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Electrospun hierarchical cancellous-bone-like microstructures composed of a crystalline TiO_2 nanonet

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ABSTRACT

Unique hierarchical cancellous-bone-like microstructures, composed of a TiO_2 nanonet (nanofiber network), have been fabricated by a facile and cost-effective process that combines the electrospinning technique with the template method. The branching three-dimensional network trabeculae that form rod- and plate-shaped scaffolds have thickness of approximately 0.5 to 2.5 μm and consist of TiO_2 nanonet. The nanonet exhibits an anatase crystalline structure and a maximum Brunauer–Emmett–Teller specific surface area of 225.9 m^2/g. This hierarchical three-dimensional nano/micro porous network material creates numerous interconnected pores with a high surface area that enhances the overall efficiency of the network due to an increase in the accessible surface area, which increases the contact with the reaction media.

1. Introduction

Recently, nanoscale titania (TiO_2) has attracted much attention because of its potential applications in environmental purification [1], photocatalysis [2], chemiresistors [3], and high-efficiency dye-sensitized solar cells [4,5]. These nanoscale TiO_2 structures have been prepared in various forms, including nanoparticles (zero-dimensional, 0-D) [6], nanofibers (1-D) [3], thin films (2-D) [7], and 3-D porous network nanostructures [8]. In particular, 3-D highly opened porous TiO_2 networks have attracted considerable attention because they offer a high surface area and provide maximum contact area between the network and the reaction media. Furthermore, the continuity of the network prevents traps or dead spots from reducing efficiency [9].

Among the various methods for fabricating 3-D porous network materials, the template method uniquely affords a variety of porous frameworks with a wide range of pore sizes, well-defined morphology, and various chemical functionalities [10,11]. On the other hand, electrospinning offers a simple, cost-effective approach to producing polymeric and inorganic nanostructures [12]. In the electrospinning process, a high-voltage electric field creates an electrostatically charged high-speed jet after forming a Taylor cone at the end of a metal needle. Before reaching the grounded collector, the solution jet evaporates and solidifies. By controlling the electrospinning parameters, some interesting polymeric nanostructures have been prepared, such as porous poly-L-lactide (PLLA) fibers [13] and beaded polyethylene oxide fibers [14].

The present research was stimulated by the exceptional structure of porous PLLA fibers and 3-D porous network materials, and this paper reports a new type of architecture: a hierarchical 3-D TiO_2 nano/micro porous network. The material was prepared by a process that combines the electrospinning technique with the template method, which creates numerous excellent interconnected pores with a high surface area, allowing maximum contact between the porous network and the reaction media. This novel approach is a facile and cost-effective fabrication process for hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet (nanofiber network), which exhibits unique morphologies.

2. Experimental section

2.1. Materials

Titanium tetraisopropoxide (TTIP), ethanol (EtOH), polyvinylpyrrolidone (PVP, Mw = 1,300,000 g/mol), acetylacetone (AcAc), amorphous hydrophilic silica powder template (SiO_2, Aerosil® 200), and polyethylene glycol (PEG, Mw = 400 g/mol) were used as received.

2.2. Electrospinning of hierarchical cancellous-bone-like TiO_2 microstructures

The scheme in Fig. 1 illustrates the procedure used to fabricate the hierarchical cancellous-bone-like TiO_2 microstructures. As in conventional electrospinning procedures, the precursor solution was prepared by mixing SiO_2 template (0.1 g), PVP (0.8 g), PEG (1 g), AcAc (0.7 g), and TTIP (6 g) in EtOH (10 ml). After the precursor solution

