IOP Conf. Series: Materials Science and Engineering **735** (2020) 012004 doi:10.1088/1757-899X/735/1/012004

Preparation and Characterization of Submicron TiO_2 Microspheres via Urea-formaldehyde Template

Shaosen Lin, Shiguo Du and Yanling Lu

The 3rd Department, Army Engineering University Shijiazhuang Campus, Shijiazhuang, Hebei 050003, PR China
E-mail: lin_shaosen@163.com

Abstract. In order to obtain sub-micron TiO_2 microspheres with good dispersibility and easy collection, urea-formaldehyde(UF)-TiO_2 hybrid microspheres were synthesized by polymerization-induced precipitation in acidic TiO_2 sol through the reaction of urea and formaldehyde. The hybrid microspheres and their calcined products were analyzed by scanning electron microscopy, laser particle size analyzer, thermogravimetric analyzer and X-ray Powder diffractometer. The results of morphological characterization showed that the UF-TiO_2 hybrid microspheres were spherical and well dispersed, and their particle size ranged from 0.8~5μm. The sub-micron TiO_2 microspheres with large pore volume and good dispersion were obtained by calcining and removing the organic components in the hybrid microspheres. Thermogravimetric analysis showed that the proportion of inorganic components in hybrid microspheres was about 20%. XRD analysis showed that the product of calcined hybrid microspheres was single anatase-type titanium dioxide.

1. Introduction

As an important broadband gap semiconductor material, TiO_2 has shown great application prospects in the fields of solar cells, photocatalysts, pigments, biological materials and sensor materials due to its excellent photocatalytic performance, chemical stability, environmental friendliness and low cost[1-3]. Monodisperse microspheric TiO_2 has become one of the hotspots in the field of materials science and engineering due to its good fluidity, high bulk density, non-reunification, easy recovery and reuse[4].

At present, sol-gel and hydrothermal methods are often used to prepare nano or sub micron pellets, which are difficult to achieve non agglomeration and easy collection[5]. UF microspheres have become templates for the preparation of micro-nano metal oxide powders and mesoporous materials due to their advantages of easy synthesis, more variable conditions and various reaction groups[6-8]. The surface of UF prepolymer contains a large number of polar functional groups such as amines, hydroxyl groups and carbonyl groups. These groups also play a guiding role in the nucleation and growth of TiO_2. Based on these considerations, this paper combined the characteristics of sol-gel method and polymerization-induced precipitation to prepare hybrid microsphere[9]. A hybrid microsphere was synthesized by the polymerization of urea and formaldehyde in acidic TiO_2 sol. The size, distribution and shape of UF-TiO_2 hybrid microspheres were controlled by polymerization-induced precipitation. TiO_2 microspheres were prepared by removing organic templates from hybrid microspheres at high temperature. This method will provide a new method and a new idea for the preparation of ultrafine inorganic materials with good dispersion and without agglomeration.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

2. Experiments

2.1. Materials
Urea (analytical reagent), Tetrabutyl titanate ($Ti(OBu)_4$, analytical reagent), Ethanol (analytical reagent) and Acetylacetone (analytical reagent) were obtained from Tianjin Yongda Chemical Reagent Co. Ltd.; Formaldehyde solution (analytical reagent, 37.0%~40.0%) and Hydrogen nitrate (analytical reagent) were purchased from Shijiazhuang Chemical Reagent Factory; Double-distilled water was used for the preparation of all solutions in this study.

2.2. Preparation of Hybrid Microspheres
6.8 g $Ti(OBu)_4$, 0.6 g acetylacetone and 25mL ethanol were mixed in beaker. Under the condition of stirring, water was added drop by drop until the precipitation was complete. Then a certain amount of nitric acid with a concentration of 30wt% was added to the turbid solution to remove the precipitation and form a transparent TiO_2 sol. After dissolving 6 g urea in 50mL water and mixing evenly with the above-mentioned TiO_2 sol, the volume of the mixed liquid was adjusted to about 200mL with water and its pH value was adjusted to about 2.5. Under the stirring condition, 20 g formalin was slowly added into the mixed liquid. After homogeneous mixing, the stirring was stopped and the reaction vessel was sealed. After the reaction was completed, the products were separated by centrifugation, washed alternately with water and ethanol for 3 to 5 times, and dried in an air blast drying chamber at 60℃ for 6 hours, resulting in the preparation of UF-TiO_2 hybrid microspheres.

