Preparation and Characterizations of TiO_2 Nanoparticles by Sol-Gel Process using DMAC Solvent

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Abstract. Titanium dioxide(TiO_2) has a good ultraviolet masking effect, antibacterial and photocatalytic function, so it is a good material for the preparation of organic inorganic composite materials, which can be widely used in industrial, food, environmental protection and other fields. In this paper, TiO_2 hydrosol was prepared by sol-gel method with Butyl titanate(TBT) as precursors N ,N-dimethyl acetamide (DMAC) as the solvent, glacial acetic acid control pH, the ratio of the precursor and the solvent and the temperature effect reaction time and stability were studied. The optimum conditions is reaction temperature 80℃, TBT/DMAC 1:4. This method can be used to prepare the composite materials and reduce influences of the later period.

1. Introduction

Titanium dioxide (TiO_2) was considered to be the most efficient functional material with photocatalytic properties, high stability, non-toxic and low cost, attracting more attentions for novel material design[1]. Consequently, it has been used widely in photovoltaics, wastewater or air purification, anti-fogging paints, fluorescrent brightening and so on [2,3]. The three polymorphs of TiO_2 are anatase, rutile and brookite. Brookite exists in an orthorhombic structure while anatase and rutile both possess tetragonal unit cells, with anatase having a more open structure[4]. The final properties of the material are highly dependent on the method of synthesis, the experimental conditions and the structure of the polymorph.

Traditionally, TiO_2 nanoparticle was usually prepared by solid-phase, liquid-phase and gas-phase processes. Considering the advantages and disadvantages of these methods, Sol-gel process became main process for TiO_2 nanoparticles because of its low reaction temperature, high particle distribution, particle-size controllable, etc. Chen Xiaoguang [5]prepared TiO_2 sol with TBT as the precursor, ethanol as solvent and hydrochloric acid as the catalyst. Wangjia et al[6], TiO_2 hydrosol was prepared by sol-gel method with $Ti(OBu)_4$ as precursors. The influence of reaction time, the dosage of $Ti(OBu)_4$,water, chelant and catalyst on the preparation was studied. However, the selection of solvent could affect the agglomeration for TiO_2 nanoparticles. Nowadays, a common variation of the sol-gel method for obtaining TiO_2 nanoparticles involves the use of organic solution at low temperatures. Compared with other solvents, the procedure in this work presents several aspects which may be an attractive alternative for obtaining TiO_2 nanoparticles with uniform size distribution and crystalline phase purity in a relatively short period of time.

In this study, DMAC was used as solvent with glacial acetic acid as the catalyst to prepare TiO_2 nanoparticles through sol-gel method. On the other hand, the influence of the ratio between four TBT and solvent was investigated.

2. Materials and experimental methods

2.1. Materials

DMAC (HPLC grade, Tianjin kemi'ou),TBT (analytical grade, Tianjin kemi'ou), Glacial acetic acid(analytical grade, Guangdong Guanghua Science and technology) were used in this study. All chemicals used as received without any further purification.

2.2. Preparation of TiO_2 sol

The TiO_2 sol was prepared through sol-gel process with DMAC as solvent. TBT was added into DMAC solution, and the pH value was controlled by adding glacial acetic acid to be 4. The ratio of TBT to DMAC was in the range from 1:1 to 1:5.

As the hydrolysis reaction progressed, the solution became milky white because of the generation of $Ti(OH)_4$ particles. After the above process was complete, hydrolysis and polymerization reactions occurred in this mixture and a sol formed. In several different gelation processes, aging is the best gelation method for the preparation of TiO_2 nanoparticles. The aging time was recorded to investigated the optimal ratio of raw materials.

The TiO_2 gel was heated in a forced convection air oven at 600 ℃ for 2 h. Then the dried TiO_2 powders were obtained by grounding and homogenized in a mortar.

2.3. Determination of crystal structure

X-ray diffractometry (XRD: Rint-Ultima+, Rigaku Corp., Japan) using monochromatic CuKα radiation was used to identify the synthetic powders. Size distribution of synthetic TiO_2 nanoparticles be analyze by Laser particle size analyzer(Nano-ZS MPT, MALVEN, America).

3. Results and Discussion

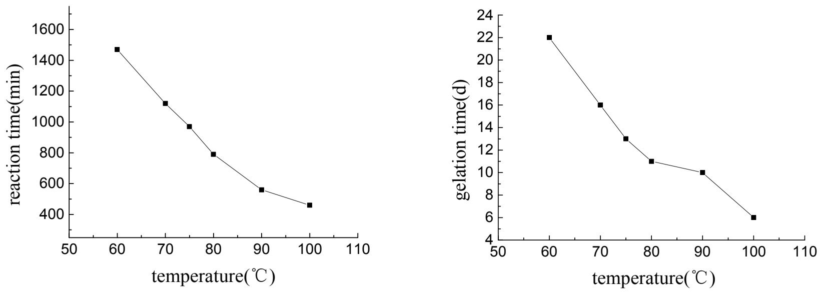

Fig.1 Influence of temperature on the hydrolysis reaction and gelation stability.(a: hydrolysis reaction; b: gelation stability)

The influence of temperature on the hydrolysis reaction and gelation was shown in Fig.1. From Fig.1(a), with the increasing temperature, the hydrolysis reaction and gelation was accelerated because of the enhancement of colloidal particles' kinetic energy. On the other hand, it can be observed that the gelation time was decreased with the increased temperature from Fig.1(b). Since the stability of TiO_2 sol could be evaluated by the gelation time, the gelation should be formed at lower temperature. Therefore, Considering the reaction time and sol stability, the reaction temperature was confirmed to be 80℃.

