromagnetism properties. Paramagnetic materials are materials that are attracted to magnetic fields, for example oxygen gas. Diamagnetic materials are materials that are unaffected by magnetic fields. Water is included in this category (Yamaguchi and Tanimoto, 2006). The magnetism properties are due to the magnetic susceptibility or magnetic energy density of material. Therefore, magnetic field is expected to give effect towards physical properties in order to control the chemical and physical processes (Young and Freedman, 2011).

From 1992 to 1994, magnetic field effects to control chemical and physical processes have been studied extensively in Japan, as the importance of high magnetic field has been recognized (Yamaguchi and Tanimoto, 2006). From the research project entitled “Innovative Utilization of High Magnetic Field”, it is stated that many interesting phenomena which can hardly be detected in low magnetic field have been observed. The marvellous finding of these results is that chemical and physical processes can be associated even with diamagnetic materials. For example, magnetic orientation of organic polymers, gels and carbon nanotubes, magnetic levitation of diamagnetic materials, and pseudo-microgravity generated by magnetic force have been observed (Yamaguchi and Tanimoto, 2006). These newly found magnetic phenomena will be very useful for processing functional molecules with improved quality.

Therefore, in this research, the magnetic field technique is a potential method because it has an advantage that all of the materials, even diamagnetic materials, can be aligned by magnetic field as long as they have magnetic anisotropy. Magnetic anisotropy is the material's magnetic properties. The material that has been utilized in this research is tetra-*n*-butyl orthotitanate (TBOT) which is a precursor of titanium dioxide (TiO₂). Titanium dioxide is currently the most important, most widespread and most investigated metal oxide due to its low toxicity, high thermal stability, and broad applicability (Lubis, 2013). With semiconductor properties, titanium dioxide

has shown outstanding performance in photocatalysis, water-splitting and self-cleaning. It is also useful in medical application due to its biocompatibility. Different shapes and sizes of titanium dioxide were reported to give different effects in various reactions such as photocatalytic reaction.

In addition, it is hypothesized that TiO_2 could be synthesized under magnetic field. It is expected that a new phenomenon will be discovered in the synthesis of materials under magnetic fields. Here, 4-pentyl-4-biphenylcarbonitrile (5CB), a liquid crystal has been used as an alignment agent since it can be aligned under magnetic field. In this research, the shape-controlled synthesis of TiO_2 with liquid crystal as a structure-aligning agent is demonstrated for the first time using sol-gel method under a magnetic field.

This research is considered as a novel approach, due to the external magnetic field used to obtain shape-controlled TiO_2 and to the best of our knowledge, there has been no publications on this yet. Figure 1.2 shows the conceptual model for the alignment of shape-controlled TiO_2 with 5CB liquid crystal under magnetic field. Based on the concept, one hypothesizes that well-aligned TiO_2 could be synthesized under the magnetic field in the presence of 5CB liquid crystal as the alignment agent.

