

Table of Contents

Abstract.....	i
Acknowledgement.....	v
Table of contents.....	vii
List of tables.....	ix
List of figures.....	x
 Chapter 1. Introduction of titanium oxides: properties and synthesis.....	1
1.1. Two of new centurial challenges: environmental protections and energy sources.....	1
1.2. Background, Applications and Synthesis of Titanium Dioxides.....	2
1.2.1. Titanium in Our World.....	2
1.2.2. Various Allotropes of TiO_2	3
1.2.3. Properties and Applications of TiO_2	9
1.2.4. Photoinduced processes and applications of TiO_2	10
1.2.5. Improving the photoactive efficiency of TiO_2	12
1.2.6. Synthesis of TiO_2	13
1.3. Synthesis and Structure of Alkali Titanates.....	16
1.4. Synthesis and Applications of Titanate Nanostructures.....	20
1.4.1. Review of synthesis of titanate nanostructure.....	20
1.4.2. Applications of titanate nanostructure.....	26
1.5. Conclusions.....	28
1.6. References.....	29
 Chapter 2. Synthesis and Characterizations of Various Titanium Oxide Nanostructures Produced by Wet Chemistry in Base Solution ($NaOH-TiO_2$).....	35
2.1. Introduction.....	35
2.2. Experimental Section.....	36
2.2.1. Reagents.....	36
2.2.2. Synthesis Method.....	44
2.2.3. Characterization.....	46
2.3. Results.....	48
2.3.1. Correlations of reactive conditions and product structures.....	48
2.3.2. The characterizations of principle morphologies.....	57
2.4. Discussions.....	65
2.4.1. Influence of the nature of TiO_2 precursors.....	65
2.4.2. Temperature effect.....	74
2.4.3. Base concentration effect.....	79
2.4.4. Sodium chloride effect.....	82
2.4.5. Carbonate effect.....	85
2.4.6. Morphologic study of nanostructurated TiO_2	92
2.4.7. Size control synthesis of potassium titanate nanofibers ($KOH-TiO_2$) by temperature effect.....	97
2.5. Conclusions.....	106
2.6. Annex.....	107
2.6.1. Chemical composition study of various products (EDX and TGA results).....	107
2.6.2. FT-IR study of various products.....	115
2.6.3. $TiOCl_2 + x NaOH$	119
2.6.4. Enlargement of nanosheet from RDH15MR by treatment of boiling in water.....	123
2.6.5. Reaction time effect of am10MR (from semi-nanotube to nanoribbon).....	127

2.6.6. 5nm5M120-xNa ₂ CO ₃	129
2.7. References.....	131
 Chapter 3. Structures, Growth and Condensation Mechanism of Titanate Nanostructures Produced by Hydrothermal Method.....	133
3.1. Introduction.....	133
3.2. Method.....	133
3.3. Structures of the lepidocrocite type products.....	134
3.3.1. nanoribbon.....	134
3.3.2. nanotube and nanosheet.....	138
3.4. Structure of the rutile type (lamellar ramsdellite) product.....	139
3.5. Growth mechanism and phase transformations of the sodium hydroxo titanates..	144
3.6. Conclusions.....	149
3.7. Annex.....	150
3.7.1. Raman study.....	150
3.7.2. X-ray absorption spectroscopy study on X-ray Absorption Near-Edge Structure.	153
3.8. Reference.....	156
 Chapter 4. Photocatalytic and Lithium Ion Intercalation Properties of Titanate Nanostructures Produced by Solvothermal Method.....	157
4.1. Introduction.....	157
4.2. Method.....	158
4.2.1. Photocatalyse.....	158
4.2.2. Lithium ion intercalation.....	160
4.3. Results and Discussions.....	162
