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Thermal Analysis for Water-Assisted Crystallization of TiO_2 Particles

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Abstract: An improved thermal treatment with dimethylsilicone fluid sealing was proposed for water-assisted crystallization of TiO_2 particles. With the amorphous titanium dioxide (TiO_2) particles fabricated using sol-gel method, an average diameter of about 200 nm was first measured by transmission electron microscopy, and then the phase transition of TiO_2 from amorphous to anatase was also identified by X-ray diffraction before and after the crystallization process. Obvious thermal behaviors obtained by thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis demonstrated that the conversion from amorphous to anatase phase of TiO_2 could be realized at low temperature in water. Meanwhile, with dimethylsilicone fluid sealing, water loss was reduced to enhance the accuracy of DSC during the crystallization of TiO_2 particles. Anatase TiO_2 can be produced with reduced temperature for higher soaking temperature and longer soaking time. This study provides an environmental method for low-temperature synthesis of anatase TiO_2 with the assistance of water.

Key words: TiO_2, phase transition, water-assisted, thermal analysis, dimethylsilicone fluid sealing
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TiO_2水助晶的热分析

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[摘要] 本文提出了一种硅油密封检测水助二氧化钛(TiO_2)结晶的热分析方法.采用溶胶-凝胶法制备了非晶态的TiO_2, 经TEM检测其平均粒径约为200 nm, X射线衍射分析表明TiO_2由非晶态向锐钛矿型的转变.热重(TG)和差热(DSC)分析表明, TiO_2有明显的热行为, 其能够在低温水浸润环境下实现非晶态向锐钛矿型的转变.同时, 硅油作为覆盖层减少了水分的挥发, 提高了TiO_2在结晶过程中DSC的测量精度.较高的浸润温度和较长的浸润时间能够降低TiO_2的结晶温度, 该研究提供了一种优化低温水浸润环境下合成锐钛矿型TiO_2的方法.

[关键词] TiO_2, 相转变, 水助, 热分析, 硅油密封

Metal oxide material titania (TiO_2) has been one of the most promising materials with various applications[1-5], such as supercapacitors, drug delivery, sensor and biomaterials, etc. Due to the high catalytic activity[6-8] with good stability, low toxicity and abundance, anatase TiO_2 attracts more and more attention for its application potential as a catalyst for environmental remediation. Several technologies have been proposed to control the size of colloidal TiO_2 and optimize the properties of high temperature calcinations and addition of surfactants

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or dopants. The performance of TiO_2 is highly dependent[9-13] on the characteristics of crystallinity, phase composition, morphology and surface area. However, the as-prepared TiO_2 product is amorphous with relatively high surface area. High temperature thermal treatment (>300 ℃) is required to obtain crystalline TiO_2 products and the porous structure will be irreversible destroyed with drastically decreased surface area.

Recent research reported that anatase TiO_2 materials could be fabricated with aging amorphous TiO_2 in water. Zhong et al[14] developed a simple strategy to synthesize hierarchically nanoporous TiO_2 samples with large surface by refluxing titanium glycolate spheres in water. Domen et al[15] reported that amorphous TiO_2 nanotubes could be converted to anatase TiO_2 nanotubes by simply soaking amorphous nanotube into water under room temperature with a long time period (up to 3 days). Owing to the advantage of avoiding high temperature thermal treatment, the fabrication strategy of aging in water has promising application potential for the preparation of anatase TiO_2 with large surface area and good crystallinity.

In this study, amorphous TiO_2 samples were first prepared with sol-gel method, and then an improved thermal analysis method was proposed to investigate the performance of the phase transition of TiO_2 in water. In the process, an additional layer of dimethylsilicone fluid was employed as the sealing of solution samples to reduce water volatilization, which was beneficial to improve the sensitivity and accuracy of thermal analytical measurements. It was also proved that the phase transition of TiO_2 would be accelerated with reduced crystallization temperature for higher soaking temperature and longer soaking time, providing a novel environmental method for low-temperature synthesis of anatase TiO_2.

1 Experiments

By employing the sol-gel method[16-17], colloidal TiO_2 particles were fabricated. In the process, hydroxypropyl cellulose (HPC, 0.2 g) was first dissolved in an ethanol (50 mL) and deionized water (0.3 mL) solution. Then, with the instillation of tetrabutyl orthotitanate (TBOT, 97%, 0.85 mL), the solution was stirred vigorously until the presence of cloudy. With 3 hours' reaction, the resulting particles were isolated through centrifugation. After three times' washing with ethanol and one time washing with water and particle dispersion in 20 mL of deionized water, the solution of amorphous TiO_2 particles was finally prepared.