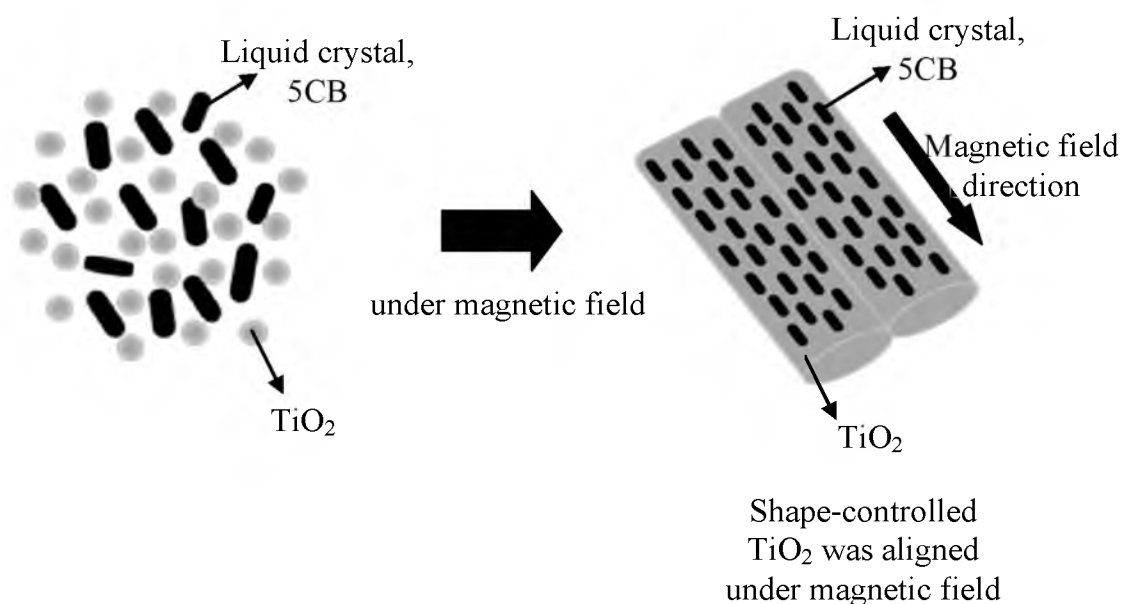


Figure 1.2: The conceptual model for the alignment of shape-controlled TiO_2 with liquid crystal, 5CB under magnetic field.

1.2 Problem Statement

This research is focused on investigating the effects and the influence of magnetic fields towards shape-controlled TiO_2 synthesized under magnetic field and the photocatalytic activity of the synthesized TiO_2 .

In previous research, it was demonstrated that TiO_2 could be synthesized under strong magnetic field using cetyltrimethylammoniumbromide (CTAB) as the alignment agent (Attan, 2013). The yarn-like, well-aligned TiO_2 was obtained where the hydrolysis of TBOT with CTAB as the alignment agent was carried out under magnetic field (Attan, 2013). However, the structure of well-aligned TiO_2 collapsed when the CTAB was removed. Therefore, this problem was overcome with the improvement of synthesizing TiO_2 under magnetic field using a different alignment agent which is 4-pentyl-4-biphenylcarbonitrile, 5CB liquid crystal.

The sol-gel method was employed to synthesize the shape-controlled TiO₂, with TBOT as the titanium dioxide precursor, 5CB liquid crystal as the alignment agent, with slow hydrolysis rate under magnetic field. 5CB is predicted to control the alignment of TBOT to produce well-aligned TiO₂ under magnetic field.

The effect of magnetic field towards the synthesized TiO₂ was characterized by several analytical instruments. The morphology and physicochemical properties of the shape-controlled TiO₂ were characterized using scanning electron microscope (SEM), Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD) spectrometer, photoluminescence spectrometer (PL), thermal gravimetric analyser (TGA), nitrogen adsorption apparatus and diffuse reflectance ultraviolet visible (DR UV-Vis) spectrometer. Figure 1.4 shows the research questions and hypothesis in this research.

Shape-Controlled Synthesis of Titania with 4-pentyl-4-biphenylcarbonitrile as a Structure-Aligning Agent under the Influence of Magnetic Field



Research Questions

- **Is there any difference between synthesized TiO_2 under magnetic field and without magnetic field?**
- **Can the shape and alignment of TiO_2 be controlled under the effects of magnetic field?**
- **What are the characteristics of the synthesized shape-controlled TiO_2 with liquid crystal as an alignment agent under magnetic field?**
- **Does shape-controlled TiO_2 with liquid crystal 5CB influence the photocatalytic activity?**

Hypothesis

- **The well-aligned TiO_2 can be synthesized under magnetic field with liquid crystal as an alignment agent. This material is more active in photocatalytic oxidation of styrene with aqueous H_2O_2 (30%) compared to that of the non-aligned TiO_2 .**

Figure 1.3: Summary of the research questions and hypothesis.

1.3 Objectives of Study

The objectives of this research are:

- to synthesize shape-controlled TiO₂ using liquid crystal as an alignment agent under magnetic field.
- to characterize the synthesized shape-controlled TiO₂.
- to evaluate the photocatalytic activity of the shape-controlled TiO₂.