2.3. Characterization
Morphology and microstructure of hybrid microspheres and TiO_2 were observed by scanning electron microscopy (SEM, Hitachi S-4800). The particle size distribution was measured using a laser particle size analyzer (Malvern, Zetasizer Nano ZS90). The X-ray diffraction (XRD) measurement of the hybrid microspheres after calcination was made using Cu Kα radiation (D8 ADVANCE, Bruker AXS). The thermal properties of hybrid microspheres were examined by a thermogravimetric analyzer (TGA, PerkinElmer Pyris Diamond, SDTQ600) at a heating rate of 10℃·min^{-1} under N_2 atmosphere.

3. Results and Discussion

3.1. Morphology
Scanning electron microscopy analysis was performed to identify the morphology of UF-TiO_2 hybrid microspheres. Figure 1 shows SEM images of UF-TiO_2 hybrid microspheres at different magnification. These pictures together confirm the good dispersion of the hybrid microspheres. As can be seen from Figure 1 (a), UF-TiO_2 hybrid microspheres possess good spherical shape and fine particle size. Figure 1 (b) shows the morphology of single hybrid microspheres. Figure 1 (c) shows high magnification SEM image of the dotted line frame in Figure 1 (b). Two high magnification photographs show that there are nano-sized porous structure on the surface of hybrid microspheres, which lays a good foundation for the next step of calcination to remove organic templates to obtain porous TiO_2 microspheres. Figure 1 (d) is the particle size distribution of UF-TiO_2 hybrid microspheres. The result shows that the particle size of UF-TiO_2 hybrid microspheres concentrated in 0.8-5μm, and the average particle size was about 2μm. It can be predicted that ultrafine TiO_2 microspheres can be obtained by calcining this type of hybrid microspheres.

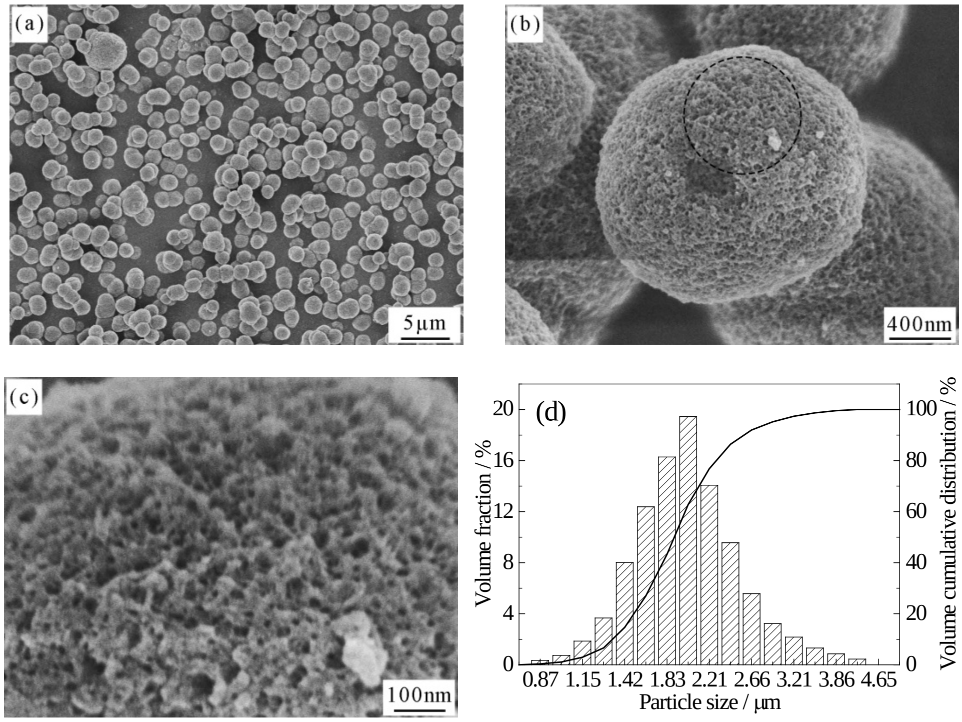

Figure 1. SEM Images and Particle Size Distribution of UF-TiO_2 Hybrid Microspheres

3.2. Thermal Analysis

The TG/DTG curves of UF microspheres (control sample, without TiO_2) and UF-TiO_2 hybrid microspheres at a heating rate of 10℃·min^{-1} were shown in Figure 2. The weight loss process of samples could be divided into three stages: slow weightlessness at room temperature to 200℃, rapid weightlessness at 200–350℃ and carbonization reaction at 350–600℃.

