SYNTHESIS OF SnO_2 NANOMATERIAL WITH VARIOUS MORPHOLOGIES BY HYDROTHERMAL METHOD

TỔNG HỢP VẬT LIỆU NANO SnO_2 VỚI CÁC DẠNG HÌNH THÁI KHÁC NHAU BẰNG PHƯƠNG PHÁP NHIỆT THUỶ PHÂN

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ABSTRACT

SnO_2 nanomaterials with various morphologies have been successfully prepared by hydrothermal method using tin chloride and ammonia, sodium hydroxide and cetyltrimethyl ammonium bromide (CTAB) as starting materials. The surfactant CTAB is a key in determining the morphologies of the products. The SnO_2 nanoparticles with diameter of 6nm were produced by hydrothermal treatment stannic acid gel in ammonium solution. Nanorods, nanotubes and bended foils and plates of SnO_2 can be formed by using NaOH and CTAB. The crystalline size and morphologies of the SnO_2 were characterized by X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). For obtained SnO_2 nanorods, the diameters of the nanorods are around 100 nm to 200 nm with lengths of several micrometers. The success of preparing various morphologies of SnO_2 nanomaterials, will improve the research and preparation of gas sensor based on SnO_2 materials.

TÓM TẮT

Vật liệu nano SnO_2 với các dạng hình thái khác nhau được chế tạo thành công bằng phương pháp nhiệt thủy phân có sử dụng các vật liệu ban đầu như $SnCl_4$, NH_4OH, NaOH và CTAB (chất hoạt động bề mặt). Chất hoạt động bề mặt CTAB đóng vai trò quan trọng trong việc xác định các hình thái của vật liệu SnO_2 cấu trúc nano. Các hạt SnO_2 với kích thước cỡ 6 nm thu được bằng việc xử lý nhiệt thủy phân gel vật liệu SnO_2 trong dung dịch NH_4OH. Các thanh, ống và lá kim của vật liệu nano SnO_2 được tổng hợp bằng việc sử dụng NaOH và CTAB. Các đặc trưng cấu trúc và kích thước tinh thể của SnO_2 được khảo sát bởi phương pháp nhiễu xạ tia X (XRD) và kính hiển vi điện tử quét phát xạ trường (FESEM). Với thanh nano SnO_2 đã được chế tạo, đường kính thanh từ 100 nm đến 200 nm với chiều dài cỡ vài micrô mét. Việc chế tạo thành công các dạng hình thái khác nhau của vật liệu nano SnO_2 giúp cho việc nghiên cứu chế tạo cảm biến khí trên cơ sở vật liệu SnO_2 ngày càng tốt hơn.

I. INTRODUCTION

Enormous efforts are being directed towards the development of nanometer sized materials in studies related on one hand to their fundamental mechanisms such as the size effect and the quantum effect, and on the other hand towards application of these materials. Tin dioxide is a versatile material with a wide variety of applications. It is well known for its application in gas sensor, optoelectronic devices, dye-base solar cells, electrode materials and catalysts [1-4]. As the gas sensing and other properties of SnO_2 materials are strongly dependent on their size and shape, it is obvious that the controlled synthesis of the morphologies of SnO_2 materials is very important for special applications. The SnO_2 materials with different morphologies have been prepared by a few methods. For example, SnO_2 nanorods were synthesized by a vapor–liquid-solid approach [5,6]. SnO_2 nanotubes were fabricated by an infiltration technique [7]. SnO_2 nanowires have been obtained in a chemical vapor deposition (CVD) process [8]. However, with our best knowledge, relatively high temperature and complicated procedure are generally required for these methods. Thus, it is still a challenge to find novel and simple synthetic route for SnO_2 nanomaterials [9]. In this paper, we report a novel and simple hydrothermal synthetic route for the preparation of SnO_2 nanomaterials with various morphologies.

II. EXPERIMENTAL

2.1 Preparation of SnO_2 nanoparticles

The SnO_2 nanoparticles were synthesized by sol-gel method with hydrothermal treatment technique.