1.4 Scope of Study

In this research, magnetic field was applied to synthesize the shape-controlled TiO₂ with liquid crystal as structure-aligning agent. The shape-controlled TiO₂ was successfully synthesized by sol-gel method by using TBOT as TiO₂ precursor in the presence of 5CB liquid crystal, with slow hydrolysis process. The solution was placed under magnetic field (up to 0.3 Tesla) and left to self-dry for 12 to 14 days.

Several techniques were used to characterize the sample, such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) spectroscopy, photoluminescence spectroscopy (PL), thermal gravimetric analyser (TGA), nitrogen adsorption apparatus and diffuse reflectance ultraviolet visible (DR UV-Vis) spectroscopy. These physicochemical properties were correlated to the photocatalytic activity in the oxidation of styrene.

1.5 Significance of Study

In this research, the shape-controlled TiO₂ with liquid crystal as a structure-aligning agent was synthesized under magnetic field for the first time. Magnetic field is one of the potential methods to align and orientate molecules, even for diamagnetic materials; it can be aligned by magnetic fields as long as they have the magnetic anisotropy.

The novelty of this research is the establishment of the synthesized shape-controlled TiO₂ obtained under strong magnetic field. It is expected to be a potential photocatalyst due to its ability to reduce the recombination process of hole and electron during ultraviolet irradiation. Therefore, the ultimate goal of this research is to synthesize a new material under magnetic field by using liquid crystals as the alignment agent.

REFERENCES

- Abbet, S., Heiz, U. (2005). *The Chemistry of Nanomaterials : Synthesis, Properties and Applications*. Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim.
- Alivisatos, A. P. (1996). Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*. 271: 933-937.
- Antonini, G. M., Calandra, C., Corni, F., Maticotta, Sacchi, M. (1987). Atomic Local Coordinations and Multivalent States in $\text{Yb}_2\text{Cu}_3\text{O}_{9-\delta}$ Superconductors. *Europhysics Letters*. 4. 851-855.
- Attan, N. (2013). *Magnetic Field Effects on the Adsorption of Dyes, Heterogeneous Oxidation Catalysis and Synthesis of Well-Aligned Titania*. Universiti Teknologi Malaysia: Ph.D. Thesis.
- Attan, N., Nur, H., Effendi, J., Lintang, H. O., Lee, S. W., Sumpono, I. (2012). Well-Aligned Titanium Dioxide with Very High Length-to-Diameter Ratio Synthesized Under Magnetic Field. *Chemistry Letters*. 41: 1468-1470.
- Bornstein, L. (1986). *Numerical Data and Functional Relationships in Science and Technology: Magnetic properties of Metals*. Springer-Verlag Berlin Heidelberg.
- Burda, C., Chen, X., Narayanan, R., El-Sayed, M. A. (2005). Chemistry and Properties of Nanocrystals of Different Shapes. *Journal of Chemical Reviews*. 105: 1025-1102.
- Carlos, M. H., Nosang, V. M. (2005). Magnetic Alignment of Nanowires. *Chemistry Materials*. 17: 1320–1324.

- Deissler, R. J. (2008). Dipole in Magnetic Field, Work and Quantum Spin. *Journal of Physical Review E*. 77. 366-376.
- Fisch, M. R. (2004). *Liquid Crystals, Laptops and Life*. World Scientific Pub. Co Inc, United State of America.
- Fujishima, A., Honda, K. (1972). Environmental Science: Organic Pollutants-Monitoring, Risk and Treatment. *Nature*. 238. 37-38.
- Fujiwara, M., Mitsuda, K., Tanimoto Y. (2006). Movement and Diffusion of Paramagnetic Ions in a Magnetic Field. *Journal of Physical Chemistry B*. 110: 13965–13969.
- Giordani, N. J. (2009). *College Physics Reasoning and Relationships*. Edition 2. Cengage Learning. Purdue University, United State of America.
- Hammond P. (1971). *Applied Electromagnetism: Applied Electricity & Electronics*. Oxford: Pergamon Press Ltd. United Kingdom.
- Hirai, T., Sato, H., Komasaawa, I. (1993). Mechanism of Formation of Titanium Dioxide. Ultrafine Particles in Reverse Micelles by Hydrolysis of Titanium Tetrabutoxide. *Journal of Industrial & Engineering Chemistry Research*. 32: 3014-3019.
- Hird, M., Collings, P. J. (1997). *Introduction to Liquid Crystals: Chemistry and Physics*. Taylor & Francais. United Kingdom.
- Ikedda, S., Nur, H., Ohtani, B. (2001). Phase-Boundary Catalysis of Alkene Epoxidation with Aqueous Hydrogen Peroxide using Amphiphilic Zeolite Particles Loaded with Titanium Dioxide. *Catalysis*. 204: 402-408.
- Jang, B. K., Sakka, Y. (2009). Influence of Shape and Size on the Alignment of Multi-Wall Carbon Nanotubes under Magnetic Fields. *Materials Letters*. 63: 2545–2547.