It can be seen from Figure 2 (a) that the UF microsphere has a weight loss of about 9% before 200℃. The main reason for weight loss in this stage is the volatilization of water adsorbed in UF microspheres and other low boiling point substances. In addition, this stage also corresponds to the thermal curing process of UF, that is, the reactive groups such as unreacted methylol group and amine group in the UF will undergo condensation reaction at high temperature to remove moisture and formaldehyde. The rapid decomposition stage of UF is 200-350℃. The weight loss of the sample is about 83%. The main reasons are the breakdown of methylene ether bond, methylene bond and the removal of other small molecules. The carbonization reaction stage is 350-600℃, and the weight loss is about 4%. The main reason is the removal of nitrogen, oxygen, hydrogen and other elements. Figure 2 (b) shows that the weight loss of UF-TiO_2 hybrid microspheres is about 10% before 200℃. The main reason is the volatilization of water adsorbed in the hybrid microspheres and other low boiling point substances, including the moisture and formaldehyde removed by the thermal curing process of UF. The weight loss of samples at 200-350℃ is about 62%, which is mainly caused by the thermal decomposition of organic components in hybrid microspheres and the transformation of TiO_2 sol to solid TiO_2. Among them, 252℃ corresponds to the thermal decomposition of UF and 290℃ corresponds to the transformation process from TiO_2 sol to solid TiO_2, The weight loss during the transformation process is caused by the loss of structural water and alcohol in the titanium dioxide sol. Carbonization occurs above 350℃, and the weight loss is about 4%. From the above analysis, it can be inferred that the content of solid TiO_2 in UF-TiO_2 hybrid microspheres is about 20%.

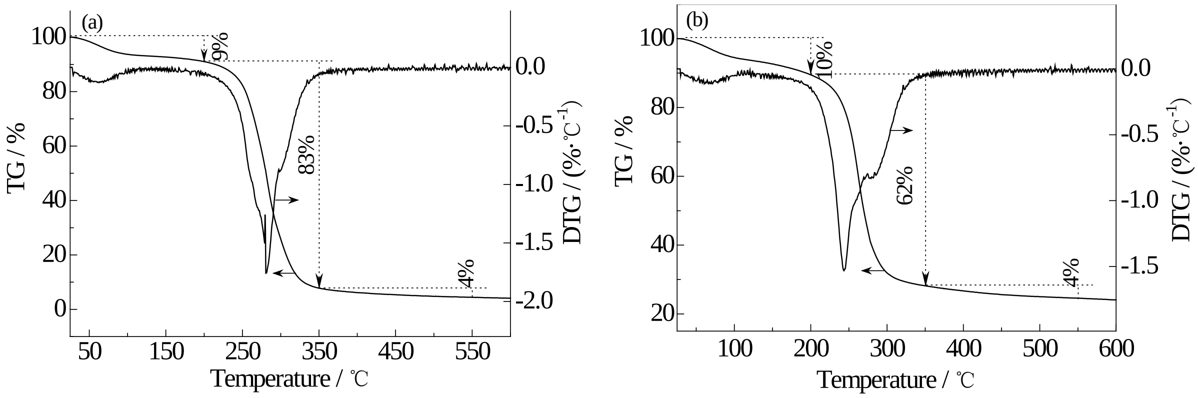

Figure 2. TG/DTG Curves of Samples: (a) UF Resin; (b) UF-TiO_2 Hybrid Microspheres

3.3. Characterization of UF-TiO_2 Hybrid Microspheres after Calcination

The as-prepared UF-TiO_2 hybrid microspheres were calcined at 600℃ for 20 minutes to remove the organic components. The calcined products were collected and their structures were observed by SEM, as shown in Figure 3. From Figure 3 (a), it can be seen that the TiO_2 microspheres have regular shape and good dispersion. Figure 3 (b) is an intervention broken TiO_2 microspheres. The broken TiO_2 microspheres show hollow structure or even double-layer structure. The shell of the broken TiO_2 microspheres is composed of multi-layer or single-layer TiO_2 particles. It is inferred that the TiO_2 microspheres are produced by calcining the hybrid microspheres whose surface is composed with UF. Due to the limitation of UF, the TiO_2 particles in the hybrid microspheres will self-assemble into TiO_2 microspheres during calcination, and the TiO_2 particles tend to migrate outward to form hollow structure due to the effect of surface tension in the process of polymerization. After the organic components was removed by calcination, the TiO_2 particles with small particle size and large specific surface area formed TiO_2 microspheres.