Stannic acid gel was synthesized by hydrolyzing 0.2M solution of tin chloride ($SnCl_4$) with ammonia.

$$SnCl_4 + 4NH_4OH \rightarrow SnO_2.nH_2O + 4NH_4Cl + (2-n)H_2O$$

In this reaction, the pH of solution was adjusted to 7 by ammonia. The resulting precipitate (wet gel) was washed thoroughly with deionized water many times to remove excess ions (Cl^- and NH_4^+). The gel was mixed with aqueous ammonia to pH=10.5, and loaded into an autoclave for the hydrothermal treatment at 200 ^oC for desired time under saturated vapor pressure. After the hydrothermal treatment processes, transparent sol suspensions with different sol particle size were obtained. A part of the sol after drying at 120 ^oC for 24 h was used to determine the average crystalline size of SnO_2, base on X-ray diffraction method and Scherrer's formula. The grain size of SnO_2 was also measured visually on an FE-SEM.

2.2 Preparation of SnO_2 nanomaterial with various morphologies

In order to prepare SnO_2 with various morphology (nanorods, nanotubes and, bended foils…), the surfactant cetyltrimethyl ammonium bromide (CTAB) and NaOH solution were used. Stannic acid gel ($SnO_2.nH_2O$) and SnO_2 sol suspensions were used as the precursor materials. In a typical procedure, SnO_2 was mixing with 10ml NaOH (0.15M) aqueous solution, stirring for 20 minute to obtain a clear solution. After that, 2 mmol of CTAB powder was added into above clear solution, followed by heating to make CTAB dissolve completely. Then the mixture was hydrothermally treated in the autoclave at 200 ^oC, 230 ^oC, and 250 ^oC for 16 h or 20h. The resulting white precipitate was collected by centrifugation, washed with ethanol several times and dried at 100 ^oC for 24 h. After that, the obtained powders were calcined at high temperature for studying the morphology and structure of the materials.

III. RESULTS AND DISCUSSION

3.1 Preparation of SnO_2 nanoparticles

For preparation of SnO_2 nanoparticles, the hydrothermal treatments were carried out for stannic acid gel suspensions of various gel contents (2 % wt. - 7% wt. SnO_2) with ammonia solution at 200^{o}C for 3 h. Stable SnO_2 sols were obtained in all cases.

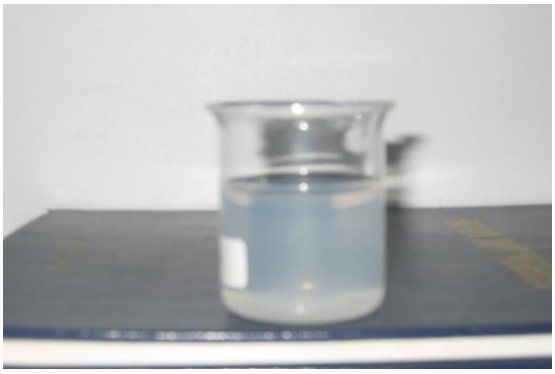


Fig.1 An image of 6%wt. SnO_2 sol suspension

The XRD patterns of SnO_2 nanoparticles are shown in Fig 2. All of the diffraction peaks can be perfectly indexed to the tetragonal SnO_2 structure with lattice parameters of a = 4.738Å and c = 3.186 Å. Furthermore, the crystallite grain size of SnO_2 derived from 6%wt. sol was estimated as 6.0 nm according to Scherrer formula $d = k\lambda/(\beta\cos\theta)$, where λ is the wavelength of the X-ray radiation ($\lambda_{CuK\alpha}$ = 0.154 nm), k is a constant taken as 0.89, β is the line width at half maximum height and θ is the diffracting angle.

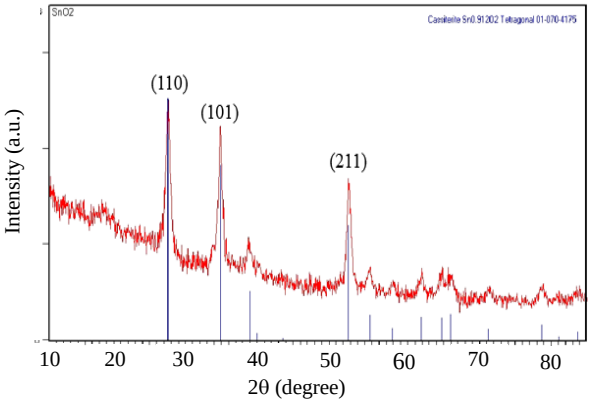


Fig.2 XRD patterns of SnO_2 nanoparticles

The morphology and size of the initial SnO_2 nanoparticles were investigated by FE-SEM. They can be seen in Figure 3. The result

showed that the SnO_2 nanopaticles were about 6.0 nm in diameter with a fairly narrow particle size distribution and were well dispersed. The obtained grain size from FESEM image was almost the same with the result from XRD analysis.