To investigate the structure and crystallinity of the fabricated TiO_2 particles, the morphology was first characterized by transmission electron microscopy (TEM, Tecnai T12, 120 kV). And then the phase compositions of TiO_2 before and after the water-assisted thermal treatment were measured by X-ray diffraction analysis (XRD, Bruker D8, Advance Diffract Meter with Cu and Kα radiation) at the scanning speed of 2°/min with the angle scope 2θ from 20° to 60°.

Thermogravimetric (TG) and differential scanning calorimeter (DSC) analytical measurements were carried out in simultaneous TGA/DSC Analyzer (TG/DTA 220, Seiko) from room temperature to the target temperature at 5 ℃/min heating rate under an argon atmosphere with 100 mL/min following rate. However, for the normal Al_2O_3 crucible without sealing, it was unable to maintain stable solution state and serious influence would be introduced in DSC measurements due to water evaporation and additional heat loss. In this experiment, 15 mL dimethylsilicone fluid (Dow Corning 200 Fluid, viscosity 1 000 cst, density 0.97 kg/m^3) was used as the sealing to reduce water evaporation to improve the accuracy of DSC measurement.

2 Results and Discussion

TEM image as shown in Fig.1, the morphology of the as-prepared TiO_2 particles synthesized by sol-gel method has a uniform size distribution with an average diameter of about 200 nm. After centrifugation and vacuum drying in room temperature for 2 hours, the TiO_2 particles were prepared to conduct X-Ray Diffraction (XRD) measurement. From the XRD patterns of the as-prepared TiO_2 particles as illustrated in Fig.2, relative flat distribution is clearly displayed, denoting the amorphous state of the synthetic sample without crystallinity.

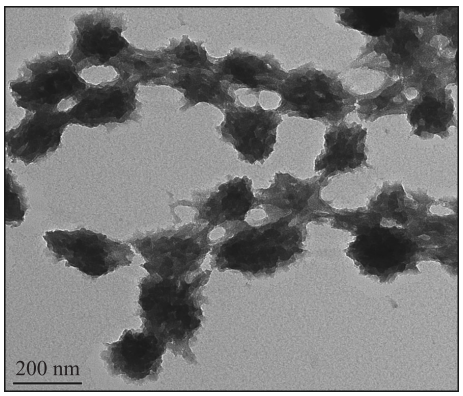

Fig.1　TEM Image of the synthetic TiO_2 samples

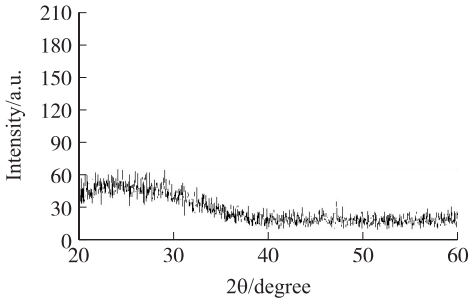

Fig. 2　XRD patterns of the synthetic TiO_2 samples

To study the thermal performance during the process of crystallization, TG tests were conducted for pure H_2O, dimethylsilicone fluid and H_2O covered with dimethylsilicone. According to the TG curves as illustrated in Fig.3, water evaporates completely before 70 ℃ without any sealing. While for the dimethylsilicone fluid, there is not any weight loss for high temperature of 85 ℃, providing good thermal stability of dimethylsilicone. In addition, due to the high dynamic viscosity and low density of dimethylsilicone fluid sealing, there is no any weight loss before 65 ℃ and only about 0.43% weight loss for 85 ℃. It is well proved that dimethylsilicone sealing can be used as effective protection layer for aqueous phase test with improved low-temperature stability without volatilization, reaction and decomposition.