4.3.1. Photocatalytic property of titanate nanostructures.....	162
4.3.2. Lithium ion intercalation property of titanate nanostructures.....	165
4.4. Conclusions.....	168
4.5. Reference.....	169
 Chapter 5. General Conclusions.....	170

List of Tables

Table 1.1. Lattice parameters of various allotropes of TiO ₂	4
Table 1.2. Some bulk properties of TiO ₂ (anatase, brookite and rutile).....	10
Table 1.3. Various alkali titanate structures: number of octahedrons repeating along c and lattice parameter.....	19
Table 2.1. Table of various titanium oxide precursors.....	37
Table 2.2. Table of various sodium sources or carbonate additives.....	43
Table 2.3. Table of various reactive conditions and product morphologies.....	49
Table A2.1. Na/Ti ratio of various morphologies of titanate by EDX/SEM.....	107
Table A2.2. TGA-MS reports of various morphologies of titanate.....	107
Table A2.3. TGA-MS reports of various morphologies of H-titanate (after proton exchanged).....	112
Table A3.1. Table of XANES results of submicrostick and nanoribbon samples.....	153



List of Figures

Figure 1.1.	Correlations of global population and greenhouse effect.....	1
Figure 1.2.	Photoinduced processes on TiO ₂	2
Figure 1.3.	Structure of TiO ₂ (B): projection along (a) [010], (b) [001] and (c) [100]; (c) structure of ReO ₃	4
Figure 1.4.	Structure of TiO ₂ anatase: projection along (a) [100] and (b) [001].....	5
Figure 1.5.	Structure of TiO ₂ rutile: projection along (a) [001] and (b) [100].....	6
Figure 1.6.	Projection along [1 0 10] of structural diagram of TiO ₂ hollandite.....	6
Figure 1.7.	Projection along [0 -1 -12] of structural diagram of TiO ₂ ramsdellite.....	7
Figure 1.8.	Structure of TiO ₂ brookite: projection along (a) [001] and (b) [100].....	8
Figure 1.9.	Structure of TiO ₂ -II: projection along (a) [001] and (b) [100].....	8
Figure 1.10.	Photoinduced process on semiconductor: (a) electron–hole generation; (b) oxidation of donor (D); (c) reduction of acceptor (A); (d) and (e) electron–hole recombination at surface and in bulk, respectively.....	11
Figure 1.11.	Diagram represents the nature of ligands on a coordinated cation with ion charge z and environmental pH.....	15
Figure 1.12.	Possible reaction routes of the formation of rutile and anatase phase TiO ₂ from aqueous solution.....	16
Figure 1.13.	Structural diagram of sodium trititanate Na ₂ Ti ₃ O ₇ (layer structure, n=3) viewing along (a) [010], (b) [100] and (c) [001].....	17
Figure 1.14.	Structural diagram of sodium hexatitanate Na ₂ Ti ₆ O ₁₃ (tunnel structure, n=6) viewing along (a) [010], (b) [100] and (c) [001].....	18
Figure 1.15.	Structural diagram of cesium hexatitanate Cs ₂ Ti ₆ O ₁₃ (lepidocrocite, γ -FeO(OH), type layer structure, n= ∞) viewing along (a) [100], (b) [010] and (c) [001].....	18
Figure 1.16.	Phased (primitive, P) and anti-phased (c-center, C) titante layer structures.....	19
Figure 1.17.	(a) side view and (b) top view of an open-end titanate nanotube; (c) HRTEM and simulation image of the wall part of (a); (d) diagram of a unit cell of Na ₂ Ti ₃ O ₇ along [010]; (e) diagram of Na ₂ Ti ₃ O ₇ nanotube rolling structure along [010]; (f) 3D view of Na ₂ Ti ₃ O ₇ nanotube.....	21