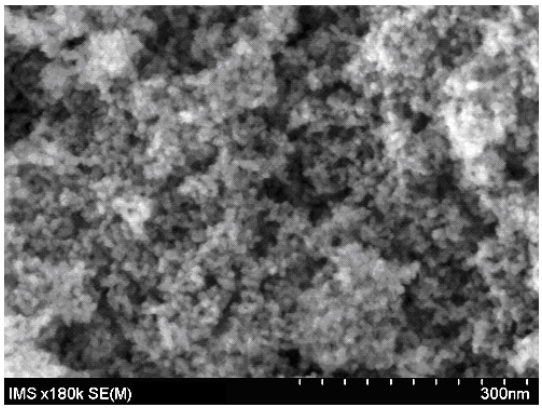
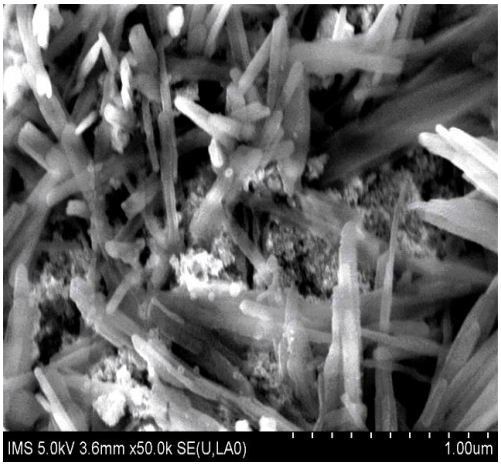


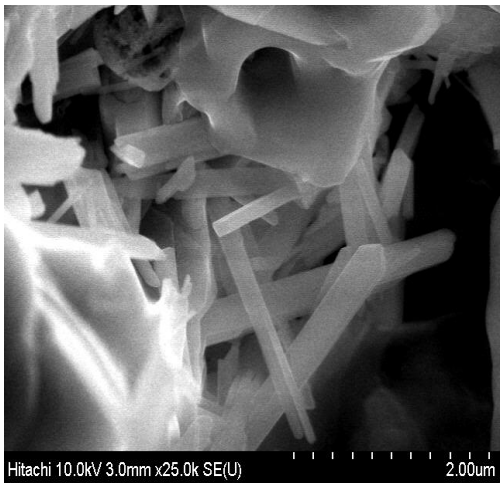
Fig.3 FE-SEM image of SnO_2 nanoparticles derived from hydrothermally treated 6%wt. SnO_2 and calcined at 600 ^oC for 30 minutes

3.2 Preparation of SnO_2 nanomaterial with various morphologies

When SnO_2 nanoparticles were treated by using NaOH and CTAB, the morphological change was observed with the growth conditions, such as changes of temperature and time of hydrothermal treatment and precusors. Fig. 4 shows the FESEM images of the powders obtained by the hydrothermal treatment at 200 ^oC for 16 h. By this process, the rod-like SnO_2 were obtained. The diameters of nanorods are around 100-200 nm and the lengths are around several micrometers. Furthermore, during the synthetic procedure, we observed that the surfactant CTAB was a key in determining the morphologies of the products. The formation of nanorods can be attributed to the following mechanism. $Sn(OH)_4$ is an amphoteric hydroxide which can be dissolved in NaOH solution and forms $Sn(OH)_6^{2-}$ anion, the CTA^+ cationscondense into aggregates in which the $Sn(OH)_6^{2-}$ anions are intercalated in the interspaces among the head groups of CTA^+ to form CTA^+- $Sn(OH)_6^{2-}$ ion pairs by electrostatic interactions. The $CTAB^+$-$Sn(OH)^{2-}_6$ ion pairs form a sandwich- like structure in water. The inter-layers may serve as micro-factors that are responsible for the ultimate formation of nanorods [3,11].



