

Size controlled synthesis and Photocatalytic activity of anatase TiO₂ hollow microspheres

Charu Dwivedi, V. Dutta

Abstract—Titanium oxide hollow microspheres were synthesized from organic precursor titanium tetraisopropoxide (TTIP) using continuous spray pyrolysis reactor. Effects of precursor concentration, applied voltage and annealing have been investigated. It was observed that the annealing of the as-synthesized TiO₂ hollow microspheres at 250°C, which had an average external diameter of 200 nm, leads to an increase in the size and also more spherical shape. The precursor concentration was found to have a direct impact on the size of the microspheres, which is also evident in the absorption spectrum. The as-prepared TiO₂ hollow microspheres exhibited good photocatalytic activity for the degradation of MO.

Keywords—TiO₂ hollow microspheres; Spray Pyrolysis; Electric Field; Microscopy; Microstructures.

I. INTRODUCTION

HOLLOW inorganic microspheres are of great interest due to wide applications in diagnostics, drug delivery, bioactive materials, and optical devices. Hollow spherical TiO₂ microspheres have emerged as a material of special interest to the researchers worldwide due to specific properties such as low density, high surface area, good surface permeability, and increased light-harvesting capacity.[1-7]

Recent progress shows that hollow TiO₂ spheres present an enhanced performance in photocatalysis, dye-sensitized solar cells and photonic crystals due to their light scattering, organic adsorption, and porous characteristics.[8-15] In the past decade, great progress has been made to fabricate hollow TiO₂ spheres with varied structural features. Among the various synthesis techniques, template based approach is most commonly used, where solid materials such as anodic alumina membranes or mesoporous silicas and soft templating materials such as ionic or nonionic surfactants, polymers, or organic ligands have been utilized as structural guiding matters.[16-17]

Herein, we report a simple technique to synthesize well defined anatase TiO₂ hollow microspheres without a template using continuous spray pyrolysis reactor with metal alkoxide precursor and ethanol as solvent. Spray pyrolysis is of considerable interest for the preparation of metals, metal oxides, non-oxides and composite powder because this method can produce particles of controlled composition and morphology, good crystallinity, and uniform size distribution, all of which can be readily obtained in only “one-step” and is also less time consuming technique as compared to other template based and hydrothermal approaches.

Also, the morphology and size of the product can be controlled by simply varying the concentration and applied voltage during spray which has been reported in this paper. The photocatalytic property of the products was evaluated by degradation of MO under UV-visible irradiation.

II. EXPERIMENTAL DETAILS

Well-defined anatase TiO₂ hollow microspheres were prepared via one step technique (Continuous Spray Pyrolysis Reactor (CoSP)) using titanium isopropoxide (TTIP) as organic precursor and ethanol as solvent. The concentration of the precursor was varied from 0.1 M to 0.2 M. Vigorous stirring with a magnetic stirrer was applied during slow addition of TTIP into the ethanol solution at room temperature for about 1 h. A milky white titanium precursor was obtained after 1 hr of stirring which was sprayed through a three zone reactor with all the three zones maintained at different temperatures viz. 600, 850 and 500 °C, respectively with N₂ as the carrier gas. [18] The solution flow rate and the gas pressure were kept constant at 2 ml/min and 2 kgf/cm².

XRD studies were done using X-ray diffractometer (Phillips X'PERT PRO), having CuK_α incident beam ($\lambda = 1.54\text{\AA}$). Phillips CM12 120KV transmission electron microscope was used for TEM and 200kV Technai G20- high-resolution transmission electron microscope was used for HRTEM studies. Surface morphology was studied using ZEISS EVO-50 model scanning electron microscope (SEM). The absorbance of the solution was measured using Lambda 1050 UV-VIS-NIR spectrophotometer.

The photocatalytic activities of the prepared TiO₂ hollow microspheres were determined by measuring the degradation of methyl orange (MO) in an aqueous solution under UV light irradiation. A 370 nm UV lamp (15 W) was used as light source. Typically, 10 mg of photocatalyst was put into 40.0 mL of MO aqueous solution (10 mg/L) and was magnetically stirred in the dark for 1 hr to reach the adsorption equilibrium of MO with the photocatalysts, and then exposed to UV light. UV/Vis absorption spectra were recorded at different time intervals, and the concentration of MO left in the aqueous system was measured by detecting the absorption at 464 nm, the maximum absorption wavelength for MO.

III. RESULTS AND DISCUSSION

Figure 1 shows the SEM image of the hollow microspheres prepared with different concentrations of TTIP ethanol solution: (a) 0.1M; (b) 0.15M and (c) 0.2M. The images clearly show that slightly larger particles are obtained for higher concentration as compared to lower ones. On the other hand, Fig. 1 (d) shows the SEM image of hollow microspheres

Authors are with the Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India (phone: 011-26591261; fax: 011-26591261; e-mail: charudwi.iitd@gmail.com; vdutta@ces.iitd.ac.in).

(0.1M TTIP ethanol solution) annealed at 250 °C. It was found that the average size of the microspheres increased to 4 µm (o.d.) & 1.8 µm (i.d.) with annealing and the shape becomes more spherical.

