Materials Science in Semiconductor Processing 75 (2018) 10–17

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Morphology transformation from titanate nanotubes to TiO_2 microspheres

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ARTICLE INFO

Keywords:
Mesoporous
TiO2
Nanotubes
Synthesis
Microspheres

ABSTRACT

Single phase TiO_2 mesoporous microspheres were synthesized using a facile one step technique from nanotubes. The prepared microspheres were crystallized in an anatase form with a tetragonal symmetry. The results of surface area measurements revealed mesoporous structure of such materials together with uniform pores. The samples possess rough surface and could be exploited in different applications. The methodology is easy, cheap, fast and could be reproduced for morphology tuning and/or transition.

1. Introduction

Titanium dioxide nanoparticles (TiO_2) represent a family of most distinguished materials, used in a variety of applications like; environmental remediation [1], solar cells [2,3], photocatalysis [4,5], hydrogen production [6,7] and energy storage [8,9]. Some of the unique physical and good chemical properties of TiO_2 are their high specific surface area, wide band gap, low toxicity, low cost and chemical stability [10]. The former could be prepared with different morphologies such as; nanowires, nanospheres, nanotubes, nanosheets and nanorods [11–21]. TiO_2 microspheres proved excellent performance in environmental and energy fields, owing to their fascinating properties such as large pore size, high surface area, large pore volume, alternative pore shapes and controllable framework compositions [22–25]. The presence of pores in nanostructures improved their physical and chemical characteristics owing to their ability to interact with atoms, ions, and nanoparticles not only on the surface but also in the bulk of the material [26].

Different methods were reported to prepare TiO_2 spheres with a mesoporous structure such as; hydrothermal, sacrificial template, precipitation, sol-gel, gas bubble and microemulsion [27–34]. Among these techniques, the hydrothermal process has offered many advantages than others such as simple equipment requirements, low cost, mild reaction conditions and less energy consumption [35]. The main drawbacks of these methods are using titanium precursors which exhibit a high reactivity towards water, causing difficulties to control the morphology of TiO_2. To avoid these drawbacks, J. Lei et. al [35], reported a simple method for morphology modification of Titanate starting with TiO_2 nanowires as a precursor to avoid the usage of the highly reactive alkoxide or chloride.

Titanate and TiO_2 nanostructures are ideal materials extensively used in photocatalytic degradation of dyes when using photocatalyst, it absorb UV radiation photons either from sunlight or UV lamp [36–38].

By performing a survey on Scopus database using "mesoporous titanium dioxide microspheres" as keywords, the results were 211 paper and 488 patents in the period (1996–2017). Fig. 1(a) illustrates the number of research papers published from 1996 to 2017. The figure inset shows the percentage of papers classified according to the subject area. Uptill now no published articles were found on the morphology transition from nanotubes to microspheres.

Herein, we developed a facile method to prepare TiO_2 microspheres from titanate nanotubes for the first time as a precursor in the presence of hydrofluoric acid (HF) and urea using the hydrothermal method.

2. Experimental

2.1. Synthesis and characterization of spherical TiO_2 microspheres

2.1.1. Preparation of nanotubes

As in our recently published work [39]; 5 g of pure TiO_2 (anatase) powder were mixed with 500 ml, 10 N NaOH using magnetic stirring till a milky solution is formed. Then, the later was transferred to a Teflon-lined stainless steel autoclave with 1000 ml capacity and heated at 160 °C for 23 h. [40,41]. The resultant white product of sodium

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https://doi.org/10.1016/j.mssp.2017.09.030
Received 3 August 2017; Received in revised form 25 September 2017; Accepted 26 September 2017

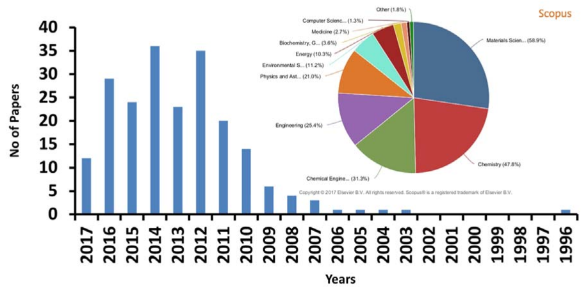

Fig. 1. (a) number of papers published from 1996 to 2017 on Mesoporous Titanium dioxide microspheres; the inset Percentage of the papers on Mesoporous Titanium dioxide microspheres according to different subjects.

Table 1
The structural parameters of S1 and S2.