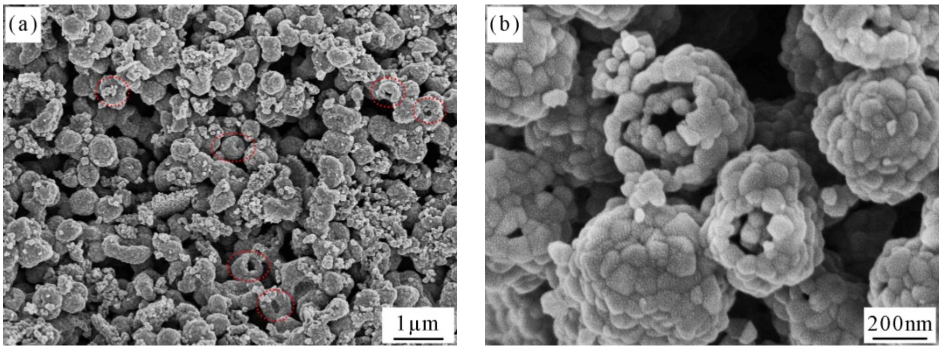

Figure 3. Morphology and Structure of UF-TiO_2 Hybrid Microspheres after Calcination

Figure 4 is the XRD pattern of the above-mentioned TiO_2 microspheres. The positions of the diffraction peaks on each crystal plane in the pattern are consistent with those on the standard anatase-type TiO_2 card (JCPDS 21-1272). This indicates that the crystalline form of TiO_2 microspheres obtained by calcining hybrid microspheres at 600℃ is anatase TiO_2.

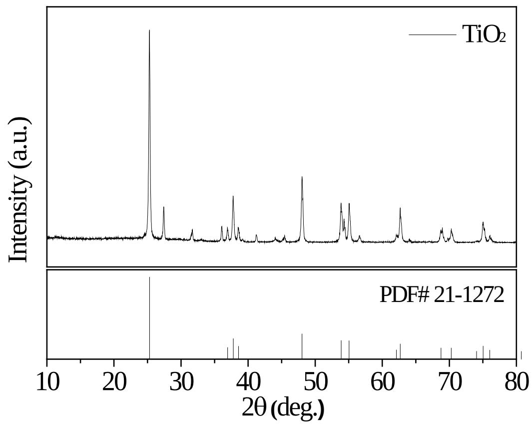

Figure 4. XRD Patterns of Hybrid Microspheres after Calcination

4. Conclusion

(1) UF-TiO_2 hybrid microspheres were successfully prepared by polymerization-induced precipitation method. The microspheres were well dispersed and no agglomeration was observed. The particle size of the microspheres ranged from 0.8-5μm. Submicron TiO_2 microspheres with good dispersion and easy collection could be obtained by removing organic template from hybrid microspheres by calcination.

(2) Thermal analysis showed that the proportion of TiO_2 in UF-TiO_2 hybrid microspheres was about 20%.

(3) XRD analysis showed that the crystalline form of TiO_2 microspheres obtained by calcining hybrid microspheres was anatase TiO_2.

5. Acknowledgements

The financial support provided by the project (51272284) of the National Natural Science Foundation of China for this work is gratefully acknowledged.

6. References

[1] Ma Y, Wang X, Jia Y, Chen X, Han H and Li C 2014 *Chem. Rev.* **114** 9987-10043
[2] Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod BF, Ashari-Astani N, Tavernelli I, Rothlisberger U, Nazeeruddin MK and Grätzel M 2014 *Nat. Chem.* **6** 242-7
[3] Wang S Q, Zhu A M, Liu Q L 2010 *Chemical Industry Times* **24** 5-8
[4] Ye C Y, Quan X J, Jiang L, Zhang, L and Tan, L 2011 *Chemical Reaction Engineering and Technology* **27** 515-20
[5] Jing M X, Yan Y Z, Ping Y H and Li L K 2014 *Journal of Materials Science & Engineering* **32** 5-9
[6] Wang, Y, Yan X, Tu M, Cheng J and Zhang J 2017 *Mater. Lett.* **191** 178-81
[7] Hao Z, Guo B, Liu H, Gan L, Xu Z and Chen L 2006 *Micropor. Mesopor. Mat.* **95** 350-9
[8] Liu Z, Du Z, Song H, Wang C, Subhan F, Xing W and Yan Z 2014 *J. Colloid. Interf. Sci.* **416** 124-32
[9] Siva T, Muralidharan S, Sathiyanarayanan S, Manikandan E and Jayachandran M 2017 *J. Inorg. Organomet. P.* **27** 1-9.