Chinese Chemical Letters Vol. 14, No. 8, pp 877 – 880, 2003 877
http://www.imm.ac.cn/journal/ccl.html

The Intelligent Properties of Micro-reactors for Preparating Nanoparticles

Gang WEI, Hai Yan HUANG, Rong Chun XIONG*

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029

Abstract: TiO_2 nanoparticles were synthesized by using micro-reactors. The shape and size of the nanoparticles produced from the original micro-reactors and the five times recycled micro-reactors mother liquor were investigated on transmission electron microscopy (TEM) by using the original sample, freeze prepared sample, and dyeing treated sample, respectively. UV-VIS spectrometry was used to study the growth process of TiO_2 nanoparticles in main reactors. The results showed that micro-reactors with nanometer magnitude had spherical or oval structures, and could restore to their original structure after they were destroyed. The products prepared in the original micro-reactors were similar to that in the micro-reactors recycled for many times, suggesting that the micro-reactors had memory function.

Keywords: Micro-reactors, nanoparticles, titanium dioxide, intelligent properties.

The micro-reactors were named as “intelligent reactors” in some references[1,2,3] for their self-assembly and self-copy properties similar to some functions of biological bacteria which can reassemble and restore automatically. Investigation on forming mechanisms[4,5] of nanoparticles in micro-reactors have focused on surfactant-related theories. No evidence has yet been reported to relate to intelligent properties of micro-reactors. No reports have been found on the direct recycling of micro-reactors mother liquor, particularly with regard to intelligent properties and economical benefits. The objective of this study was to synthesize TiO_2 nanoparticles by using micro-reactors. The intelligent properties of micro-reactors were investigated in the original reaction liquid and multi-recycled mother- liquors.

Experimental

n-Hexanol was mixed with cyclohexane at a mass ratio of 1: 1, then TX-100 was added under stirring to form a micro-reactors matrix (I) with TX-100 concentration of 0.67mol/L. The titanium-reactors system (II) was prepared by adding 5 mL of $TiCl_4$-HCl solution (0.1031 mol/L) to 12 mL of the micro-reactors matrix (I). The ammonium-reactors system (III) was prepared by adding 5 mL of aqueous ammonium (3.5 mol/L)

*E-mail: xiongrongchun@263.net

into 12 mL of (I) under stirring. The ammonium-reactors system (III) was added drop by drop into the solution II with vigorous stirring and reacted for 3 hours to form the main reactors system (IV). (IV) was transferred into two centrifuge tubes, and placed in a centrifuge at 4000 rpm for about 10 min. The supernatant was collected. The precipitate was thoroughly washed with an alcohol: acetone mixture (50:50 v/v) for three times to remove surfactant residues and solvent, then dried at 100°C and calcined at 480°C in a Mafu furnace. The product was white TiO_2 powders.

The shape and size distribution of the calcined particles were observed on a Hitachi H-800 transmission electron microscope (TEM). The preparation of TEM samples was done by ultrasonically dispersing the powders in alcohol prior to deposition on a copper-net. The micro-reactors sample was frozen in a BALZERS BAF-4000D high air freezing etch apparatus. The outer shape and size distribution of micro-reactors were then observed by using the frozen samples on a JEM-100CX TEM (Japan). Small quantity of micro-reactors sample was taken in a Petri dish, and dyed with a drop of acetic dioxy-uranium solution, for 90s prior to deposition on a copper-net. The inner shape and size distribution of micro-reactors were then observed by using the dyed samples on a JEM-100CX TEM (Japan). DR400/U UV-VIS spectrophotometer (American, Hach Co.) was used to measure UV-VIS absorption spectra of the micro-reactors systems.

Results and Discussion

The TEM photograph of the freeze prepared samples showed the outer shape of the micro-reactors, indicating that the micro-reactors system was composed of plenty of single micro-reactors with spherical or oval structure. The size of micro-reactors was of nano-meter magnitude (diameter: 24-40 nm). Their actual size could be controlled by changing experimental conditions, especially water content. The micro-reactors were destroyed during the separation of nanoparticles synthesized, from the micro-reactors system. But they could restore or reassemble automatically to form their original spherical or oval structures. The size of the restored micro-reactors, however, increased to 60-100 nm in diameter due to the increase in water content. The results indicated that micro-reactors had memory and auto-restoring functions.

