

PREPARATION AND CHARACTERIZATION OF INORGANIC NANOPARTICLES AND NANOCOMPOSITES FOR SENSING MATERIALS

S.J. Cha^{1,2}, C.W. Heo^{1,2}, D.J. Lee^{1*}, H.M. Lim¹, D.H. Suh², S.K. Lim³, H.D. Kim⁴, H.S. Kim⁴

¹ Eco-Composite Material Center, Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea

² Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

³ Division of Nano & Bio Technology, Daegu Gyeongbuk Institute of Science & Technology, Daegu 711-873, Korea

⁴ Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea

* Corresponding author(dongjlee@kicet.re.kr)

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1 Introduction

Semiconductor metal oxides (SMOs) such as SnO₂, ZnO, TiO₂, In₂O₃ and WO₃ have been of interests as solid-state gas sensing materials due to their high sensitivity, good reproducibility, low cost, etc. Their gas sensing performances are attributed to the variation of electrical conductivity upon exposure to toxic and flammable gases. Notably, the performances are heavily dependent on the surface to volume ratio, porosity, and granularity of the gas sensing materials [1–3]. For this reason, current researches focus on the preparation of the advanced gas sensors using nanostructures which have exceptional functions and potential applications.

Nanostructured titania have been found to be very attractive materials because of their superior physicochemical properties as active materials for photocatalysis [4], electrochemical capacitors [5], and dye-sensitive solar cells [6, 7]. In all the applications, the structure of TiO₂ employed must have sufficiently high surface area for interaction and optimum pore size to allow diffusion of active species. Therefore, how to enlarge the surface area and control the pore size are important issues for the application of TiO₂.

Also, carbon nanotubes are materials with special carbon nanostructures, electronic and mechanical properties, which are promising for many technological applications. And, the main advantages of car-

bon nanotubes are high mechanical strength, the mesoporous nature, which makes them interesting to promote a variety response. Moreover, due to their surfaces obtaining a good interfacial bonding is a requirement in order to achieve efficient load transfer across the CNT–matrix interface. Formation of a proper treatment on the surface of CNTs could offer a valuable alternative [9].

In this work, we describe that the calcination of the titanate nanotubes at different temperatures could yield products with different crystal-phase compositions, morphologies, and pore structures, and it will be of great interest to understand how the electrochemical performance of sensing materials. Also, we describe that preparation and characterization of CNT/TiO₂ nanocomposites with electronic and mechanical properties compared to oxidized CNT.

2 Experimental

2.1 Preparation of Titanate and Titania Nanotubes and Nanorods

The TiO₂ source used for nanotube and nanorod productions was commercial-grade TiO₂ powder (ST-21, Ishihara, Japan) with anatase crystalline structure and primary particle size of ca. 20 nm. In nanotube and nanorod preparation, 2g of the TiO₂ powder was mixed with 70 mL of 10 N NaOH solutions, followed by thermal treatment of the mixture at 110–150 °C in a Teflon-lined autoclave for 24 h.

After the treatment, the filtered sample was then neutralized by mixing with 1 L of 0.1 N HCl solutions for several times until the pH value of the rinsing solution was less than 7. After being dried at 60 °C for at least 2 days, the as-prepared sample was calcined in an oven at 200, 300, 400, and 500 °C for 6 h in air, respectively.

2.2 Preparation of CNT/TiO₂ Nanocomposites

MWCNT was selected as a starting material and was received from JEIO. *m*-Chloroperbenzoic acid (MCPBA) was used as an oxidized reagent, which was purchased from Aldrich.

The as-received MWCNTs were refluxed at 80 °C for 6 h in MCPBA–benzene solution. The MWCNT were recovered by filtration, rinsed with ethanol and dried overnight at 70 °C. And then the oxidized MWCNT was put into TTIP–benzene solution (2 mL of TTIP in 50 mL benzene). The mixture was refluxed at 70 °C for 5 h. These were heat treated at 600 °C for 1 h with a heating rate of 6 °C /min to form the CNT/TiO₂ nanocomposites.

2.3 Characterization of Titanate and Titania Nanotubes and Nanorods and Nanocomposites

Investigations on morphology and crystallinity were done by field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (TEM, Jeol) and powder X-ray diffraction (XRD, X'Pert Philips instrument). The inclusion of TiO₂ into the CNTs was confirmed by UV–visible spectroscopy, Fourier-transform infrared spectroscopy (FT-IR). Surface area of TiO₂ and the composite was measured by Brunauer–Emmett–Teller (BET) method

3 Results and discussion

3.1 Characteristics of Titanate Nanotubes and Nanorods

The pore structures of TiO₂ nanotube prepared from NaOH treatment on commercial nanoparticle ST-21 can be regulated by adjusting either the treatment temperature or the concentration of neutralization HCl solutions. The function of the NaOH treatment is to convert the starting TiO₂ particles into sheets composed mainly of anatase phase that is more feasible for rolling of the sheets to form nanotubes. The treatment temperature determines the extent of precursor conversion, which eventually influences not