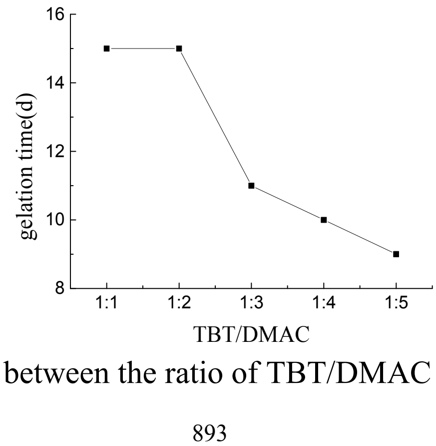

Fig.2. Relationship between the ratio of TBT/DMAC and gelation time.

Fig.2 shows the relationship between the gelation time and TBT/DMAC ratio. The gelation time was decreased with the increased amount of DMAC, because the volatilization of organic solvent was decreased and the TiO_2 sol formed network structure.

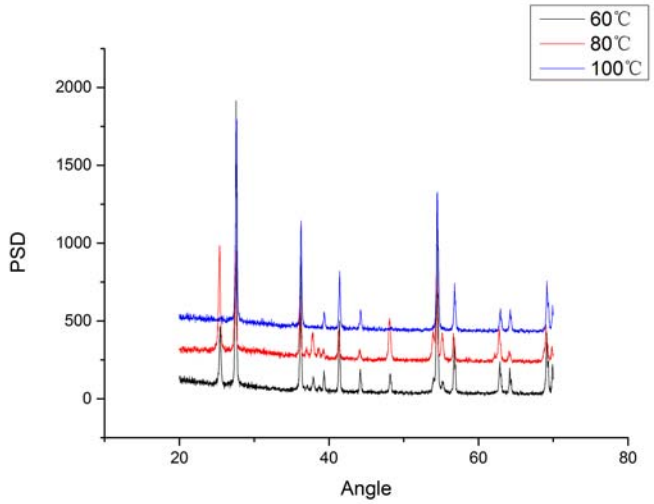

Fig.3 XRD patterns for synthetic TiO_2 nanoparticles.

These amorphous TiO_2 nanoparticles exhibited XRD patterns with no sign of any peak tendencies especially at 2 =25°-30°. The diffraction pattern for S60 and S80 included both the anatase phase with ICSD #98-004-0606 and rutile phase with ICSD #98-004-1027, while S100 shown only rutile phase. A significant difference in the intensity, however, was obvious for the dominant rutile characteristic peaks at 2 =27.43°.

Fig.4 indicated the size distribution of synthesized TiO_2 nanoparticles. The average size of TiO_2 nanoparticles was about 90.6 nm, and the TiO_2 particle size was in the range from 68.06 nm to 105.7nm. The high dispersity of TiO_2 was caused through the existence of DMAC solvent, which could decreased the surface energy of nanoparticles, decreasing the agglomeration of synthesized TiO_2 nanoparticles.

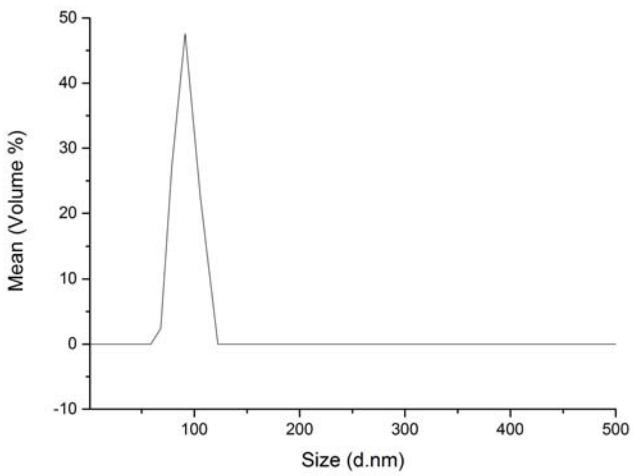

Fig.4 Size distribution of synthetic TiO_2 nanoparticles .

Summary

Sol-gel is more common、universal method that to prepare TiO_2 sol. This is more diversity choice about precursor, solvent and stabilizer . Many chose ethanol and water as solvent, hydrochloric acid, nitric acid, glacial acetic acid as stabilizer. In this paper ,this is slightly different from predecessor in the solvent and stabilizer. Especially solvent, choose DMAC that is not attempt, the reagent can dissolve more organic and inorganic substances, high boiling point.

Sol-gel method is used to prepare TiO_2, the optimum conditions is reaction temperature 80 ℃, TBT/DMAC 1:4.In this condition, the reaction time is shorter and sol stability time is relatively long. Both can obtain good effect, which can be as much as possible to reduce energy consumption and also the cost.

Acknowledgements

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Reference

[1] Fujishima A, Honda K, Electrochemical photolysis of water at a semiconductor

electrode, Nature, 1972, 238: 37-38

[2] AlbericiRM , JardimW F. Photocatalytic destruction of VOCs in the gas- phaseusingtitanium dioxide1 .Appl CatalB: Environ, 1997, 14 (1 - 2):55-68

[3] Duan Xiaodong , Sun Dezhi , Yu Zhengzhe , Zhu Zhibin , Shi Pengfei. Study on Photocatalytic Oxidation of Volatile Benzene Homologue,J. Environmental protection of chemical industry,2003,05:253-257

[4] ZhangYulong editor. Nanocomposite manual. China petrochemical press, 2005.

[5] Cheng Xiaoguang. Study on anti-ultraviolet performance of cotton textiles with sol-gel technology,J.Chemical Fiber and Textile Technology,2008(3):4-6.

[6] Wang Jia, Chen Ying, Yang Yue. Preparation and Application of TiO_2 Hydrosol,J. Journal of Beijing Institute of Clothing Technology,2011,04:46-51.