The inner structure of micro-reactors was also spherical or oval as shown in the TEM photograph of dyeing treated samples. The inner diameter was 15-62 nm, 40-80 nm, 70-160 nm for the ammonium reactors, main reactors and auto-restored reactors, respectively.

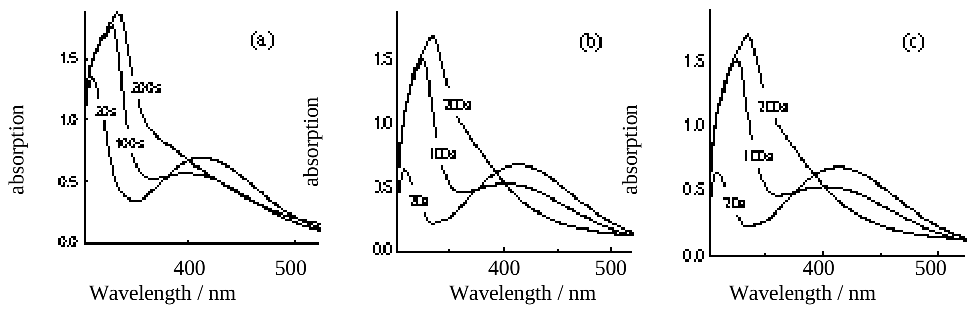
The mother liquor was recovered directly from the micro-reactors system, and renewed by adding extra amount of ammonium and matrix, which were lost due to dilution and loss. The resulting liquid was reused as ammonium reactors to synthesize TiO_2 nanoparticles. Surprisingly, the diameter still lied between 13-14 nm for the TiO_2 nanoparticles prepared from the mother liquor that had been recycled for five times. After being recovered directly for 5 times, the mother liquor contained by-products such as ammonia chloride. The diameter of TiO_2 nanoparticles obtained from the recycled mother liquors with the presence of ammonia chloride was still similar to that obtained in the original ammonium reactors system. This suggested that the function of ammonium reactors system had restored automatically after the recycled mother-liquid was renewed by adding some ammonium and matrix.

The direct recycling capability of micro-reactors mother liquor is the key intelligent property of micro-reactors, which has theoretical and practical significance. Various synthesis processes have been reported for the synthesis of nanoparticles in micro-reactors, but to the best of our knowledge no previously reported processes were similar to the process used in this study, particularly with regard to the direct recycling of the micro-reactors mother liquor. In contrast, the method of normal decompressed distill mother-liquid could recover the solvent, but micro-reactors system was destroyed. The method had only economical significance.

The function of main reactors produced from the original ammonium reactors and restored ammonium reactors was similar. The results showed that main reactors had memory and auto-restoring functions.

According to the quantum effect of nanoparticles and Brus formula[6], UV-VIS spectrometry was used to study the growth process of TiO_2 nanoparticles in main reactors (**Figure 1**). Nano-size particles were very small in the initial stage of reaction, so that characteristic absorption peaks were observed within UV wave-length due to the quantum effect. Nanoparticles grew gradually with reaction time, and red shift in absorption spectrum was observed, leading to an increase in absorbence. The fact of that the spectra for both the original and restored main reactors were similar indicated that the growth course and velocity were similar in both systems, suggesting that the main reactors had memory and auto-restoring functions.

Figure 1 Growth of nanoparticles in main-reactors



(a. the original reactors, b. the first restored reactors, c. the second restored reactors)

All of the above results suggested that micro-reactors had memory and auto-restoring functions.

Acknowledgments

This work was supported by the China National Key Technologies R&D Programme Item (2002BA313B05).

References

1. M. P. Pileni, *J. Phys. Chem.,* **1993,** *97,* 6961.
2. M. P. Pileni, *Advanced in Colloid and Interface Science,* **1993,** *46,* 139.
3. G. Beck, P. Francois, *Journal of the society of non-traditional technology,* **1992,** *3,* 42.
4. V. Chhabra, V. Pillai, B. K. Mishra, *et al.*, *Langmuir,* **1995,** *11,* 3307.
5. E. W. Joselvich, *J. Phys. Chem.,* **1994,** *98*, 7628.
6. L. E. Brus, *J. Chem. Phys.*, **1983,** *79,* 5566.

Received 27 August, 2002