TiO_2 Hollow Nanofibers Templated by Electrospun Polyethylene Oxide (PEO) Aqueous Solutions

Shinsuke Nagamine[*]*, Yoshitaka Tanaka, Masahiro Ohshima*
Department of Chemical Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto 615-8510, Japan
* Tel: +81-753832686, Fax: +81-753832646, E-mail: nagamine@cheme.kyoto-u.ac.jp

Abstract

A new and simple method of fabricating TiO_2 hollow nanofibers which employs electrospinning was developed. An aqueous solution of polyethylene oxide (PEO) was electrospun and thread-like liquid jets were introduced directly into a titanium tetraisopropoxide (TTIP) / hexane solution. This induced the formation of a core – sheath structure due to the rapid hydrolysis and condensation of TTIP at the interface between the PEO solution and TTIP solution. As a result, mat-like samples were obtained, which was composed of nanofibers with a diameter of several hundreds nanometers and a length of several tens to hundreds micrometers. Hollow spherical micron particles with a diameter of several micrometers and thick hollow fibers could also be synthesized by varying the molecular weight and concentration of PEO solution. It was suggested that the product morphology was governed by two parameters relating to properties of PEO solution, Berry number $C[\eta]$ and κ / γ, representing the degree of overlap of polymer chains and the strength of electric charge repulsion against the surface tension, respectively.

Introduction

Hollow microparticles and microfibers of inorganic materials have a wide range of applications, e.g. microcapsules for controlled release, catalysts, sensors, and electric devices. The most effective strategy for preparing the hollow structure is to utilize the precipitation of solids at the interfaces, such as spray drying (liquid droplet – gas interface), the emulsion method (water – oil interface stabilized by surfactant), and the solid templating method (solid particle – liquid interface). We have previously developed another simple synthetic method for creating TiO_2 hollow microparticles, what we call "spray hydrolysis". In this method, water is atomized and introduced into an organic solution containing titanium tetraisopropoxide (TTIP) as the precursor of TiO_2 [1, 2]. The rapid hydrolysis and condensation of TTIP at the interface of the water droplets – organic phase leads to the formation of a TiO_2 shell and keep the droplets from coalescing. The merits of this method are as follows: (1) Spherical hollow microparticles can be produced quickly at ambient temperature and pressure; (2) The synthesis process is free from contamination and there is no complicated post-treatment to remove additives such as surfactants.

Our present purpose is to produce hollow fibers based on the concept of spray hydrolysis. As a simple synthetic method of micro and nanofibers, electrospinning has attracted

considerable attention and is well studied [3]. Hollow fibers of metal oxides [4, 5] were prepared using co-axial electrospinning, where two immiscible liquids were simultaneously electrospun from the co-axial double-tube spinneret. Another synthetic method for creating hollow fibers which also employs electrospinning is to use preformed polymer fibers as templates [6]. This method consists of three steps: (1) the formation of template polymer fibers by electrospinning, (2) the coating of the fibers with the target solid, and (3) the removal of the template fibers by the thermal treatment.

In this study, a new and simple method of fabricating TiO_2 hollow nanofibers is proposed. This method consists of electrospinning a viscous aqueous solution of polyethylene oxide (PEO) and the direct introduction of elongated jets into the organic solution of TTIP. The core-sheath structure is formed via the hydrolysis of TTIP at the interface between the aqueous PEO solution and the TTIP solution. This method may appear similar to the above-mentioned method which uses the electrospun fibers as templates. The difference is that our method enables the formation of the thread-like templates and the TiO_2 core-sheath structure in a single process. The product morphology would reflect that of electrospun jet, which strongly depends on the properties of PEO solution, such as viscosity, surface tension, and electric conductivity. Therefore the effects of those properties determined by molecular weight and concentration on the product morphology were investigated.

Experimental Section

PEO (M_W = 500,000, 2,000,000, and 4,000,000), TTIP and hexane were purchased from Wako Chemical, Japan and were used as supplied. Aqueous solutions of PEO with different concentrations (C = 0.1 – 10 wt%) were prepared. Viscosities of PEO solutions were measured using capillary viscometer. The measurements of surface tensions were performed by Wilhelmy plate method using Kyowa CBVP-A3. Electric conductivities were measured using conductance meter (HORIBA ES-51). The measurements of these properties were conducted at 298 K.

