Characterization of Titanium Dioxide by Microwave Assisted Homogeneous Precipitation

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Abstract. Nanoparticulate TiO_2 microspheres were synthesized by microwave assisted homogeneous precipitation. The effect of concentration of oxysulfate sulfuric acid complex hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$), urea and temperature were investigated. The obtained powder was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM). The results showed that obtained TiO_2 were pure-phase anatase with diameters of about 2μm with 5.4383g $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$, 12.24g urea and 2% Span20 and 5% PEG600 in 20mL deionized water.

Introduction

Titanium dioxide (TiO_2) presents in three main phases, namely anatase, rutile and brookite. It is well known that rutile is the stable phase because of different distortion degree and connection mode (two edges are shared in rutile, four edges in anatase) while anatase shows higher photocatalytic activity due to the lower recombination rate of photogenerated electron-hole pair than rutile and has high adsorption capacity towards organic contaminates [1]. Numerous efforts have been devoted to synthesize TiO_2 with different morphology including sol-gel process, hydrothermal treatment, micro-emulsion and anodization method [2]. Nevertheless, these methods described above require expensive precursors and strict equipment condition and greatly limit the application of TiO_2. Homegeneous precipitation method, has been widely applied to synthesize variety of metallic oxide such as TiO_2, Al_2O_3, ZnO because of its simple operation, cheap precursors and ease for mass production [3], urea is demonstrated as a precipitation agent in this method which can slowly release ammonia to ensure the nucleation rate is greater than growth rate during precipitation and obtain better crystallinity, regular shape and size of particles.

Besides, microwave irradiation had drawn much attention since the first report of microwave-assisted synthesis in 1986 [4] due to its volumetric heating, simultaneous heating and rapid heating rate, different from the conventional annealing process which temperature rise through convection, conduction and irradiation. To the best of our knowledge, the method combined homogenous precipitation with microwave irradiation has not been investigated to prepare anatase.

In the present work, anatase was synthesized through homogenous precipitation assisted by microwave irradiation, taking titanium oxysulfate sulfuric acid complex hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) as Ti source and urea as precipitation agent with 2% Span20 and 5% PEG600 as surfactant. The effect of concentration of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ and urea, temperature were all investigated.

Materials and Methods

Chemicals. Titanium oxysulfate sulfuric acid complex hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) was

purchased from Aladdin, urea was purchased from Tianjin Zhiyuan Co., Ltd, urea and ethanol were of analytical grade and used without further purification.

Synthesis of Anatase. Firstly, appropriate amount of urea, 2% Span 20 and 5% PEG600 were added into the dilute aqueous solution of titanium oxysulfate sulfuric acid complex hydrate which was filtered by adding some activated carbon. Then, the mixture solution was transferred into three-necked flask and placed in microwave field at different temperature for 20 min, the resulting solution was washed for several times with 60°C deionized water to remove Fe^{2+} and then washed with absolute ethanol, the white precipitate was dried in a vacuum at 80°C for 2 h and calcined in muffle at 600°C for 2 h. Finally, the obtained powders were kept in dryer for further investigation.

Results and Discussion

Effect of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ Concentration. To determine the impact of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ concentration on crystallinity, 4.08g urea, 2% Span20 and 5% PEG600 were put into the diluted $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ (5.4383g, 2.7192g and 0.9597g) aqueous solution with 20mL deionized water. The subsequent operations were in line with previous described. Fig. 1a shows XRD patterns of synthesized TiO_2 with different $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ concentration. Before calcination, the sample exhibited a weak peak corresponding to the (001) diffraction plane of anatase and the calcined samples all showed no peak shift and other new crystalline phase, clearly existed six characteristic peaks indexed to (001), (004), (200), (105), (211), (204) diffraction planes which are matched well with JCPDS file No. 21-1272, indicating that calcined samples were phase-pure anatase and the intensity of diffraction peaks increased by varying $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ quality from 0.9597g to 5.4383g, the peaks after 60° were not obvious with low precursor concentration. With the dilute concentration of reactants, the hydrolysis rate of urea increased and lead to the little and big grain product. Therefore, the concentration of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ is a crucial factor to this process and 5.4383g $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ which FOM reached 9.5 with particle size of 17.58nm calculated from (101) plane was chosen for next experiments. For each case, one parameter was changed and analyzed while the other factors were kept constant.