- Jianguo, G., Gongqin, Y., Wei, W., Jun, L. (2012). External Field–Assisted Solution Synthesis and Selectively Catalytic Properties of Amorphous Iron Nanoplatelets. *Materials Chemistry*. 22. 3909–3915.
- Jun, W., Min, Y., Chuanhui, X., Yuejin, Z., Gaojie, X., Ping, C. (2008). Magnetic Chains of Co Spheres Synthesized by Hydrothermal Process under Magnetic Field. *Materials Letters*. 62: 3431–3433.
- Kamat, P. V., Tvrdy, K., Baker, D. R., Radich, J. G. (2010). Beyond Photovoltaics: Semiconductor Nanoarchitectures for Liquid-Junction Solar Cells. *Chemical Reviews*. 110: 6664-6688.
- Khoo, I. C., Wu, S. T. (1993). *Optics and Nonlinear Optics of Liquid Crystals*. World Scientific Publishing. United State of America.
- Kouveliotou, C., Duncan, R. C. (2003). *Magnetors*. Scientific American Inc. Khoo, I. C., Wu, S. T. (1993). *Optics and Nonlinear Optics of Liquid Crystals*. World Scientific Publishing Co. Inc. London.
- Kroes, G. J., Gross, A., Baerends, E. J., Scheffler, M., McCormack, D. A. (2002). Quantum Theory of Dissociative Chemisorption on Metal Surfaces. *Accounts of Chemical Research*. 35: 193-200.
- Li, P., Nan, C., Wei, Z., Lu, J., Peng, Q. (2010). Mn₃O₄ Nanocrystals : Facile Synthesis, Controlled Assembly and Application. *Chemistry of Materials*. 22. 4232-4236.
- Lin, P. T., Wu, S. T., Chang, C. Y., Hsu, C. S. (2004). *Molecular Crystals and Liquid Crystals: UV Stability of High Birefringence Liquid Crystals*. Taylor & Francis. United Kingdom.
- Linsebigler, A. L., Lu, G., Yates, J. T. (1995). Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews*. 95: 735-758.

- Loon, L. W. (2010). *Field-Induced Director Alignment of Liquid Crystals in Controlled Porous Glasses (CGPs)*. Universiti Teknologi Malaysia. M.Sc. Thesis.
- Lubis, L. (2013). *Porous Carbon-Coated Titania Prepared by In-Situ Polymerization of Styrene and Its Catalytic and Photocatalytic Activities in Oxidation of Alkenes*. Universiti Teknologi Malaysia: Ph.D. Thesis.
- Mao, Y., Park, T. J., Zhang, F., Zhou, H., Wong, S. S. (2007). Environmentally Friendly Methodologies of Nanostructure Synthesis. *Small*. 3: 1122-1139.
- Michael, H. N., Jonathan, R. I. L., Qiaona, H., Thomas, Y. H., James, J. Y. (2012). Structural Evolution, Formation Pathways and Energetic Controls during Template-Directed Nucleation of CaCO₃. *Faraday Discussions*. 159: 105–121.
- Miguel, A. C. D., Marek, G., Verónica, S. M., Michael, G., Luis, M. L., Michael, F., Karl, S., Rodolfo, D. (2005). Alignment of Carbon Nanotubes under Low Magnetic Fields through Attachment of Magnetic Nanoparticles. *Journal Physical Chemistry B*. 109: 19060–19063.
- Monica, T., Laura, A. B., Anne, H., Daniel, M. S., Li, S., Daniel, H. R., Peter, C. S., Gerald, J. M. (2001). Magnetic Alignment of Fluorescent Nanowires. *Nano Letters*. 1: 155–158.
- Mulay, L. N. (1963). *Magnetic Susceptibility*. John Wiley & Sun. United State of America.
- Nguyen, T. D., Dinh, C. T., Do, T. O. (2010). Shape and Size-Controlled Synthesis of Monoclinic ErOOH and Cubic Er₂O₃ from Micro to Nanostructures and Their Upconversion Luminescence. *ACS Nano*. 4. 2263-2273.
- Prasai, B., Cai, B., Underwood, M. K. (2012). Properties of Amorphous and Crystalline Titanium Dioxide from First Principles. *Materials Science*. 10: 1008-1013.