The electrospinning of these PEO solutions was conducted using a commercial electrospinning device (Kato-Tech NEU). The schematic of experimental setup is illustrated in Fig. 1. A PEO solution was loaded in a downward plastic syringe with a steel spinneret (inner diameter: 0.8 mm). A TTIP solution in hexane (1.0 mol L^{-1}) in a petri dish was located on the ground electrode. The distance from the tip of spinneret to the top of the TTIP solution is fixed at 11.4 cm. The PEO solution was then fed at the rate of 3.8 cm^3 h^{-1} and a positive voltage of 10 kV was applied to the spinneret. The jetted PEO

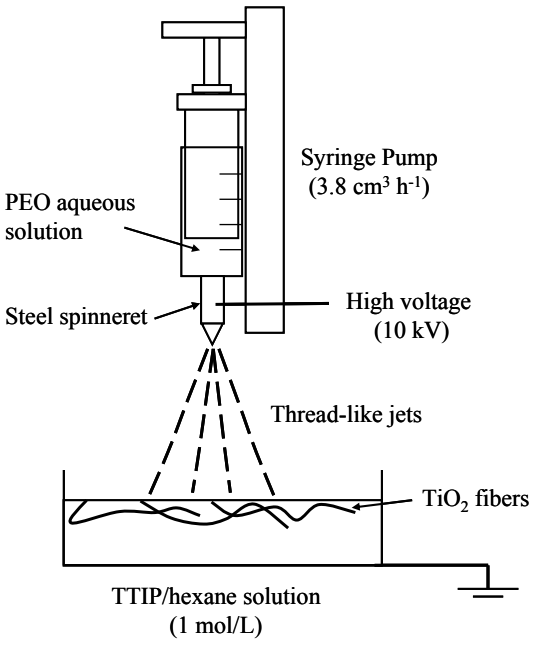

Fig. 1. Schematic illustration of sample preparation process.

solution was introduced into the TTIP solution, resulting in the immediate formation of a mat-like structure that floated on the surface of the TTIP solution. The products were recovered by filtration, washed with hexane, and dried at 363 K for several hours. A part of sample was calcined at 773 K to remove PEO completely and to convert it to crystalline TiO_2. The products were observed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6340FS).

Results and Discussion

Fig. 2a shows a photograph of a sample prepared with a PEO having M_W = 500,000 and *C* = 5 wt%. The SEM observation reveals that the mat-like sample is mainly composed of fibers, although micrometer-sized spheres are also present as by-products (Fig. 2b). The diameters of fibers are on a submicron scale and the lengths are greater than tens of micrometers. The outer morphologies of the fibers are a little larger when compared to those of PEO nanofibers prepared by the conventional electrospinning method. However, the inner structure significantly differs from that of PEO fiber, that is, the fibers possess a hollow core-sheath structure as shown in the magnified SEM image of fractured fibers in Fig. 2c. This result suggests that the TiO_2 sheaths were formed by the hydrolysis of TTIP at the interface between the elongated PEO aqueous solution and the organic TTIP solution. An interesting feature is that the hollow structure is formed without the removal of PEO. This is probably because the template was composed mostly of water and had a low concentration of PEO. After drying, the volume of precipitated PEO was too small to fill the space inside the sheath of TiO_2, which led to the creation of hollow structure. Fig. 2d presents the SEM image of calcined sample. The hollow fibrous structure is maintained even after calcination.