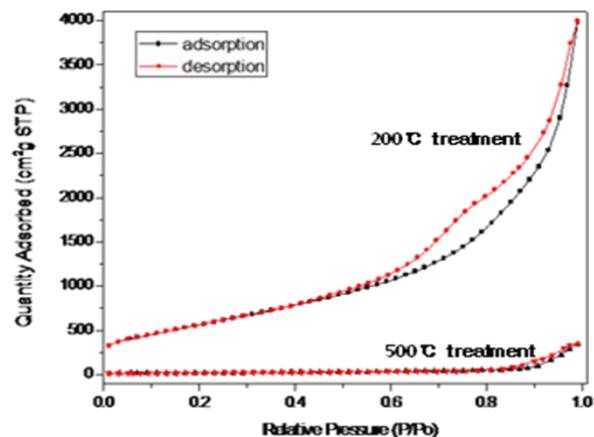


Fig.1. BET surface area of heat treatment at 200 and 500 °C.

only the pore structure of the nanotube aggregates but also the structural stability of crystalline anatase at high temperatures. The process of TiO₂ sheets rolling into nanotubes upon acid washing removes electrostatic charges [8].

Since the morphology of TiO₂ nanotubes strongly depends on the size and crystalline phase of the TiO₂ source, use of the ST-21 as the starting material has the advantage in the property control of the nanotube products for subsequent application or even mass production.

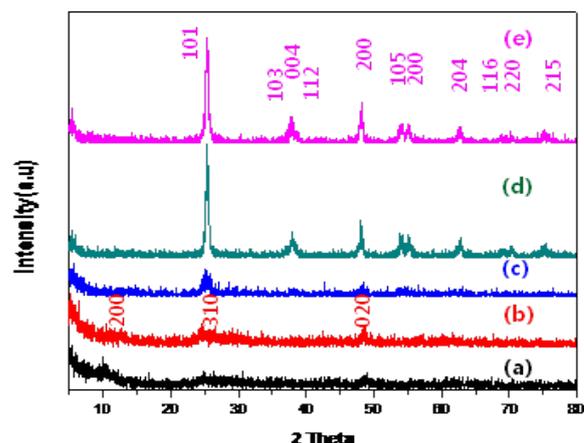


Fig.2. The XRD patterns of protonated titanate nanotubes (a) and the samples calcined at 200 (b), 300 (c), 400 (d), and 500 °C (e).

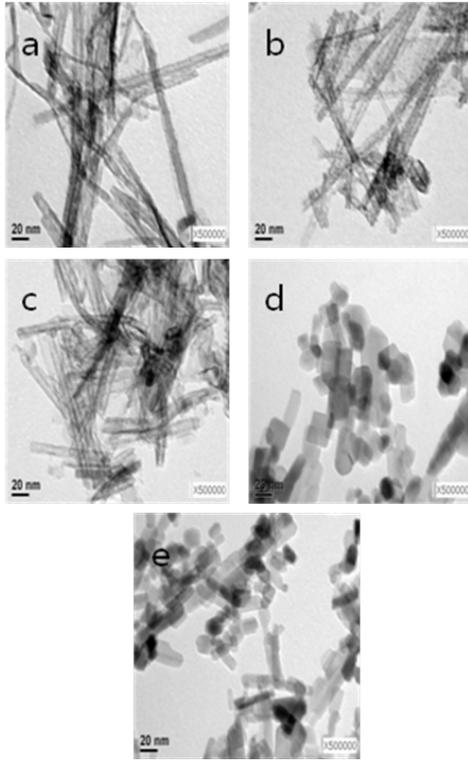


Fig.3. TEM images of original protonated titanate nanotubes (a) and the samples calcined at 200 (b), 300 (c), 400 (d), and 500 °C (e)

Figure 1 shows the BET surface area onto the nanotube products from calcination at 200 and 500 °C. These isotherms exhibit obvious hysteresis behavior, indicating that the products are mainly mesoporous at 200°C, which has a surface area of ca. 2168 m²/g. The surface area decreases with further temperature increase (surface area of 76 m²/g at 500 °C). Nanotubes with high surface area prepared from hydrothermal treatment using NaOH. XRD patterns of as-prepared and calcined samples are given in Figure 2. It is found that the pattern of the as-prepared sample with a relatively low intensity should be assigned to layered protonated titanate with poor crystallinity. It is also shown that after the calcination at 400 °C, the anatase phase seems to coexist with anatase nanorods are formed when the titanate nanotubes are calcined at 500 °C. The as-prepared nanotubes are several hundred nanometers in length with the outer diameter of about 10-15 nm, as shown in Figure 3a. Such hollow tubular morphology could be converted to the solid nanorod morphology when calcined at 500 °C in air (Figure 3e).