Figure 1.18.	Schematic drawing of an anatase single layer and the tube wall structure formed by the single-layer sheets. Shadowed area indicates the unit cell of the anatase phase.....	22
Figure 1.19.	Schematic diagram of formation process of titania nanotube.....	22
Figure 1.20.	Schematic diagram of formation process for nanotube Na ₂ Ti ₂ O ₄ (OH) ₂	22
Figure 1.21.	Schematic diagram showing proposed transformation of multilayered nanosheets to nanotubes.....	23
Figure 1.22.	Overall scheme for the formation and transformation of nanotubes induced by the NaOH treatment and the post-treatment washing.....	23
Figure 1.23.	SEM images for: (a) raw materials (calcined at 673 K), (b) treated by 5M NaOH, (c) treated by 10M NaOH, and (d) calcined at 1173K followed by 10M NaOH at 423K for 20h.....	24
Figure 1.24.	(a) Low-magnification TEM image of titanium oxide nanomaterials, showing well-interlinked structure; (b) HRTEM image of a nanofiber, revealing the layered structure.....	25
Figure 1.25.	TEM images of the samples. (a) H-titanate wires, (b) HRTEM image of the wires, (c) the product of the phase conversion reaction at 373 K and (d) the product obtained at 393 K.....	25

Figure 1.26. Variation of potential, vs. Li/Li ⁺ (1 M) electrode, with Li content (charge passed) for TiO ₂ -B nanotubes and nanowires cycled.....	26
Figure 1.27. Photocatalytic activity of pristine trititanate nanotubes (solid squares) and CdS doped trititanate nanotubes (open squares).....	27
Figure 1.28. (a) P-C isotherms of TiO ₂ nanotubes and bulk TiO ₂ at room temperature. (b) P-C isotherms of TiO ₂ nanotubes at 24, 70, and 120 °C.....	27
Figure 2.1. XRD diagrams of (a) amorphous TiO ₂ , hydrate from TiOCl ₂ ; (b) TiO ₂ , hydrate from TTIP; (c) 5nm anatase; (d) Degussa P25; (e) RDH anatase and (f) Aldrich rutile.....	38
Figure 2.2. FT-IR ATR spectra of (a) amorphous TiO ₂ hydrate from TiOCl ₂ ; (b) TiO ₂ hydrate from TTIP; (c) 5nm anatase; (d) Degussa P25; (e) RDH anatase and (f) Aldrich rutile.....	39
Figure 2.3. TEM image of (a) survey, (b) particle-like part and (c) plate-like part of amorphous TiO ₂ hydrate from TiOCl ₂	40
Figure 2.4. (a) low magnification and (b) high resolution TEM image of TiO ₂ hydrate from hydrolysis of TTIP.....	41
Figure 2.5. TEM image of (a) Alfa 5nm anatase and (b) Degussa p25 TiO ₂	42
Figure 2.6. TEM image of (a) RDH anatase and (b) Aldrich rutile TiO ₂	43
Scheme 2.1. Preparation procedure of nanostructured TiO ₂ samples obtained by exchanged and calcination of titanate nanostructures from chimie-douce synthesis.....	44
Scheme 2.2. Relation of titanate monolayer width and various product morphologies.....	57
Figure 2.7. XRD diagrams of sodium hydroxo titanate (a) nanosheet (am1M120), (b) semi-nanotube* (rut10MR), (c) nanotube (RDH10M140), (d) nanoribbon (RDH10M180) and (e) submicrostick (rut10M220).....	58
Figure 2.8. (a) The SEM image and (b) the magnified one of titanate nanosheets (am1M120).....	59
Figure 2.9. (a) The TEM image and (b) the magnified one of titanate nanosheets (RDH15MR).....	59