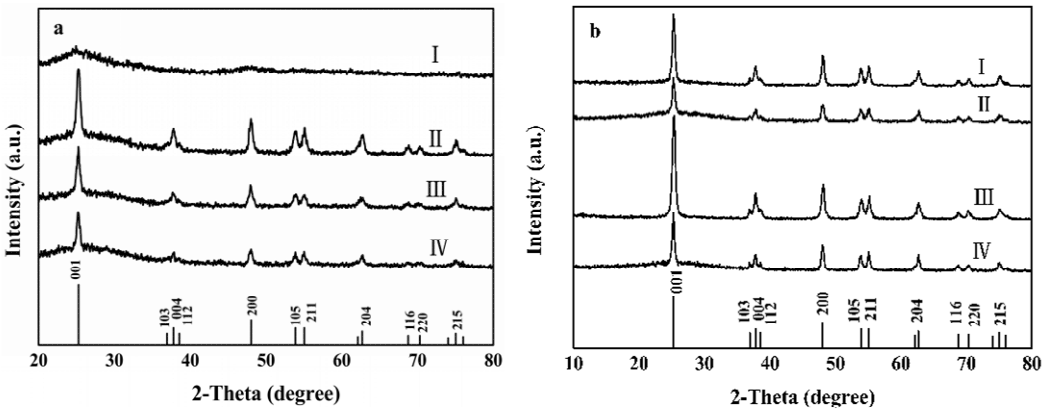

Figure 1. The XRD Patterns of Synthesized TiO_2: (a) with different dosages of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$: I5.4383g before calcinations; II5.4383g calainated at 600°C; III2.7192g; IV0.9597g. (b) with different temperature:I85°C; II90°C; III95°C; IV100°C

Effect of Urea Dosage. In order to study the effect of urea concentration on particle size and dispersion property. $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ was fixed at 5.4383g whereas the urea quality varied from 4.08g to 20.4g, the other conditions are the same as mentioned above. SEM images of titania

obtained from homogeneous precipitation assisted by microwave irradiation are shown in Fig. 2. It can be found that spherical agglomerates were obtained with appropriate urea/$TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ ratio, when urea quality increased to 12.24g, the roughly spherical particles with a diameter of about 1μm were observed while the dispersion property of agglomerates became worse with a further increase of urea/$TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ ratio. The concentration of OH^- increased in aqueous with larger urea/$TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ ratio, and caused the greater degree of supersaturation which is beneficial to the formation of small particles. Therefore, 12.24g urea was used for further investigation.

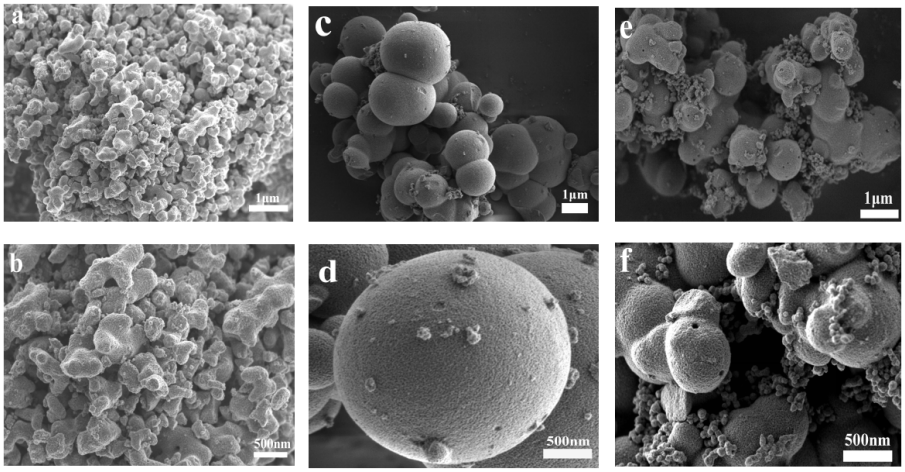

Figure 2. SEM images of representative TiO_2 samples synthesized with different urea qualities: (a) 4.08g; (b) the enlarged SEM image with 4.08g urea (c) 12.24g; (d) the enlarged SEM image with 12.24g urea; (e) 20.4g; (f) the enlarged SEM image with 20.4g urea