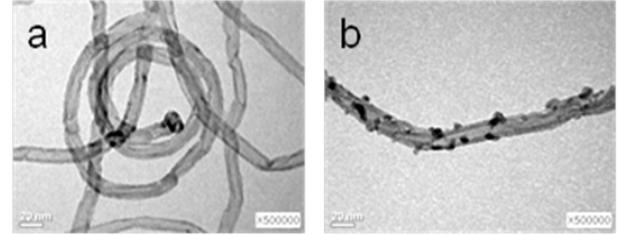


Fig.4. TEM images of oxidized CNT (a) and CNT/TiO₂ nanocomposite (b)

Moreover, the nanorods are shortened or broken to some extent during the calcination. When the calcination is conducted between 200 and 300 °C, most of the products still remain with the tubular morphology with the inner diameter of about 4-6 nm. The nanotubes calcined at 400 °C are curved or collapsed to some extent as compared to the parent uncalcined nanotubes.

3.2 Characteristics of CNT/TiO₂ Nanocomposites

CNT/TiO₂ nanocomposites were prepared by MWCNTs and titanium (IV) isopropoxide through a sol-gel method. Fig. 4 shows the TEM images for the oxidized CNT and CNT/TiO₂ nanocomposite. In Fig. 4(a), after treatment of CNTs with MCPBA under reflux, the nanosized tube networks were opened, oxidized and shortened, and exhibited regular morphology. Fig. 4(b) shows that TiO₂ particles are uniformly dispersed on the surface of CNTs. TiO₂ particles of 15–20 nm size were regularly and individually distributed on the CNTs surface. The results of BET surface area are shown in Table.1. from the data of the BET surface area of the Original

Table. 1. BET surface area of CNT, Oxidized CNT, and CNT/TiO₂ nanocomposites.

| Samples | TTIP (ml) | Heat treatment (°C) | S _{BET} (m ² /g) |
|--------------|-----------|---------------------|--------------------------------------|
| Original CNT | - | - | 188.7 |
| Oxidized CNT | - | - | 284.1 |
| C/T 1 | 2 | 400 | 261.0 |
| C/T2 | 2 | 600 | 164.4 |
| C/T3 | 4 | 600 | 119.5 |

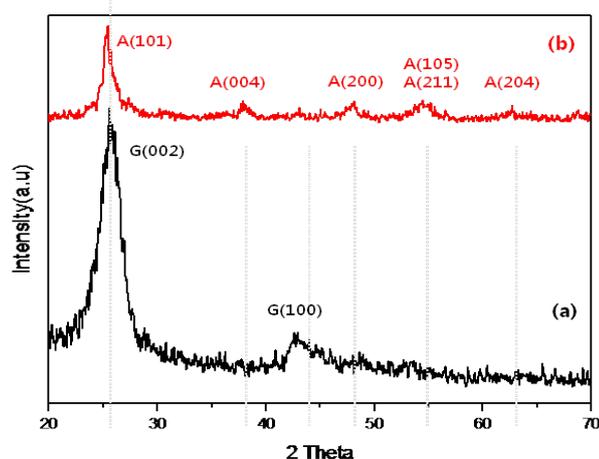


Fig.5. XRD patterns of bare CNT (a) and CNT/TiO₂ nanocomposite (b).

CNT is 188.7 m²/g. When treated by MCPBA to obtain the Oxidized CNT, surface area is increased to 284.1 m²/g. Furthermore, the surface areas of CNT/TiO₂ introduced to TiO₂, decreased as order of 261.0 m²/g, 164.4 m²/g and 119.5 m²/g corresponding to samples C/T1, C/T2 and C/T3. And introduction of TiO₂ particles is one kind of factor for the decrease of the surface area of CNT/TiO₂ nanocomposites. The XRD patterns of CNT and CNT/TiO₂ nanocomposite are shown in Fig. 5. The strong (002) diffractions of the hexagonal graphite at 2 θ of about 25.888 with the weak (100) diffractions indicate. For the CNT/TiO₂ nanocomposite, we can find the peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase at 873 K.

4 Conclusion

In this work, we prepared that the vast surface created from the hydrothermal alkali treatment is accessible to the reacting molecules. The calcination at low temperature leads to the formation of inner hollow nanotubes with the large specific surface area and nanorods structure. The solid anatase nanorods with the reduced specific surface area can be obtained by the calcination at 500°C. The present paper has studied composition, especially the carbon-metal oxide hybrid system. We expect to the activity of the CNT/TiO₂ nanocomposite is larger than that of other TiO₂. Therefore, we will be investigated sensing materials for enhancing the sensing properties of the

sensor based on the prepared TiO₂. In particular, the effects of sensor will be discussed in terms of higher response, fast response recovery, good selectivity and good stability.

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