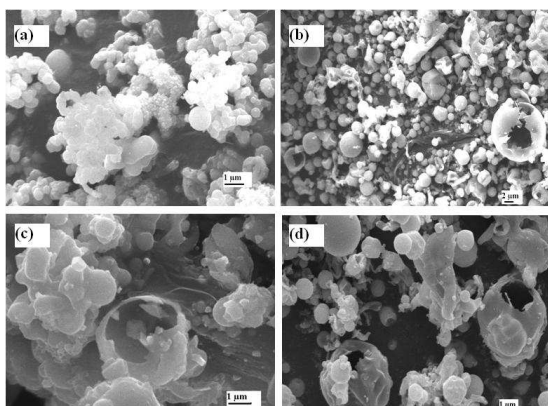


Fig. 1 SEM images of TiO₂ microspheres at (a) 0.05 M; (b) 0.1 M; (c) 0.15 M; (d) annealed at 250 °C

The porous hollow structure was further investigated by the TEM image as shown in Fig. 2 and the intensive contrast between center and edge of the spheres indicates the formation of hollow structure in the final products and the shell thickness of the spheres is about 55-60 nm.

The particle size as calculated from the TEM image clearly indicates an increase in the size from 170 to 250 nm external diameter as the concentration changes from 0.1 to 0.2 M which is also confirmed from the size calculated by the XRD data. The high-resolution TEM (HRTEM) image also shows clear lattice fringes which reveal a distance between lattice planes of 0.35 nm, corresponding to the (101) lattice planes of anatase TiO₂. [19]

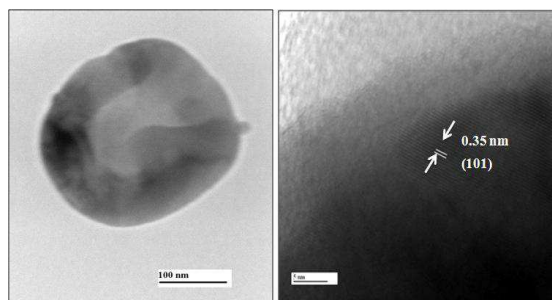
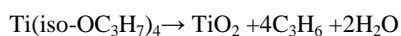


Fig. 2 TEM images of TiO₂ microspheres at (a) 0.1 M; (b) HRTEM image

The crystal structure of the TiO₂ sample was determined by XRD analysis as shown in Fig 3. All the diffraction peaks can be well indexed to anatase phase of TiO₂ (JCPDS 71- 1169). No peaks of impurities were detected in the XRD patterns, indicating the high purity of the products.

The possible growth mechanism of the hollow microspheres may be as follows with the possible pyrolysis reaction as suggested below: [20]



At the beginning for smaller precursor concentrations, titanium dioxide crystallized gradually and formed lots of small nanocrystallites as can be seen in the SEM image (Fig. 1(a)). At the same time, the above mentioned pyrolysis reaction takes place leading to the formation of C₃H₆ (propene gas). These gas bubbles and TiO₂ nanoparticles tend to aggregate together to minimize the interfacial energy and the spherical aggregates are then formed by aggregation of original nanocrystallites nucleated on the gas-liquid interface.

The solid aggregates is followed by a solid core evacuation and a hollowing effect can take place at such a high reaction temperature, which is due to the continuous outward growth of the fine nanocrystallites and the gas bubbles gathered in the center of spheres.²¹

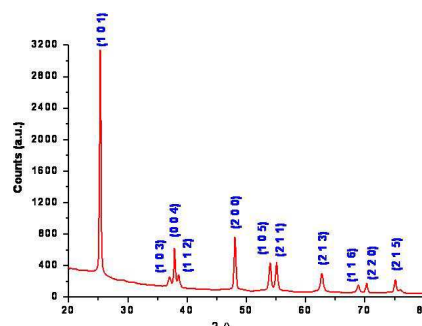


Fig. 3 XRD spectra of TiO₂ microspheres (0.1M)

Fig 4 shows the optical absorption spectrum of the TiO₂ samples w.r.t concentration. The absorption spectrum shows that the band gap of 0.1M sample is 3.40 eV and that of 0.2 M is 3.35 eV. The decrease in the band gap is due to increase in the particle size with increasing concentration.

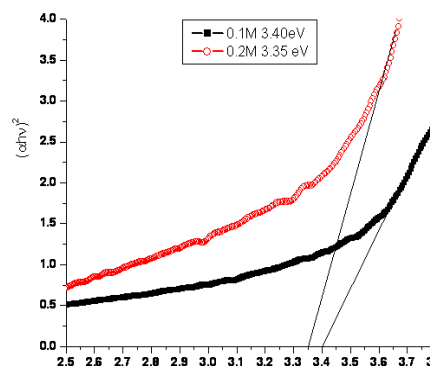


Fig. 4 Optical absorption spectra w.r.t. concentration

Figure 5 shows the decrease of the concentration of MO with irradiation time in the presence of TiO₂ hollow microspheres (0.1- 0.2 M). As-synthesized TiO₂ hollow spheres showed about 60.0% photocatalytic decomposition for MO after 90 mins of irradiation.

