Preparation of self-supporting hierarchical nanostructured anatase/rutile composite TiO_2 film†

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***Via* the combination of an electrospinning method with a hydrothermal reaction, a large-scale cedar-like hierarchical nanostructured TiO_2 film with an anatase/rutile composite phase was fabricated.**

Metal oxide nanostructures have attracted considerable attention because their unique physical and chemical properties make them suitable for diverse applications in catalysis, hydrogen storage, sensors and many others. In particular, TiO_2, which is one of the most attractive materials among metal oxide semiconductors, has been intensely studied in recent years for its wide variety of applications in photocatalysis, solar cells and self-cleaning coatings.[1–4] TiO_2 has three crystal forms: brookite, anatase and rutile; the latter two crystal phases have wide applications in catalysts, solar cells and so on. Compared with common one-phase TiO_2 nanomaterials, composite nanocrystals possess better photocatalytic abilities compared to the pure crystals because vectorial charge transfer at rutile/anatase heterostructured interfaces is promoted.[5–7] Various synthetic strategies have been established to generate micro/nanostructured TiO_2 with different crystal phases, such as the electrochemical method, template methods, chemical or physical vapor deposition and the hydrothermal/solvothermal method.[8–19] Compared with other methods, the hydrothermal method has proven to be a powerful approach owing to its environmentally friendly approach, low cost and the controllable morphology obtained. However, a troublesome disadvantage of this method is the post-separation and purification of the product from the reaction solution. Although the hydrothermal product may have a continuous one-dimensional structure in the nano- or microscale, it usually exhibits a random dispersed state on the macroscopic scale, which brings limitations in some applications. In comparison, the electrospinning method, which has flourished in the past decade, has been proven to be a powerful and versatile technique for the fabrication of micro/nanofibers using the aid of Coulomb force.[20–25] Electrospinning possesses several attractive advantages, such as comparatively low cost, applicability to various materials and the ability to generate relatively large-scale continuous films. Many inorganic micro/nanofibers have been fabricated using the electrospinning method.[23–25] However, the phase structure of the nanofibers is hardly controlled such that amorphous rather than crystalline nanofibers are obtained in most cases. To solve this problem, herein we describe a simple and effective route that combines the electrospinning approach with a hydrothermal method to fabricate a self-supporting TiO_2 fibrous film on a large-scale, which is of a novel, highly-branched structure with anatase and rutile composite crystal phases.

The experimental process is shown in Fig. 1. First, titania fiber was electrospun from a $Ti(OBu)_4$ sol at an appropriate high voltage (Fig. 1a), and then the obtained non-woven film was calcined at 500 °C to form an anatase TiO_2 film (Fig. 1b). This electrospun film worked as a substrate to guide the growth of TiO_2 nanorods in the next hydrothermal step. Note that the as-obtained TiO_2 film is very brittle and special caution is needed to handle it. Then the suitably-sized TiO_2 fibrous film was put into an autoclave containing a $Ti(OBu)_4$–HCl–H_2O solution. The hydrothermal reaction

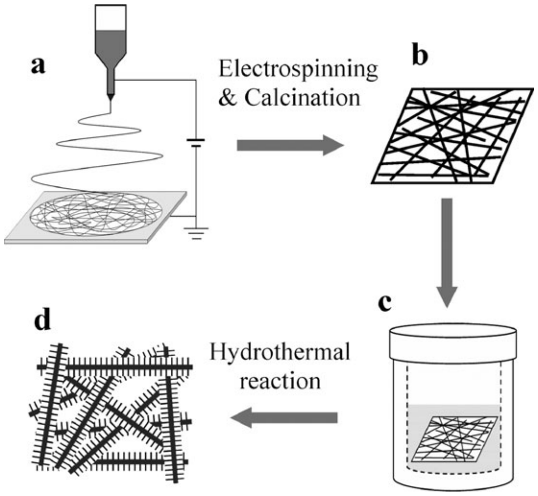

Fig. 1 Schematic illustration of the synthetic route for making branched TiO_2 fibrous films. (a) The hybrid titania nanofibers were fabricated by electrospinning; (b) the titania nanofibers were calcined to obtain an inorganic TiO_2 nanofibrous film; (c) the TiO_2 nanofibrous film was transferred to an autoclave for hydrothermal reaction; (d) the hydrothermal treated electrospun film.

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was carried out at 150 °C to obtain the hierarchical nanostructured TiO_2 film (Fig. 1c). The as-fabricated product could be easily clamped out of the autoclave with tweezers and then flushed with de-ionized water (Fig. 1d). The profile of the untreated electrospun membrane was inherited whereas the robustness was increased. (See ESI for the detailed experimental processes†).

