# Fabrication of Hollow $TiO_2$ Fibers Templated by Electrospun Aqueous Poly(ethylene oxide) (PEO) Solution

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Hollow $TiO_2$ fibers were fabricated by electrospinning an aqueous solution of poly(ethylene oxide) (PEO) and introducing the thread-like droplets directly into a titanium tetraisopropoxide (TTIP)/hexane solution, inducing the rapid hydrolysis and condensation of TTIP at the interface between the PEO solution and TTIP solution. Various hollow structures including submicron hollow fibers, thick fibers with a diameter of tens of micrometers, and spherical micron particles could be systematically synthesized by varying the molecular weight and concentration of PEO solution.

Hollow micro- and nanofibers of inorganic materials have a wide range of applications, e.g. microcapsules for controlled release, catalysts, sensors, and electric devices. Recently, electrospinning has attracted considerable attention as a simple fabricating method for micro- and nanofibers, and its application to the production of inorganic hollow fibers has been well studied. There are two major strategies for fabricating inorganic hollow fibers related to electrospinning. One is a templating method by preformed electrospun polymer fibers.[1,2] 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 thermal treatment. The other is coaxial electrospinning, where two immiscible liquids are simultaneously electrospun from a coaxial double-tube spinneret.[3,4]

We have previously developed a simple synthetic method for creating hollow $TiO_2$ microparticles utilizing water droplet–oil spherical interfaces.[5,6] In this method, water is atomized and introduced into an organic solution containing titanium tetraisopropoxide (TTIP) as the precursor of $TiO_2$. 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.

In this study, we attempt to develop a fabricating method of hollow $TiO_2$ fibers based on a similar strategy. The basic idea is to substitute thread-like droplets of polymer aqueous solution generated by electrospinning for spherical water droplets. The method consists of electrospinning a viscous aqueous solution of poly(ethylene oxide) (PEO) and the direct introduction of elongated droplets into an organic solution of TTIP. The core–sheath structure is formed via the hydrolysis and condensation of TTIP at the interface between the aqueous PEO solution and the TTIP solution. The product morphology would reflect that of an electrospun droplet, which strongly depends on the viscoelastic properties of a PEO solution that are determined by molecular weight and concentration of PEO.

PEO ($M_w = 500000$, 2000000, and 4000000), TTIP and hexane were purchased from Wako Chemical. PEO having a viscosity average molecular weight ($M_v$) of 1000000 was supplied by Aldrich. All the chemicals were used as supplied. Aqueous solutions of PEO with different concentrations ($C = 0.1$–10 wt %) were prepared. The electrospinning of these PEO solutions was conducted using a commercial electrospinning device (Kato-Tech NEU). The schematic of experimental setup is illustrated in Figure 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 $L^{-1}$, 20 $cm^3$) 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 solution was introduced into the TTIP solution, resulting in the immediate formation of a mat-like structure (Figure 2a) 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.

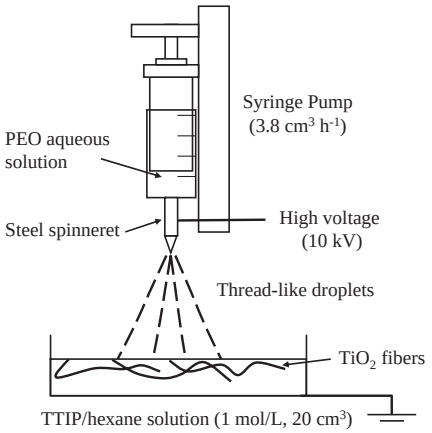


**Figure 1.** Schematic illustration of sample preparation process.

The products were observed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6340FS). Figure 2b shows a SEM image of a sample prepared with a PEO having $M_w = 500000$ and $C = 5$ wt %. The sample is mainly composed of fibers, although micrometer-sized spheres are also present as by-products. The diameters of fibers are on a submicron scale and the lengths are greater than tens of micrometers. The fibers possess a hollow core–sheath structure as shown in the magnified SEM image of fractured fiber in Figure 2c. This result suggests that the $TiO_2$ sheaths were formed by the hydrolysis of TTIP at the interface between the aqueous elongated-PEO 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 of the low concentration of PEO aqueous solution that served as a template. After drying, the volume of