The products with other morphologies were also obtained by varying M_W and *C*. Fig. 3a shows SEM image of sample prepared with M_W = 500,000 and *C* = 0.5 wt%. The main products are the spherical particles with a diameter of 10 to 20 micrometers and smaller distorted

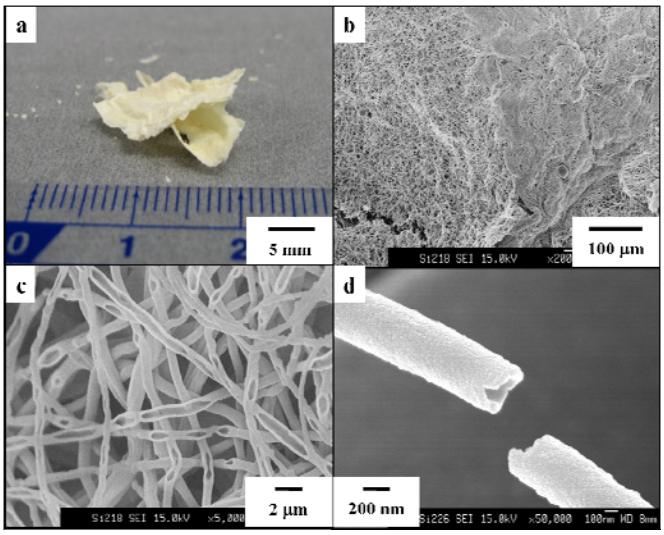

Fig. 2. (a) a photograph of a mat-like morphology and (b, c) SEM images of hollow nanofibers prepared with M_W = 500,000 and *C* = 5 wt% at different magnifications. (d) a SEM image of hollow nanofibers calcined at 773 K.

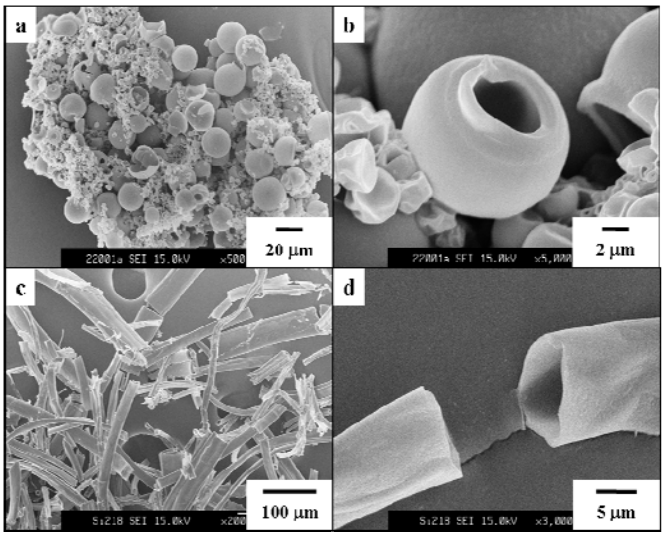

Fig. 3. SEM images of products prepared with (a, b) M_W = 500,000 and *C* = 0.5 wt%, (c, d) M_W = 2,000,000 and *C* = 5 wt% at different magnifications.

particles. The magnified SEM image reveals the formation of hollow core-shell structure in the larger particles (Fig. 3b). In this case, the projected PEO solution could not take the thread-like shape due to low viscosity, and the generated spherical droplets served as templates to yield hollow particles. Hollow fibers with a diameter of several micrometers were also obtained with M_W = 2,000,000 and C = 5 wt% (Fig. 3c, d). During the electrospinning process of this PEO solution, it was observed that a single thread-like jet with a visible thickness traveled continuously from the tip of spinneret to the TTIP solution. Probably the strong entanglement of PEO chains inhibited the disruption of the jet of the PEO solution, and led to the formation of thick hollow fibers. The dependence of the product morphology on M_W and C is summarized in Fig. 4. As a general tendency, the low M_W and low C lead to the formation of spherical particle. As C increases, the product morphology turns to hollow fiber. Hollow nanofiber could be obtained at M_W = 500,000, while thick fibers were formed at the higher M_W.

The morphology of electrospun jet is determined by the properties of spinning solution. Intuitively, when the surface tension is low and the charge density, relating to the electric conductivity, is high, the charged droplet tends to deform to increase surface area. If the viscosity is sufficiently high, the elongation occurs, while at the low viscosity, the droplet is disrupted to smaller droplets. The results of surface tension measurements are shown in Fig. 5. The surface tension γ is almost independent of C and M_W in the tested range. As shown in Fig. 6, the electric conductivity κ continues to increase with C for M_W = 500,000, while it stops increasing at 0.5 wt% for M_W = 2,000,000 and 4,000,000. Here κ / γ is regarded as a rough index representing the electrostatic repulsion against the surface energy.