Fig. 2a is an SEM image of the calcined electrospun TiO_2 fibrous film. The fibers, several hundreds of nanometres in diameter, interweave to form a non-woven fibrous film. There is apparently no secondary structure on the fibers. After the calcined film was further hydrothermally treated, the TiO_2 nanorods were formed on the fibers. As illustrated in Fig. 2b, the shape of as-treated product preserved the initial non-woven state except for the increase in diameter, while the diameter increased to several microns—several times larger than that of the original electrospun fibers. Fig. 2c shows the detailed morphology of the fibers, it is obvious that countless TiO_2 nanorods regularly array on the surface of the fibers to form a compact sheath. They are very similar to the branches of a cedar. The TiO_2 nanorods were relatively uniform, with about 50–100 nm diameter and several microns in length.

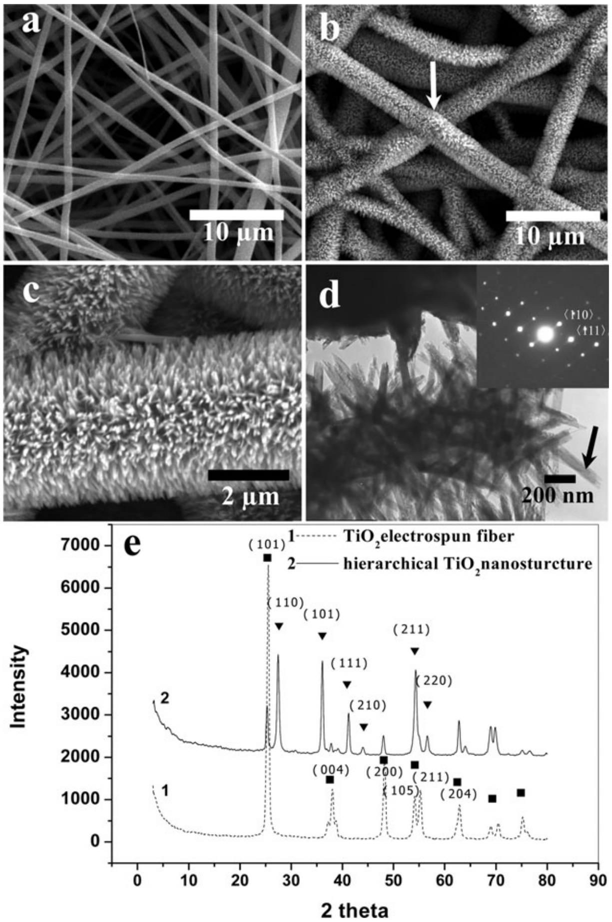

Fig. 2 SEM image of (a) TiO_2 fiber fabricated by the electrospinning method then calcined at 500 °C; (b) hierarchical brushy TiO_2 film synthesized by the hydrothermal approach; (c) high magnification image of highly-branched TiO_2 nanostructures; (d) TEM image of a single branch of hierarchical TiO_2 nanostructure (inset is the EDS pattern); (e) XRD pattern of a TiO_2 fiber fabricated by the electrospinning method (curve 1) and the composite structure synthesized by the combination of the electrospinning method and the hydrothermal approach (curve 2): ■ indicates the anatase phase and ▼ indicates the rutile phase.

Further characterization was carried out by TEM (Fig. 2d), which illustrates the highly-branched TiO_2 nanostructures similar to that of SEM images. Electron diffraction spectroscopy (EDS) showed that the nanorods are single-crystalline TiO_2 in the rutile-phase.

The X-ray diffraction (XRD) pattern of the pure calcined electrospun film and the hydrothermally treated hierarchical nanostructured TiO_2 film were compared to reveal their crystal structures, shown in Fig. 2e. The calcined fibrous film fabricated by the electrospun method was anatase crystal phase. Whereas the hierarchical nanostructured TiO_2 film after hydrothermal treatment was of both anatase and rutile crystal structure simultaneously. This composite crystal phase is caused by the anatase phase TiO_2 fiber from electrospinning and the rutile phase TiO_2 nanorod shell from the hydrothermal reaction. It means that a highly-branched TiO_2 film of composite crystal phase was successfully synthesized by a facile combination of the electrospinning technique and the hydrothermal method.