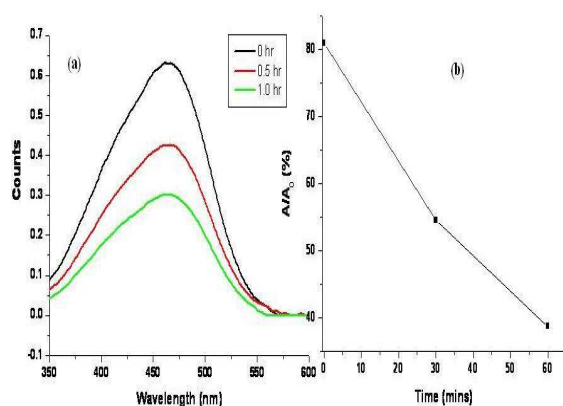


Fig. 5(a) Absorption Spectra of MO solution before and after irradiation; (b) Photodegradation of MO solution over TiO_2 hollow spheres; A_0 and A is the initial concentration of MO before and after irradiation over a period of time, respectively.

IV. CONCLUSIONS

TiO_2 hollow microspheres with anatase phase were prepared by continuous spray pyrolysis reactor. SEM and TEM investigations reveal that the products have an average diameter and shell thickness of about 200 nm and 55-60 nm, respectively. The technique is a “one step” approach to synthesize hollow microspheres as compared to other methods reported which require either several steps or longer reaction times. The microspheres showed good photocatalytic activity and their size can be controlled by simply controlling the process parameters.

REFERENCES

- [1] J. G. Yu, S. W. Liu, M. H. Zhou, *J. Phys. Chem. C*, vol. 112, 2008, pp. 2050.
- [2] J. G. Yu, S. W. Liu, H. G. Yu, *J. Catal.*, vol. 249, 2007, pp. 59.
- [3] H. Li, Z. Bian, J. Zhu, D. Zhang, G. Li, Y. Huo, H. Li, Y. Lu, *J. Am. Chem. Soc.*, vol. 129, 2007, pp. 8406.
- [4] X. Li, Y. Xiong, Z. Li, Y. Xie, *Inorg. Chem.*, vol. 45, 2006, pp. 3493.
- [5] J. H. Pan, X. Zhang, A. J. Du, D. D. Sun, J. O. Leckie, *J. Am. Chem. Soc.*, vol. 130, 2008, pp. 1256.
- [6] Z. Liu, D. D. Sun, P. Guo, J. O. Leckie, *Chem. Eur. J.*, vol. 13, 2006, pp. 1851.
- [7] S. Shang, X. Jiao, D. Chen, *ACS Appl. Mater. Interfaces.*, dx.doi.org/10.1021/am201535u.
- [8] H. J. Koo, Y. J. Kim, Y. H. Lee, W. I. Lee, K. Kim, N. G. Park, *Adv. Mater.*, vol. 20, 2008, pp. 195.
- [9] S. Nishimura, N. Abrams, B. A. Lewis, L. I. Halaoui, T. E. Mallouk, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, *J. Am. Chem. Soc.*, vol. 125, 2003, 6306.
- [10] Y. X. Yin, Z. G. Jin, F. Hou, *J. Am. Ceram. Soc.*, vol. 90, 2007, pp. 2384.
- [11] D. Chen, F. Huang, Y. Cheng, A. R. Caruso, *Adv. Mater.*, vol. 21, 2009, pp. 2206.
- [12] J. H. Pan, X. Zhang, A. J. Du, D. D. Sun, J. O. Leckie, *J. Am. Chem. Soc.*, vol. 130, 2008, pp. 11256.
- [13] H. J. Koo, Y. J. Kim, Y. H. Lee, W. I. Lee, K. Kim, N. G. Park, *Adv. Mater.*, vol. 20, 2008, pp. 195.
- [14] X. Feng, L. Yang, Y. Liu, *Materials Letters*, vol. 64, 2010, pp. 2688.
- [15] J. Fu, *Materials Letters*, vol. 68, 2012, pp. 419.
- [16] F. Caruso, R. A. Caruso, H. Mo'hwald, *Science* vol. 282, 1998, pp. 1111.
- [17] C. G. Go'ttner, *Angew. Chem, Int. Ed.*, vol. 38, 1999, pp. 3155.
- [18] C. Dwivedi, V. Dutta, *Adv. Nat. Sci: Nanosci. Nanotechnol.*, vol. 3, 2012, pp. 015011.
- [19] J. H. Pan, X. Zhang, A. J. Du, D. D. Sun, J. O. Leckie, *J. Am. Chem. Soc.*, vol. 130, 2008, pp. 1125.
- [20] W. N. Wang, I. W. Lenggoro, Y. Terashi, T. O. Kim, K. Okuyama, *Materials Science and Engineering B*, vol.123, 2005, pp. 194.
- [21] G. Yang, P. Hu, Y. Cao, F. Yuan, R. Xu, *Nanoscale. Res. Lett.*, vol. 5, 2010, pp. 1437.