Fig. 7 shows the viscosity η greatly increasing with C and M_W. The viscosity reflects the configuration of polymer chains. The spinnability of PEO solution is considered to be determined by the degree of overlap of polymer chains. It is known that the concentration C^* at

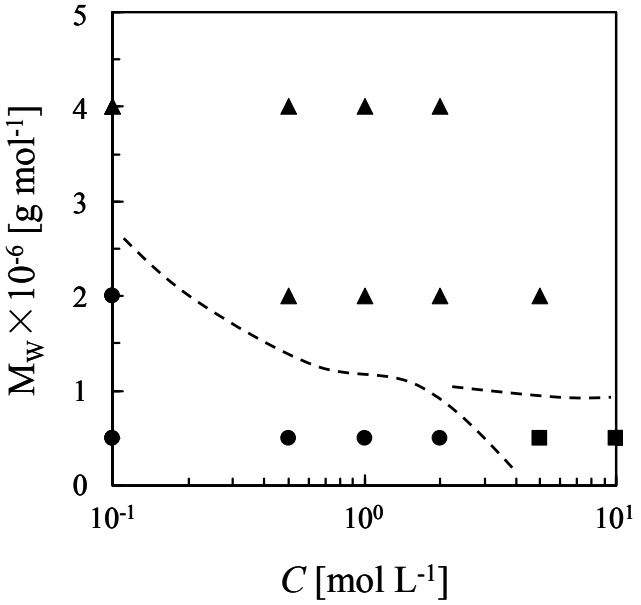

Fig. 4. The dependence of product morphology on molecular weight M_W and concentration C of PEO. (●) hollow particle, (▲) thick hollow fiber, and (■) hollow nanofiber.

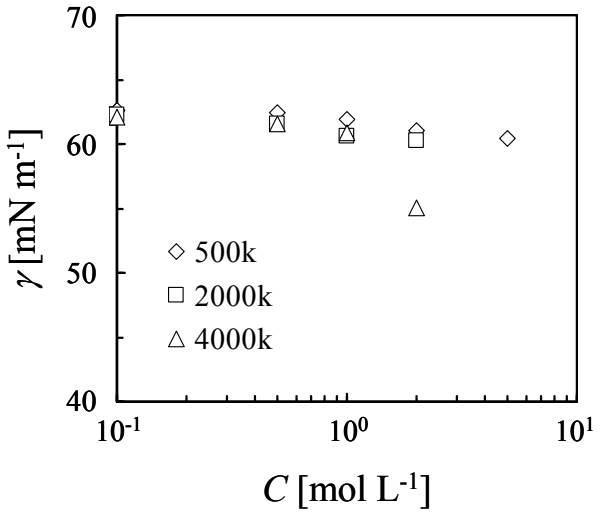

Fig. 5. Plot of surface tensions γ of PEO solutions with C for different M_W.

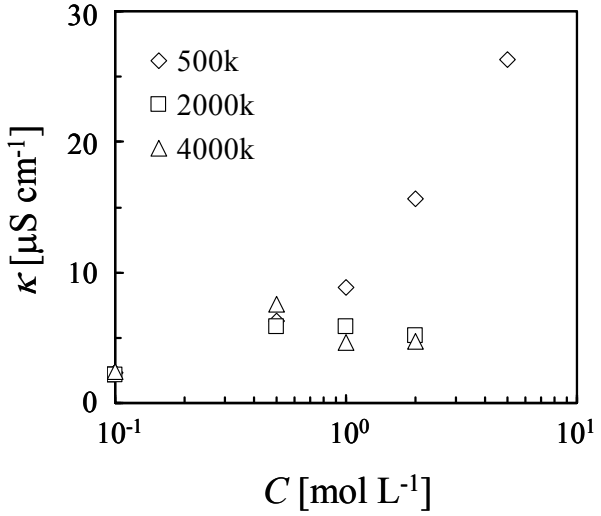

Fig. 6. Plot of electric conductivities κ of PEO solutions with C for different M_W.