By heating TiO_2 samples from room temperature to 75 ℃, 80 ℃, 85 ℃ at 5 ℃/min heating rate and holding the temperature for 60 min, DSC tests were conducted and the corresponding DSC curves were recorded as plotted in Fig.4. Three exothermic events are observed at 54 min, 40 min and 33 min with obvious heat flow peaks, which can be claimed to be the crystallization event of TiO_2 from the amorphous to anatase. Considering the different heating times of 10 min, 11 min, 12 min, obvious time delays of 13.7 min and 8 min can be observed between the holding temperatures of 75 ℃, 80 ℃ and 85 ℃, which indicate that the phase transition process is accelerated for higher soaking temperature due to the improved solubility of oligomers during the crystallization process. After being soaked in water for 0, 8 hours and 25 hours, DSC tests were conducted for TiO_2 samples from room temperature to 85 ℃ at 5 ℃/min heating rate with the holding temperature for 45 min. From the DSC curves as shown in Fig.5, three exothermal reactions are observed at 38 min, 35 min and 33 min, suggesting that soaking time in water can affect the crystallization process of TiO_2. Owing to the enhanced solubility of oligomers in water for longer soaking time, the process of crystallization is proved easier to happen with lower phase transition temperature. Meanwhile, the results of DSC also indicate that along with the increase of soaking time, partly crystallization of amorphous TiO_2 to anatase can also be observed with inconspicuous phase transition peaks, which agree well with the mechanism of spontaneous crystallization reported in literature[15].

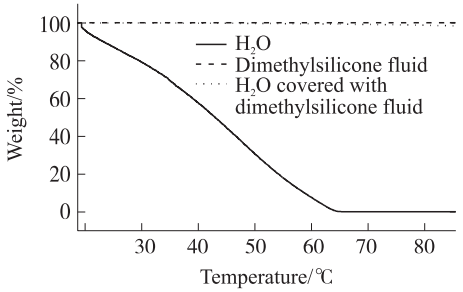

Fig.3　TG curves of H_2O, dimethylsilicone fluid and H_2O covered with dimethylsilicone fluid

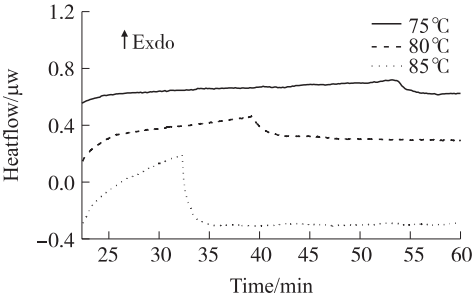

Fig. 4　DSC curves of TiO_2 samples at different soaking temperatures in water

To study the performance of phase transition for water-assisted crystallization, amorphous TiO_2 soaked in water was first heated in oven at 85 ℃ for 1 hour, and then it was centrifuged and vacuum dried at room temperature to achieve TiO_2 powder. To compare with the amorphous TiO_2 particles, XRD analysis was conducted to confirm the exothermal event detected in DSC, which was related to the crystallization of TiO_2. XRD patterns as shown in Fig.6 are quite different form that as displayed in Fig.2, four peaks are clearly displayed at 25.3°, 38°, 47.7° and 54.5°. The XRD patterns clearly show the (101), (004), (200) and (105) reflections of anatase TiO_2. Combing with the DSC curves in Fig.4, only one exothermic peak in each DSC curve provides solid evidence for phase transition of TiO_2 from amorphous to anatase after the water-soaking treatment.