(a) 2 % wt. SnO_2



(b) 5 %wt. SnO_2

Fig.4 FESEM image of the nanorods derived from different sol suspensions

It is noteworthy that the SnO_2 sol particle size, the changes of temperature and time of hydrothermal treatment led to a dramatic change in the diameters of these rods. Hydrothermal temperature is an important factor affecting the growth of SnO_2. If the reaction was carried out at a low temperature of 140 ^oC, only irregular nanoparticles were obtained. However, when increasing the hydrothermal temperature to 180 ^oC, short nanorods were prepared. And if the hydrothermal temperature increased to 200 ^oC, long nanorods were obtained. Moreover, the time reaction is also an important factor that influences the diameter of SnO_2 nanorods. Prolong time reaction, the length of SnO_2 nanorods seems to be increasing.

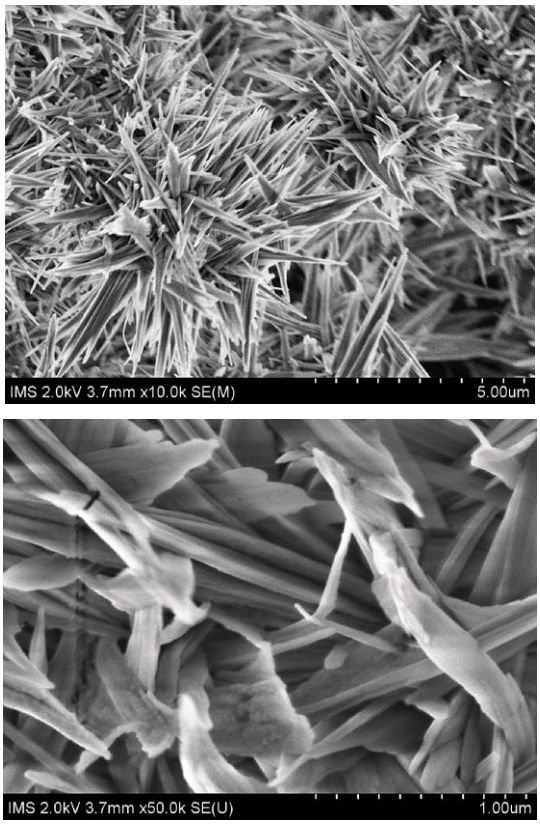


Fig.5 FESEM image of the SnO_2 the bended foils and plates from untreated sol 2%wt. SnO_2, hydrothermal treatement at 230 ^oC in 20h

If the sample was prepared from untreated sol of 2%wt. SnO_2, after hydrothermally treated at 230^{o}C for 20 h, the bended foils and plates of SnO_2 were produced (Figure 5). The results pave the way for further research to produce other morphologies of SnO_2 material for different applications.

Besides, when the sol treatment temperature was risen up to 250 ^{o}C for 16 h, nanotube of SnO_2 was obtained (Figure 6). This is a new discovery to prepare SnO_2 nanotubes by sol-gel method with hydrothermal technique.

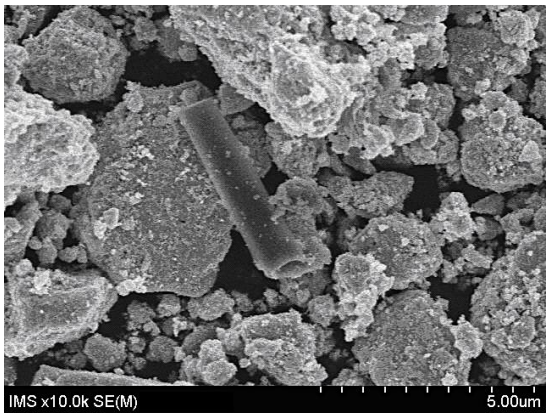


Fig.6 FESEM image of the nanotube derived from 7%wt. SnO_2 sol suspension at 250 ^oC for 16 h.

IV. CONCLUSIONS

Different morphologies of SnO_2 material have been successfully synthesized by sol- gel method with hydrothermal technique. The SnO_2 nanoparticles were prepared by hydrothermal treatment of stannic acid gel in ammonium solution. Nanorods, bended foils and plates and nanotubes of SnO_2 can be formed by using NaOH and CTAB. The surfactant CTAB plays an important role in the formation and growth of the nanorods. The results revealed that the concentration of the sol, temperature and time reaction influence on the diameter and morphology of SnO_2.

ACKNOWLEDGMENT

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