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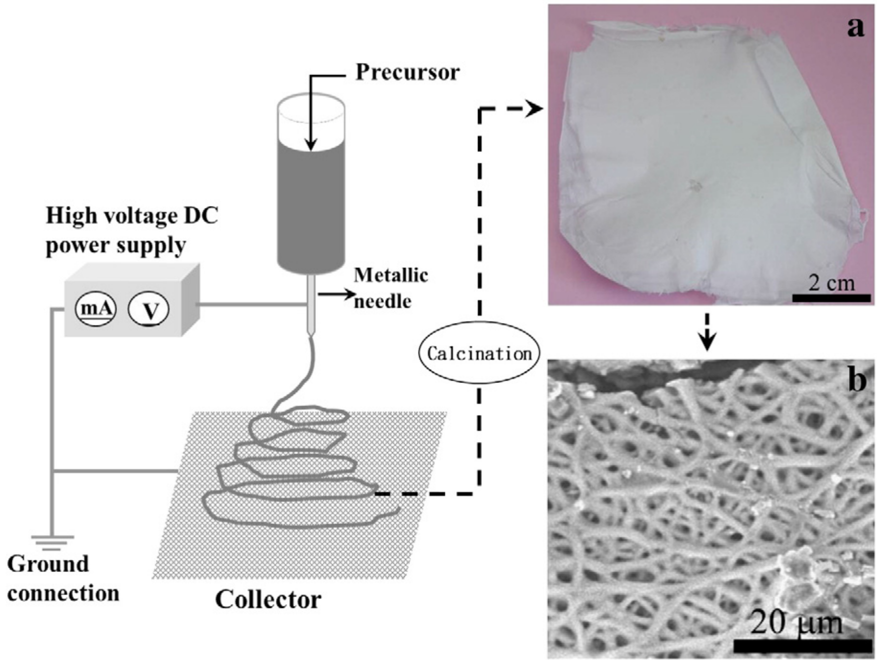

Fig. 1. Schematic illustrating the electrospinning of hierarchical cancellous-bone-like TiO_2 microstructures. (a) Optical micrograph. (b) SEM image.

was stirred well, its viscosity was about 137 cps, which was higher than that of the precursor solution without added SiO_2 template (68 cps). This precursor solution was loaded into a syringe with a 22-gauge stainless steel needle and connected to a high-voltage power supply. The flow rate of the precursor solution was 2 ml/h. An electric field of 16 kV was applied between the needle and the ground, which were at a distance of 9 cm, and the precursor solution was directly electrospun on the stainless steel mesh collector. The as-electrospun TiO_2 fiber mats were peeled off from the collector and transferred to an alumina tube furnace for calcination under atmosphere at 550 °C (heating rate = 5 °C/min) for 2 h, after which the SiO_2 template was dissolved with 3% NaOH solution. The resulting product was recovered by filtration, rinsed in DI water, and subsequently oven dried at 110 °C.

2.3. Characterization

Qualitative analyses were performed by X-ray diffractometry (XRD) with CuKα radiation. The microstructures were analyzed by field-emission scanning electron microscopy (FE-SEM) and field

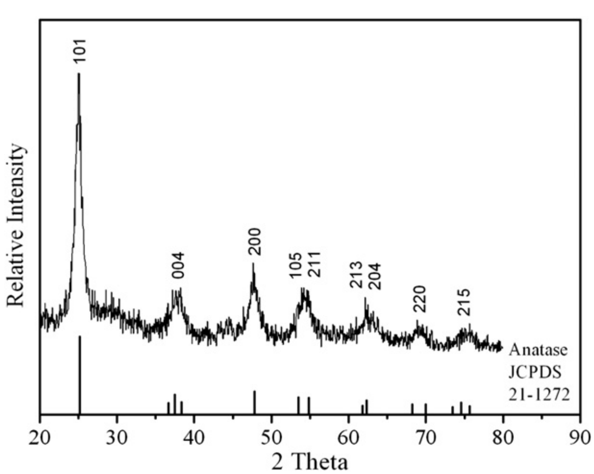

Fig. 2. XRD pattern of the hierarchical cancellous-bone-like TiO_2 microstructures.