Parameters	S_1	S_2
a (Å)	3.8067	3.7990
c (Å)	9.4557	9.4363
c/a	2.4839	2.4838
V(cm^3)	1.37023*10^{-22}	1.36189*10^{-22}
D_x (g/cm^3)	3.8709	3.8946
Calculated crystallite size(nm)	49.3	63.7
pore volume(cm^3/gm)	0.0445	0.0404
pore size (nm)	3.5 and 7.9	3.6 and 10.5
BET surface area(m^2/g)	27.06	20.2
crystal phase	Anatase	Anatase
band gap (eV)	3.25	3.25

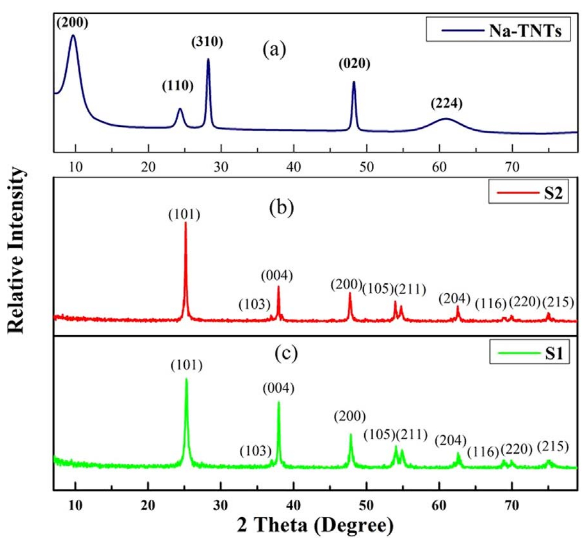

Fig. 2. (a-c) XRD patterns of Na-TNTs, S2 and S1, respectively.

titanate nanotubes (Na-TNTs) was thoroughly washed with distilled water, followed by 0.1 N HCl to prepare H-titanate nanotubes (H-TNTs) [42]. The obtained H-titanate precipitate was washed with distilled water and finally dried at 80 °C for 2 h.

2.1.2. *The synthesis of mesoporous TiO_2 microspheres*

H-titanate nanotubes (as a precursor) were mixed with 650 ml of distilled water using magnetic stirrer for 30 min, then 10 ml of HF and 19.5 g of Urea were added. After continuous stirring for 1hr slight turbid solution is obtained. This mixture was divided into two halves. The first half (S1) was placed into Teflon-lined stainless steel autoclave with 500 ml capacity to prepare the first sample. The second part (S2) was filtered using filter paper, then was placed into another autoclave with the same capacity to prepare the other sample. The two autoclaves were kept at 180 °C for 12 h., then cooled down to room temperature. After hydrothermal reaction, the resulting samples were filtrated and washed several times with distilled water and then dried at 80 °C for 2 h.

2.2. *Characterization*

The morphology and microstructure of samples were examined by FESEM (Quanta FEG 250, Switzerland) and HRTEM (JEOL-JEM 2100,Japan). XRD patterns were recorded on a PANalytical (Empyrean) X-ray diffraction using Cu Kα_1 radiation (wavelength 1.5406 Å) at an accelerating voltage of 40 kV, current of 30 mA, scan angle 5–80° range and scan step 0.02°.

3. Results and discussion

Fig. 2(a)-(c) represents XRD patterns of Na-TNTs, S2 and S1, respectively. As shown in the Fig. 2(a), the reflections at (9.68°, 24.35°, 28.20°, 48.20° and 60.86°) confirmed the tubular structure of Na-TNTs ($Na_2Ti_4O_9$) [ICDD card no. 04-009-1210] with space group *c2/m* [40]. Moreover, the data in Fig. 2(c), (d) reveals strong reflections from 10 planes. The patterns were indexed and compared with the ICDD card (01-075-2546). The former indicates the formation of anatase TiO_2 in a single phase with tetragonal symmetry characterized by the space group *I41/amd*. The large intensity, as well as sharp planes (101), (004), (200), (105) and (204), point to the very good crystallinity of the synthesized samples. The lattice parameters were calculated for S1 and S2 according to the tetragonal symmetry from the following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where d is the interplanar spacing, (*hkl*) are the Miller indices and a, c are the lattice parameters. The theoretical density was computed from the following equation:

$$D_X = \frac{ZM}{NV} \quad (2)$$

where (Z = 4) represents the number of molecules per unit cell, M is the molecular weight, N is Avogadro's number and V is the calculated