Though the as-fabricated TiO_2 film exhibits complex branched structures, the length and diameter of the TiO_2 nanorods can be easily controlled by changing the experimental parameters, such as reaction time, solution concentration and reaction temperature, *etc.* The growth process of nanorods on the surface of TiO_2 fibers is demonstrated in Fig. 3, showing the dependence of the nanorod scales with the reaction time. When the reaction system was kept at 150 °C for only one hour, layers of sparse TiO_2 nanoparticles were formed and deposited on the surfaces of the electrospun TiO_2 stems. These TiO_2 nanoparticles are tens of nanometres in diameter, which served as crystal seeds to guide the TiO_2 nanorods' subsequent growth. With the reaction time increased to 2 h, a thin layer of slim TiO_2 nanorods appeared surrounding the primal electrospun fibers. Prolonging the duration to 4 h, the length and the diameter of the TiO_2 nanorods further increased up to about 2 μm and 300 nm, respectively. Generally, both the length and diameter of the TiO_2 nanorods augment proportionately along with hydrothermal reaction time (see Fig. S1†), which means that it is feasible to control product morphologies by simply tuning the reaction time. Besides, the precursor concentration also affects the morphologies of the TiO_2 nanorods. When the $Ti(OBu)_4$ precursor was added from 0.5 mL to 4 mL, *i.e.* the concentration of Ti^{4+} was increased, the diameters of the grown nanorods changed gradually from 50 nm to 500 nm. At the same time, the density of the nanorods is also dramatically increased from sparse fuzz-like thin nanowires to thick solid coatings (see Fig. S3†).

Compared with electrospun TiO_2 films or hydrothermal TiO_2 nanorods, an outstanding advantage of the combined electrospinning method and hydrothermal approach lies in the ability to fabricate hierarchical nanostructured TiO_2 films with self-supporting properties (Fig. S2†). This greatly enhanced mechanical strength is a benefit from the grown TiO_2 nanorods. It is known that the electrospun inorganic films usually

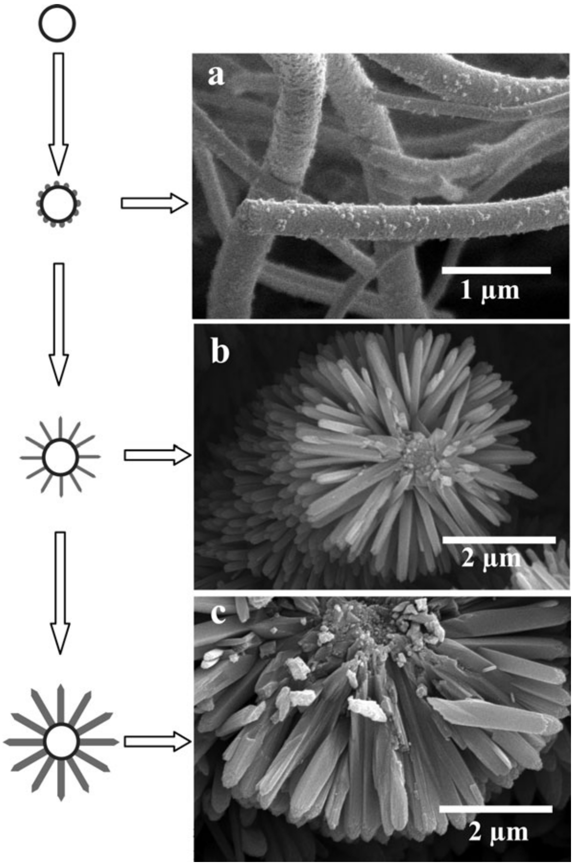

Fig. 3 The time-dependence schematic diagram of growing hierarchical TiO_2 nanostructures. Right: SEM images of TiO_2 nanostructures after hydrothermal treatment for (a) 1, (b) 2 and (c) 4 h.

are of very poor mechanical strength, mainly because there are no joints between different fiber layers. In hydrothermally treated film, however, countless TiO_2 nanorods interweave with each other at the intersections of fibers (as the white arrow indicates in Fig. 2b), which join the fragile fibers into a solid monolith. Therefore, the product is durable for clipping, flushing and nitrogen blowing. It could remarkably simplify the post-treatment process of the product.

In summary, we have synthesized novel cedar-like highly-branched TiO_2 self-supporting films that are generated from the combination of the electrospinning method with the hydrothermal reaction. The as-obtained films possess a dispersion-controlled anatase phase and a rutile phase simultaneously. The advantages of this strategy lie in its ability to fabricate a product with tunable morphologies and designed phase crystal structure. This simple and powerful strategy has established an avenue for producing diverse metal oxide hierarchical nanostructures, which could remarkably simplify the post-treatment processes of the traditional solution route. These functional materials of novel structures may find use in a broad variety of applications.

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