Effect of Temperature. In this part, 12.24g urea, 2% Span20 and 5% PEG600 were put into 5.4383g $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ in 20mL deionized water, the resulting solution was placed in a microwave field at different temperature (85°C, 90°C, 95°C, 100°C) for 20 min. XRD results in Fig. 1b showed that prepared TiO_2 were pure-phase anatase, the crystallite size calculated from (101) diffraction peak were 19.78nm, 21.24nm, 17.13nm and 23.82nm at 85°C, 90°C, 95°C and 100°C, respectively. Although the diffraction peaks at 95°C was sharpest, its agglomeration is serious and can not see the spheres from SEM images in Fig. 3c. Temperature is an important factor for nucleus formation and crystal growth, with an increase of temperature, the rate of nucleus formation increased but the super-saturation declined and the kinetic energy of molecules increased which is not beneficial for stabilization and leads to a decrease of nucleation rate. The reaction between $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ and urea started at about 80°C whereas the isomerization of urea will happen with high temperature. Therefore, an appropriate temperature is vital to this process. Consequently, 90°C was chosen as an appropriate temperature through comprehensive consideration to synthesize TiO_2. Besides, there are many literatures investigated the type of surfactant used in this reaction [5]. In the process of forming metatitanic acid, the particle surface was positively charged due to the dissociation of hydroxyl, and was easy to attract the anionic, exclude cationic from the solution. Therefore, the anionic surfactants are easier to parcel the particle surface and have very good dispersion effect theoretically, 1.5% DBS was regarded as comparison object in this experiment, the SEM image was shown in 3d, the more irregular micro-sphere was observed compared with 3b, and the dispersion property was not improved. So, 2% Span20 and 5% PEG600 were employed as surfactants in this study.

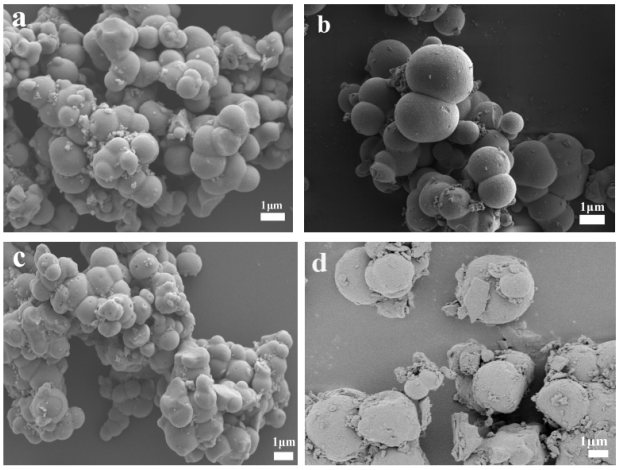

Figure 3. SEM images of different temperatures: (a) 85°C; (b) 90°C; (c) 95°C and (d) of 1.5% DBS as surfactant under 90°C

Conclusion

Nanostructured TiO_2 micro-spheres were synthesized with homegeneous precipitation method assisted by microwave irradiation. The raw materials concentration, temperature and the type of surfactant are crucial to the process of preparing nanostructured TiO_2 micro-spheres. The particles with uniform granularity and good dispersion are obtained when the $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ quality is 5.4383g, and 12.24g urea, 2% Span20 and 5% PEG600 in 20ml deionized water are placed in microwave field at 90°C for 20 min.

Acknowledgments

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