Figure 2.10. (a) The TEM image and (b) the magnified one of titanate semi-nanotubes (rut10MR).....	60
Figure 2.11. (a) The SEM image and (b) the magnified one of titanate nanotubes (RDH10M140).....	61
Figure 2.12. (a) The TEM, (b) HRTEM and cross-section images of titanate nanotubes (RDH10M140).....	62
Figure 2.13. (a) The SEM image and (b) the magnified one of titanate nanoribbons (RDH10M180).....	63
Figure 2.14. (a) The TEM, (b) HRTEM and (c) selected area electron diffraction pattern images of titanate nanoribbons (RDH10M180).....	63
Figure 2.15. (a) The SEM image and (b) the magnified one of titanate submicro-sticks (am10M220).....	64
Figure 2.16. (a) The TEM, (b) HRTEM and (c) selected area electron diffraction pattern images of titanate submicro-sticks (am10M220).....	64
Figure 2.17. XRD diagrams of sodium hydroxo titanate from (a) amorphous (am10M120), (b) TiO ₂ hydrate from TTIP (TO10M120), (c) 5nm (5nm10M120), (d) P25 (P2510M120), (e) RDH (RDH10M120) and (e) rutile (rut10M120) in 10M NaOH aqueous solution at 120° C during 72 hours.....	66
Figure 2.18. SEM images of sodium hydroxo titanate from (a) amorphous (am10M120), (b) TiO ₂ hydrate (TO10M120), (c) 5nm (5nm10M120), (d) P25 (P2510M120), (e) RDH (RDH10M120) and (f) rutile (rut10M120).....	67

Figure 2.19. TEM images of sodium hydroxo titanate from (a) amorphous (am10M120), (b) TiO ₂ hydrate (TO10M120), (c) 5nm (5nm10M120), (d) P25 (P2510M120), (e) RDH (RDH10M120) and (f) rutile (rut10M120).....	68
Figure 2.20. XRD diagrams of sodium hydroxo titanate from (a) amorphous (am10M140), (b) 5nm (5nm10M140), (c) P25 (P2510M140), (d) RDH (RDH10M140) and (e) rutile (rut10M140) in 10M NaOH aqueous solution at 140° C during 72 hours.....	69
Figure 2.21. SEM images of the product from (a) amorphous (am10M140), (b) 5nm (5nm10M140), (c) P25 (P2510M140), (d) RDH (RDH10M140) and (e) rutile (rut10M140).....	70
Figure 2.22. TEM images of sodium hydroxo titanate from (a) amorphous (am10M140), (b) 5nm (5nm10M140), (c) P25 (P2510M140), (d) RDH (RDH10M140) and (e) rutile (rut10M140).....	71
Figure 2.23. XRD diagrams of titanate nanoribbon from (a) amorphous (am10M180), (b) RDH (RDH10M180) and (c) rutile (rut10M180) at 180° C.....	73
Figure 2.24. SEM images of titanate nanoribbon from (a) amorphous (am10M180) and (b) RDH (RDH10M180).....	73
Figure 2.25. XRD diagrams of titanate nanoribbon from (a) amorphous (am10M220), (b) RDH (RDH10M220) and (c) rutile (rut10M220) at 220° C.....	74
Figure 2.26. XRD diagrams of product from amorphous in 10M NaOH _(aq) autoclaved at (a) 120°C (am10M120), (b) 140°C (am10M140), (c) 180°C (am10M180) and (d) 220°C (am10M220)	75
Figure 2.27. SEM images of product from amorphous in 10M NaOH _(aq) autoclaved at (a) 120° C (am10M120), (b) 140° C (am10M140), (c) 180° C (am10M180) and (d) 220° C (am10M220)	77
Figure 2.28. TEM images of product from amorphous in 10M NaOH _(aq) autoclaved at (a) 120° C (am10M120), (b) 140° C (am10M140), (c) 180° C (am10M180) and (d) 220° C (am10M220)	78
Figure 2.29. XRD diagrams of product from amorphous 120° C autoclaved in (a) 0M (am0M120), (b) 0.1M (am0.1M120), (c) 0.5M (am0.5M120), (d) 1M (am1M120), (e) 5M (am5M120), (f) 10M (am10M120) and (g) 15M (am15M120) NaOH aqueous solution.....	80