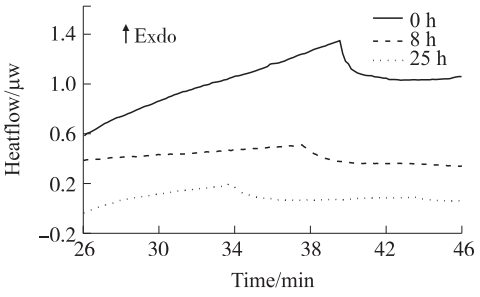

Fig. 5 DSC curves of TiO2 samples for different soaking times

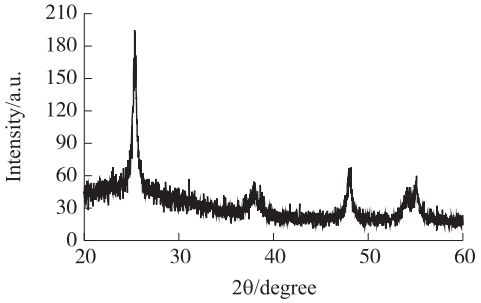

Fig. 6 XRD patterns of TiO_2 samples after soaking in water at 85 ℃ for 1 hour

3 Conclusions

In this paper, amorphous TiO_2 particles were first synthesized using sol-gel method and the phase transition from amorphous to anatase was systematically studied using DSC in water. Herein, to study the performance of water-assisted crystallization for TiO_2 particles, a simple but effective DSC approach for detecting the small exothermal event in sample solutions was proposed and dimethylsilicone fluid was also introduced as the sealing to avoid water evaporation. It is proved that the phase transition of TiO_2 from amorphous to anatase was sensitive to both temperature and soaking time. The higher the soaking temperature, the easier the phase transition of TiO_2 particles. Meanwhile, the lower the phase transition temperature can be achieved for longer soaking time. So the efficiency of crystallization for TiO_2 can be accelerated with appropriate soaking temperature control. The proposed method provides experimental basis for low-temperature water-assisted crystallization of TiO_2 particles and also suggests potential applications in environmental synthesis.

[参考文献]

[1] LU X H, WANG G M, ZHAI T, et al. Hydrogenated TiO_2 nanotube arrays for supercapacitors[J]. Nano Lett, 2012, 12: 1 690-1 696.

[2] ROZHKOVA E A, ULASOV I, LAI B, et al. A high-performance nanobio photocatalyst for targeted brain cancer therapy[J]. Nano Lett, 2009(9): 3 337-3 342.

[3] DE M, GHOSH P S, ROTELLO V M. Applications of nanoparticles in biology[J]. Adv Mater, 2008, 20: 4 225-4 241.

[4] FENG X J, ZHU K, FRANK A J, et al. Rapid charge transport in dye-sensitized solar cells made from vertically aligned single-crystal rutile TiO_2 nanowires[J]. Angew Chem Int Ed, 2012, 51: 2 727-2 730.

[5] SONG Y Y, SCHMIDT-STEIN F, BAUER S, et al. Amphiphilic TiO_2 nanotube arrays: an actively controllable drug delivery system[J]. J Am Chem Soc, 2009, 131: 4 230-4 232.

[6] MA Q, QIN T P, LIU S J, et al. Morphology and photocatalysis of mesoporous titania thin films annealed in different atmosphere for degradation of methyl orange[J]. Appl Phys A, 2011, 104: 365-373.

[7] QI J, CHEN L, ZHOU X. Advances in research of TiO_2 photo-catalytic oxidation technique for treatment of environmental pollutants[J]. Water resources protection, 2006, 22: 15-18.

[8] ROBBEN L, ISMAIL A A, LOHMEIER S J, et al. Facile Synthesis of highly ordered mesoporous and well crystalline TiO_2: impact of different gas atmosphere and calcination temperatures on structural properties[J]. Chem Mater, 2012, 24: 1 268-1 275.

[9] ZHANG Y F, ZHANG Z G, FANG X M. Synthesis of one-dimensional TiO_2, nanomaterials and their nanostructures[J]. Process Chem, 2007, 19: 494-501.

[10] JOO J B, ZHANG Q, DAHL M, et al. Control of the nanoscale crystallinity in mesoporous TiO_2 Shells for enhanced photocatalytic activity[J]. Energy Environ Sci, 2012(5): 6 321-6 327.

[11] HARIKRISHNAN S, MAGESH S, KALAISELVAM S. Preparation and thermal energy storage behaviour of stearic acid-TiO_2 nanofluids as a phase change material for solar heating systems[J]. Thermochimica Acta, 2013, 565: 137-145

[12] JOO J B, ZHANG Q, LEE I, et al. Mesoporous anatase titania hollow nanostructures though silica-protected calcination[J]. Adv Funct Mater, 2012, 22: 166-174.

[13] DAHL M, DANG S, JOO J B, et al. Control of the crystallinity in TiO_2 microspheres through silica impregnation[J]. Cryst Eng Comm, 2012, 14: 7 680-7 685.

[14] ZHONG L S, HU J S, WAN L J, et al. Facile synthesis of nanoporous anatase spheres and their environmental applications[J]. Chem Commun, 2008(10): 1 184-1 186.

[15] WANG D A, LIU L F, ZHANG F X, et al. Spontaneous phase and morphology transformations of anodized titania nanotubes induced by water at room temperature[J]. Nano Lett, 2011, 11: 3 649-3 655.

[16] JEAN J H, RING T A. Nucleation and growth of monosized titania powders from alcohol solution[J]. Langmuir, 1986(2): 251-255.

[17] HU Y X, GE J P, SUN Y G, et al. A self-templated approach to TiO_2 microcapsules[J]. Nano Lett, 2007, 7: 1 832-1 836.

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