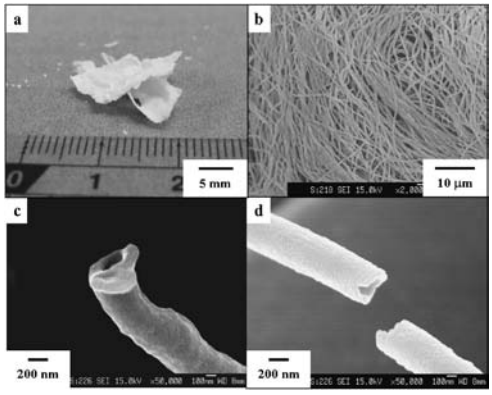


**Figure 2.** (a) Photograph of a mat-like morphology of a sample. (b, c) SEM images of hollow fibers at different magnifications. (d) SEM image of hollow fibers calcined at 773 K. The sample was prepared with $M_w = 500000$ and $C = 5$ wt %.

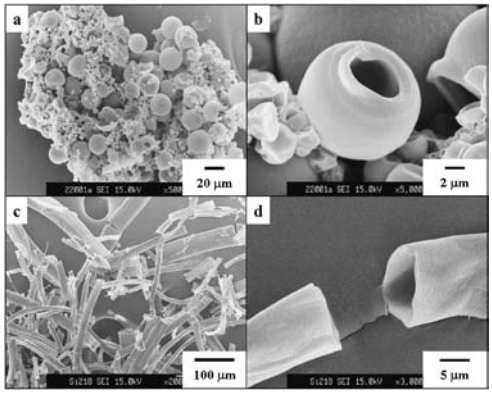


**Figure 3.** SEM images of products prepared with (a, b) $M_w = 500000$ and $C = 0.5$ wt %, (c, d) $M_w = 2000000$ and $C = 5$ wt % at different magnifications.

residual PEO was too small to fill the space inside the sheath of $TiO_2$, which led to the creation of hollow structure. The sample was calcined at various temperatures to remove PEO and to crystallize $TiO_2$. The mat-like morphology as well as the hollow fibrous microstructure was maintained even after calcination (Figure 2d). Powder X-ray diffraction analysis demonstrated that the sample was amorphous and was converted to anatase crystal structure by calcination at 673 K. and the mixture of anatase and a small portion of rutile at 773 K.

Products with other morphologies were also obtained by varying molecular weight and concentration of PEO. Figure 3a shows SEM image of sample prepared with $M_w = 500000$ and $C = 0.5$ wt %. The main products are the spherical particles with a diameter of 10 to 20 micrometers and smaller distorted particles. The magnified SEM image reveals the formation of hollow core–shell structure in the larger particles (Figure 3b). In this case, the projected PEO solution could not take a thread-like shape owing to low viscosity, and the generated spherical droplets served as templates to yield hollow particles. Hollow fibers with a diameter of tens of micrometers were obtained with $M_w = 2000000$ and $C = 5$ wt % (Figures 3c and 3d). 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 molecular weight and concentration of PEO is summarized in Figure 4. As a general tendency, the low molecular weight and low concentration lead to the formation of spherical particles. As the concentration increases, the product morphology turns to hollow fiber. Submicron hollow fiber could be obtained when molecular weight is 500000 or 1000000, while thick hollow fibers were formed at the higher molecular weights of 2000000 and 4000000.

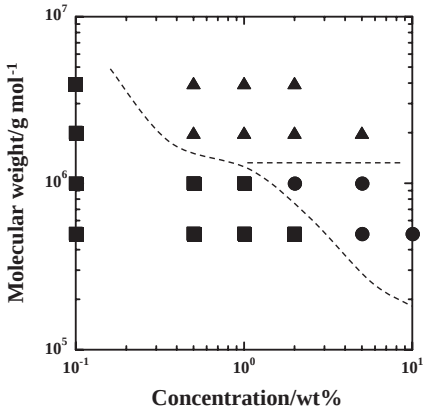


**Figure 4.** Dependence of the product morphologies on molecular weight and concentration of PEO, ●: submicron hollow fibers, ▲: thick hollow fibers, ■: spherical hollow particles.

In summary, a novel and simple fabricating method of hollow $TiO_2$ fibers was developed, which consisted of direct introduction of the electrospun aqueous PEO solution into the TTIP/hexane solution. The morphologies of product including hollow submicron fibers, hollow spherical microparticles, thick hollow fibers (OD: tens of micrometers) could be systematically controlled by varying the molecular weight and the concentration of PEO. The produced $TiO_2$ fibers have potential applications as photocatalysts and solar cells. Moreover water-soluble chemicals can be encapsulated just by dissolving them in the polymer spinning solution.

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