Figure 2.30. SEM images of product from amorphous 120° C autoclaved in (a) 0M (am0M120), (b) 0.1M (am0.1M120), (c) 0.5M (am0.5M120), (d) 1M (am1M120), (e) 5M (am5M120) and (f) 10M (am10M120) NaOH aqueous solution.....	81
Figure 2.31. TEM images of 3 types of product in am5M120: (a) small lamellar, (b) semi-tubular (major) and (c) (band-like) lamellar.....	82
Figure 2.32. XRD diagrams of (a) product from 5nm in 5M NaOH _(aq) autoclaved at 120°C (5nm5M120) and (b) specially weighed 0.02 mole NaCl in.....	83
Figure 2.33. SEM images of (a) product from 5nm in 5M NaOH _(aq) autoclaved at 120°C (5nm5M120) and (b) specially weighed 0.02 mole NaCl in.....	84
Figure 2.34. XRD diagrams of (a) RDH5M120 and (b) specially weighed 0.05 mole NaCl in (RDH5M120-4NaCl); (c) RDH10M120 and (d) RDH10M120-4NaCl.....	84
Figure 2.35. XRD diagrams of (a) am10M120 (autoclave) and (b) am10MR (reflux).....	85
Figure 2.36. (a) the TEM image, (b) cross-section image and (c) the SEM image of titanate nanofibers. (am10MR).....	86
Figure 2.37. XRD diagrams of (a) RDH15M120, (b) RDH15MR and (c) RDH15M120-2CO ₃ (2.64g Na ₂ CO ₃ added).....	87
Figure 2.38. TEM images of (a), (b) RDH15MR and (c), (d) RDH15M120-2CO ₃	88

Figure 2.39. XRD diagrams of (a) 5nm5M120, (b) 5nm5M120-1.6NaCl, (c) 5nm5M120-0.5CO ₃ , (d) 5nm5M120-0.8CO ₃ , (e) 5nm5M120-0.4HCO ₃ and (f) 5nm5M120-0.8HCO ₃	89
Figure 2.40. XRD diagrams of peak (100) ($2\theta=10^\circ$) of (a) 5nm5M120, (b) 5nm5M120-1.6NaCl, (c) 5nm5M120-0.5CO ₃ , (d) 5nm5M120-0.8CO ₃ , (e) 5nm5M120-0.8HCO ₃ and (f) 5nm5M120-1.6HCO ₃	90
Figure 2.41. XRD diagrams of am10M180 (black) and am10M180-0.8CO ₃ (red).....	91
Figure 2.42. SEM images of (a) am10M180 and (b) am10M180-0.8CO ₃ (supported on grid with carbon film).....	91
Figure 2.43. XRD diagrams of (a) nanosheet (RDH15MR-B), (b) after proton exchanged one and then (c) annealed at 400° C.....	93
Figure 2.44. TEM images of (a) nanosheet after proton exchanging and then (c) annealed at 400° C.....	93
Figure 2.45. XRD diagrams of (a) nanotube (RDH10M140), (b) after proton exchanged one and then (c) annealed at 400° C.....	94
Figure 2.46. TEM images of (a) nanotubes after proton exchanging and then (c) annealed at 400° C.....	94
Figure 2.47. XRD diagrams of (a) nanoribbon (RDH10M180), (b) after proton exchanged one and then (c) annealed at 400° C, (d) at 800° C.....	95
Figure 2.48. TEM images of (a) nanoribbons after proton exchanging and then (c) annealed at 400° C.....	95
Figure 2.49. XRD diagrams of (a) submicro-sticks (am10M220), (b) after proton exchanged one and then (c) annealed at 400° C.....	96
Figure 2.50. TEM images of (a) submicro-sticks after proton exchanging and then (b) annealed at 400° C.....	96
Figure 2.51. (a) Diagram of the formation of KTiO ₂ (OH) in the Ti-KOH-H ₂ O system; (b) SEM photograph of KTiO ₂ (OH).....	97