- Purcell, E. (2011). *Electricity and Magnetism*. Edition 2. Cambridge University Press. United Kingdom.
- Redl, F. X., Cho, K. S., Murray, C. B., O'Brien, S. (2003). Three-Dimensional Binary Superlattices Of Magnetic Nanocrystals and Semiconductor Quantum Dots. *Nature*. 423: 968-971.
- Seshadri, O. (2001). *Oxide Nanoparticles*. Wiley-VCH Verlag GmbH & Co. KgaA.
- Shah, P. R., Khader, M. M., Vohs, J. H., Gorte, R. J. (2008). A Comparison of the Redox Properties of Vanadia-Based Mixed Oxides. *Journal of Physical Chemistry C*. 112. 2613-2617.
- Skitek, G. G. (1982). *Electromagnetic Concepts and Applications*. Prentice Hall. United State of America.
- Tenne, R. (2004). Materials Physics: Doping Control for Nanotubes. *Nature*. 431. 640-641.
- Tsunehisa, K., Masafumi, Y., Wataru, K., Minako, K., Takahiko, K. (2000). Magnetic Orientation of Polymer Fibers in Suspension. *Langmuir*. 16: 858–861.
- Umar, M., Aziz, A. H. (2013). Photocatalytic Degradation of Organic Pollutants in Water. In-Tech Published. United of State.
- Wade, J. (2005). *An Investigation of TiO₂-ZnFe₂O₄ Nanocomposites for Visible Light Photocatalysis*. University of South Florida, Tampa. Graduate School Theses and Dissertations.
- Wang, X., Zhuang, J., Peng, Q., Li, Yi. (2005). A General Strategy for Nanocrystal Synthesis. *Nature*. 437. 121-124.
- Wen, C. H., Gauza, S., Wu, S. T. (2005). Photostability of Liquid Crystals and Alignment Layers. *Society for Information Display*. 13: 805-811.

- Yamaguchi, M., Tanimoto, Y. (2006). *Magneto Science. Magnetic Field Effects on Materials: Fundamentals and Applications*. Springer-Verlag Berlin Heidelberg.
- Yin, Y., Alivisatos, A. P. (2005). Colloidal nanocrystal synthesis and the organic-inorganic interface. *Nature*. 437: 664-670.
- Yong, S. W. (2012). *Synthesis of Nanocrystalline Bismuth Titanate Photocatalysts via Modified Hot Injection Method*. Universiti Teknologi Malaysia. M.Sc. Thesis.
- Yoshitake, M. (2011). *Nanocrystal: Chapter 2: Size and Shape-Controlled Synthesis of Monodisperse Metal Oxide and Mixed Oxide Nanocrystals*. In Tech Published. Canada.
- You, X. F., Chen, F., Zhang, J. L. (2005). Effects of Calcination on the Physical and Photocatalytic Properties of TiO₂ Powders prepared by Sol-Gel Template Method. *Sol-Gel Science and Technology*. 34: 181-187.
- Young, H. D., Freedman, R. (2011). *Physics with Modern Physics*. Edition 13. Addison-Wesley. United State of America.