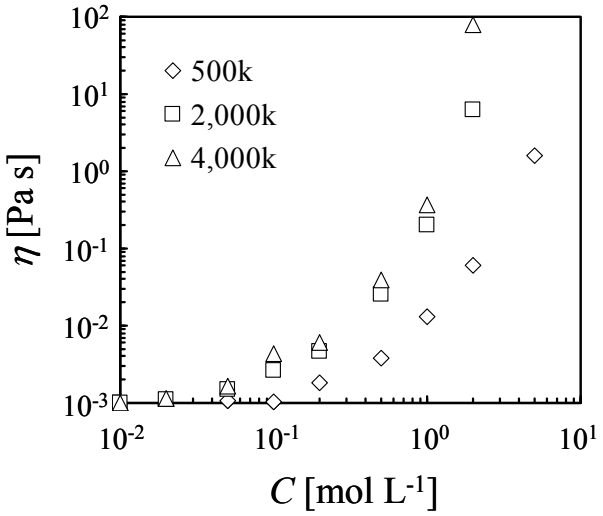

Fig. 7. Plot of viscosities η of PEO solutions with C for different M_W.

which overlap starts is associated with the intrinsic viscosity [η] by the following equation [7].

$$C^* \sim [\eta] \quad (1)$$

[η] can be calculated by applying the Huggins equation to the dependence of η on C.

$$\eta / \eta_S = 1 + [\eta]C + k([\eta]C)^2 + \cdots \quad (2)$$

Here Berry number *Be* defined by the following equation is introduced as an index of the degree of overlap of polymer chains.

$$Be = [\eta]C \quad (3)$$

Fig. 8 shows the dependence of product morphology on *Be* and κ / γ. This map could be successfully partitioned into three zones associated to the morphologies. When *Be* was large, overlap of polymer chains induced the formation of fiber. When κ / γ was large, the electric charge repulsion surpassed the surface tension. As a result, the disruption of droplet led to the production of thin nanofibers or spherical particles.

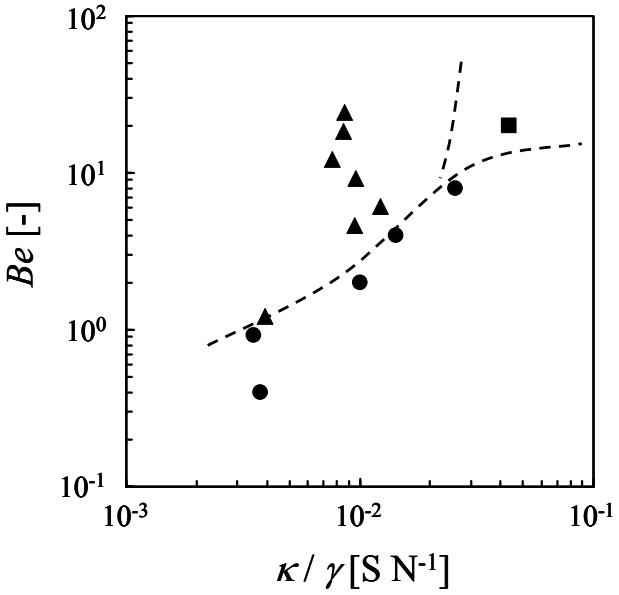

Fig. 8. The dependence of product morphology on Berry number Be = [η]C and κ / γ. (●) hollow particle, (▲) thick hollow fiber, and (■) hollow nanofiber.

Conclusion

A novel and simple method to synthesize hollow TiO_2 nanofibers was developed, which based on electrospinning and an interfacial sol-gel reaction. The introduction of the electrospun PEO aqueous

solution into the TTIP / hexane solution resulted in the formation of TiO_2 hollow nanofibers. Hollow microparticles and thick microfibers were also obtained by varying the molecular weight and the concentration of PEO. The dependence of product morphology on the properties of PEO solution could be summarized in a diagram using *Be* and κ / γ as indexes. Spherical particles were produced with small *Be*. As *Be* increased, the products tended to be fibers due to the overlap of polymer chains. When κ / γ was large, strong electric charge repulsion caused the disruption of droplets and therefore thin nanofibers were produced.

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