Figure 2.52. (a) The charge-discharge curves of the block products (made from Ti plate) (labeled by B) and the powder products (made from Ti powder) (labeled by P) showing good electrochemical performance of the products as anode materials for lithium ion battery. (b) The cycle performance of the products showing excellent reversible capacities of the block products (labeled by B) and the powder products (labeled by P).....	98
Figure 2.53. XRD diagrams of product by the reaction TiOCl ₂ ·1.4HCl·7H ₂ O + (3.4+x) KOH at 180° C 24 hours: (a) x = 0, (b) x = 0.5 and (c) x = 1.....	100
Figure 2.54. XRD diagrams of product by the reaction TiOCl ₂ ·1.4HCl·7H ₂ O + 4.4 KOH at (a) 110° C, (b) 120° C, (c) 150° C, (d) 180° C and (e) 220° C 24hours.....	100
Figure 2.55. TEM images of potassium titanate nanoribbons obtained at (a) 110° C, (b) 150° C, (c) 180° C and (d) 220° C.....	101
Figure 2.56. FT-IR-ATR spectrum of potassium titanate nanoribbon obtained at 220° C.....	103
Figure 2.57. XRD diagrams of (a) potassium titanate nanoribbon, (b) after 0.1M HNO ₃ washing and then (c) annealed to 400° C.....	103
Figure 2.58. FT-Raman spectra of potassium titanate nanoribbon obtained at (a) 110° C and (b) 220° C; (c) K ₂ Ti ₆ O ₁₃ ; (d) K ₂ Ti ₄ O ₉ ; (e) K ₂ Ti ₂ O ₅	104
Figure A2.1. (a) TG weight loss % diagram and (b) TG-Mass spectra of raw nanosheets (RDH15MR).....	109
Figure A2.2. (a) TG weight loss % diagram and (b) TG-Mass spectra of nanosheets (RDH15MR-B).....	109
Figure A2.3. (a) TG weight loss % diagram and (b) TG-Mass spectra of nanotubes (RDH10M140).....	110

Figure A2.4. (a) TG weight loss % diagram and (b) TG-Mass spectra of nanofibers (small ribbon) (am10MR).....	110
Figure A2.5. (a) TG weight loss % diagram and (b) TG-Mass spectra of nanoribbons (RDH10M180).....	111
Figure A2.6. (a) TG weight loss % diagram and (b) TG-Mass spectra of submicro-sticks (rut10M220).....	111
Figure A2.7. (a) TG weight loss % diagram and (b) TG-Mass spectra of proton exchanged nanosheets (RDH15MR-B-H).....	112
Figure A2.8. (a) TG weight loss % diagram and (b) TG-Mass spectra of proton-exchanged nanotubes (RDH10M140-H).....	113
Figure A2.9. (a) TG weight loss % diagram and (b) TG-Mass spectra of proton-exchanged nanofibers (small ribbon) (am10MR-H).....	113
Figure A2.10 (a) TG weight loss % diagram and (b) TG-Mass spectra of proton-exchanged nanoribbons (RDH10M180-H).....	114
Figure A2.11 (a) TG weight loss % diagram and (b) TG-Mass spectra of proton-exchanged submicro-sticks (am10M220-H).....	114
Figure A2.12 Various types of carbonato groups.....	115
Figure A2.13 The FT-IR spectra of (a) nanosheet (RDH15MR-B), (b) nanotube (RDH10M140), (c) nanofiber (am10MR), (d) nanoribbon (RDH10M180) and (e) submicrostick (rut10M220).....	116
Figure A2.14 The FT-IR spectra in range of 1000cm^{-1} - 1900cm^{-1} of (a) nanosheet (RDH15MR-B), (b) nanotube (RDH10M140), (c) nanofiber (am10MR), (d) nanoribbon (RDH10M180) and (e) submicrostick (rut10M220).....	117
Figure A2.15 The FT-IR spectra of proton exchanged (a) nanotube (RDH10M140-H), (b) nanofiber (am10MR-H), (c) nanoribbon (RDH10M180-H) and (d) submicrostick (am10M220-H).....	117
Figure A2.16 The FT-IR spectra in range of 1000cm^{-1} - 1900cm^{-1} of proton exchanged (a) nanotube (RDH10M140-H), (b) nanofiber (am10MR-H), (c) nanoribbon (RDH10M180-H) and (d) submicrostick (am10M220-H).....	118
Figure A2.17 (a) low and (b) high magnification of TEM images of titanate nanosheets from $\text{TiOCl}_2 + (x+3.4)\text{NaOH}$, $x=0.63$, 180°C autoclaved 24h; (c), (d) nanosheets and demi-tube with $x=1.26$; (e), (f) ribbon-like nanosheet and demi-nanotubes with $x=1.5$	120
Figure A2.18 XRD diagrams of products from TiOCl_2 180°C autoclaved with stoichiometric $(x+3.4)\text{NaOH}$, $x = (a) 0$, (b) 0.5, (c) 0.63, (d) 1, (e) 1.26, (f) 1.5, (g) 2, (h) 2.5, (i) 3, (j) 3.5, (k) 4, (l) 5.....	122
Figure A2.19 XRD diagrams of (a) nanosheet (RDH15MR) and (b) enlarged one after boiling in water during 48 hours (RDH15MR-B).....	124
Figure A2.20 SEM images of (a) nanosheet (RDH15MR) and (b) enlarged one after boiling in water during 48 hours (RDH15MR-B).....	124
Figure A2.21 TEM images of (a), (b) nanosheet (RDH15MR) and (c), (d) nanosheet enlarged after boiling in water during 48 hours (RDH15MR-B).....	125
Figure A2.22 FT-IR spectra of (a) nanosheet (RDH15MR) and (b) nanosheet enlarged after boiling in water during 48 hours (RDH15MR-B).....	126
Figure A2.23 FT-IR spectra in range of 1000 cm^{-1} - 1900 cm^{-1} of (a) nanosheet (RDH15MR) and (b) nanosheet enlarged after boiling in water during 48 hours (RDH15MR-B).....	126
Figure A2.24 XRD diagrams of am10MR reflux during (a) 24 hours, (b) 48 hours and (c) 72 hours.....	127

Figure A2.25 TEM images of am10MR reflux during (a), (b) 24 hours, (c), (d) 48 hours and (e), (f) 72 hours.....	128
Figure A2.26 XRD diagrams of products from 5nm anatase TiO ₂ in 120°C autoclave with (a) 5M NaOH, (b) specially add 0.66g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=0.5), (c) 1.06g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=0.8), (d) 1.33g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=1), (e) 2.65g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=2), (f) 5.30g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=4).....	129
Figure A2.27 the SEM images of products from 5nm anatase TiO ₂ in 120°C autoclave with (a) 5M NaOH, (b) specially add 0.66g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=0.5), (c) 1.06g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=0.8), (d) 1.33g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=1), (e) 2.65g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=2), (f) 5.30g Na ₂ CO ₃ (CO ₃ ²⁻ /Ti=4).....	130
Figure 3.1. (a) SAED, (b) HRTEM and (c) FT pattern (above is inversed FT pattern) of HR image of nanoribbon (RDH10M220) viewing along [010].....	135
Figure 3.2. Possible structure expressed as ball and stick mode of the nanoribbon as “Cs ₂ Ti ₆ O ₁₃ ” type titanate NaTi ₂ O ₄ (OH) viewing along (a) [010] and (b) [100]..	136
Figure 3.3. Series of HRTEM simulation of NaTi ₂ O ₄ (OH) perform by Mac Tempas with I2/m space group : a = 3.65 Å, b = 17 Å, c = 20 Å, β = 87°; Focal serie: Δf (beg.-700 ; inc. 50 ; end -850) vertical ; Thickness (beg. 42.5 nm; inc. 1.7 nm; end 51 nm) horizontal.....	137
Figure 3.4. (a) ED simulation and (b) HRTEM images: observed and simulated (focal -850; Thickness 42.5 nm) from idealized structural model of “Cs ₂ Ti ₆ O ₁₃ ”-type NaTi ₂ O ₄ (OH) viewing along [010].....	138
Figure 3.5. (a) Small angle XRD and (b) powder XRD diagrams of the submicrosticks (rut10M220).....	140
Figure 3.6. The diagram of reciprocal lattice reconstructed by tilting single crystallite along [010] of the submcrostick.....	141
Figure 3.7. HRTEM image and the FT and inverse FT patterns of the submicrostick viewing along [100].....	142
Figure 3.8. The possible structure viewing along [010] of the microstick as lamellar ramsdellite with lattice parameters: monoclinic, Primitive, a=40.9Å, b=2.9Å c=9.4Å, β=80°.....	143
Figure 3.9. Possible growth mechanism from anatase to lepidocrocite.....	145
Figure 3.10. Possible growth mechanism from brookite to lepidocrocite.....	146
Figure 3.11. Possible growth mechanism from rutile to lepidocrocite.....	147
Figure 3.12. Possible growth mechanism of lamellar ramsdellite type titanate.....	148
Figure A3.1. Raman spectra of (a) nanosheets (am1M120), (b) nanotubes (RDH10M140), (c) nanowires (RDH10M180) and (d) submicro-sticks (rut10M220).....	151
Figure A3.2. Raman spectra of (a) RDH5M120-0.8CO ₃ , (b) am10MR, (c) am10M180.....	151
Figure A3.3. Raman spectra of (a) nanotubes (RDH10M140), (b) lepidocrocite Cs ₂ Ti ₆ O ₁₃ , (c) K ₂ Ti ₂ O ₅ , (d) K ₂ Ti ₄ O ₉ , (e) K ₂ Ti ₆ O ₁₃ , (f) Na ₂ Ti ₃ O ₇ and (g) Na ₂ Ti ₆ O ₁₃	152
Figure A3.4. XANES of anatase TiO ₂	154
Figure A3.5. XANES of titanate submicrostick (rut10M220).....	154
Figure A3.6. XANES of titanate nanoribbon (RDH10M180).....	155
Figure A3.7. XANES of proton-exchanged titanate nanoribbon (RDH10M180-H).....	155
Figure 4.1. Photoreacter of photocatalysis.....	159
Figure 4.2. Photocatalytic activity of H-nanotube (RDH10MR-H), annealed H-nanotube (RDH10MR-H-400° C), H-nanosheet (RDH15MR-H), annealed H-nanosheet (RDH15MR-H-400° C) and Degussa P25 as reference sample.....	163

Figure 4.3. Photocatalytic activity of 400° C annealed H-nanowire (RDH10M180-H-400° C), 800° C annealed H-nanowire (RDH10M180-H-800° C), 800° C annealed H-nanofiber (am15MR-H-800° C), 400° C annealed H-K ₂ Ti ₂ O ₅ and Degussa P25 as reference sample.....	164
Figure 4.4. Cyclic voltammogram on the (a) bulk TiO ₂ (B) produced from K ₂ Ti ₄ O ₉ , (b) TiO ₂ from nanotube (RDH140-H-400° C) and (c) nanofiber (am10MR-H-400° C) electrode (rate of charge: 2C).....	166
Figure 4.5. Charge-discharge curve on the (a) bulk TiO ₂ (B) produced from K ₂ Ti ₄ O ₉ , (b) TiO ₂ from nanotube (RDH140-H-400° C) and (c) nanofiber (am10MR-H-400° C) electrode (rate of charge: 2C).....	166
Figure 4.6. Cyclic voltammogram on the (a) nanoribbon (RDH10M180-H-400° C, reversible capacity: 140 mAhg ⁻¹), (b) small nanoribbon (am10MR-H-400° C, reversible capacity: 140 mAhg ⁻¹) and (c) longer nanoribbon (am10M180-0.8CO ₃ -H-400° C, reversible capacity: 95 mAhg ⁻¹) electrode (rate of charge: C).....	167
Figure 4.7. Cyclic voltammogram on the (a) nanoribbon (RDH10M180-H-400° C, reversible capacity: 170 mAhg ⁻¹), (b) small nanoribbon (am10MR-H-400° C, reversible capacity: 165 mAhg ⁻¹) and (c) longer nanoribbon (am10M180-0.8CO ₃ -H-400° C, reversible capacity: 150 mAhg ⁻¹) electrode (rate of charge: C/10).....	167