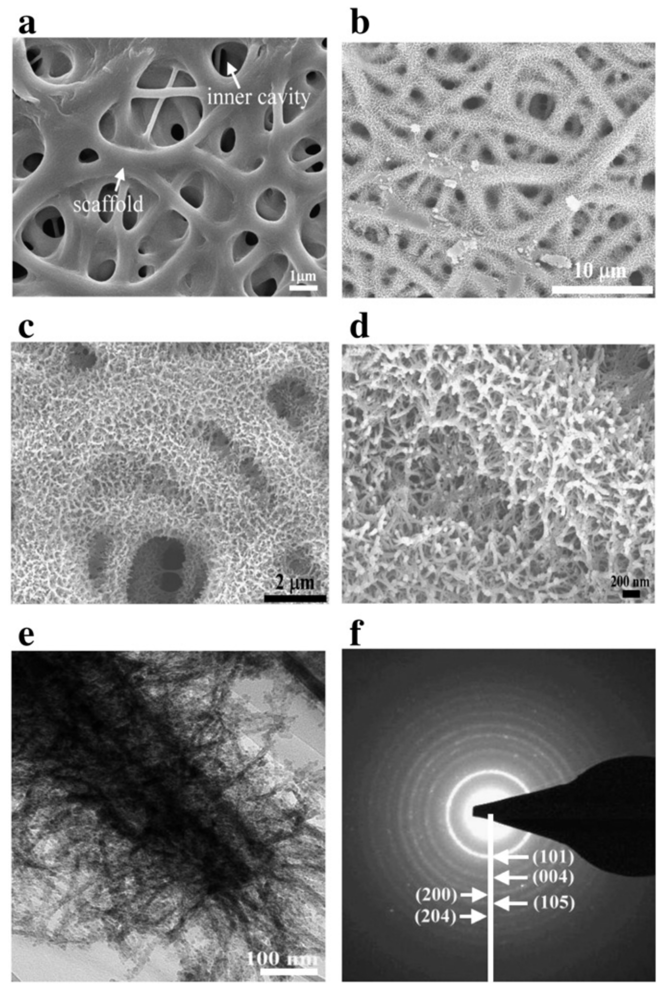

Fig. 3. Morphology of the hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet. FE-SEM images of the nanonet (a) as-spun and (b–d) after calcination and removal of the SiO_2 template. (c, and d) Magnification of (b). (e) TEM image and (f) SAED pattern.

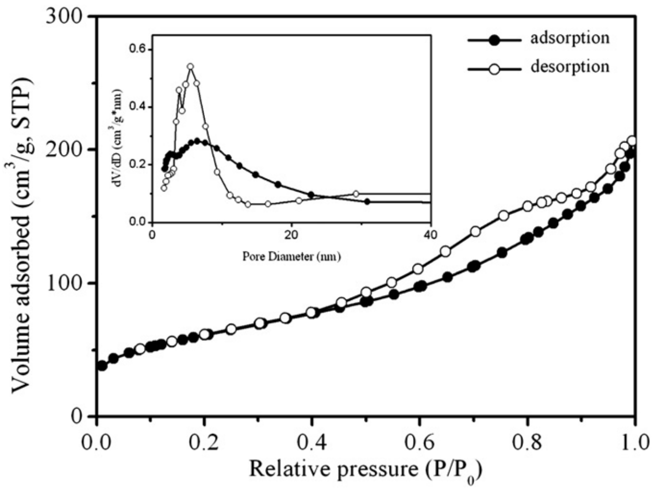

Fig. 4. Nitrogen adsorption/desorption isotherms and BJH pore size distribution (inset) for the hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet.

emission gun transmission electron microscopy (TEM). The Brunauer–Emmett–Teller (BET) specific surface area was determined by nitrogen adsorption apparatus (Micromeritics, ASAP 2020).

3. Results and discussion

The wide-angle XRD pattern of the resultant product is displayed in Fig. 2. Several diffraction peaks that can be assigned to the anatase phase (tetragonal $I4_1/amd$, No.141) are unambiguously identified. These assignments are further confirmed via the reference database (JCPDS No. 21-1272). This suggests that the as-electrospun TiO_2 fiber mats after calcination under atmosphere at 550 °C exhibit an anatase crystalline structure.

As shown in Fig. 3, the unique morphologies are reminiscent of those seen in cancellous bone, which is composed of a network of trabeculae form rod- and plate-shaped scaffolds. The FE-SEM images clearly show that the fiber mats comprised hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet. These branching 3-D network trabecular-form scaffolds have thickness approximately 0.5 to 2.5 μm and inner cavity size in 0.3–2.7 μm range (Fig. 3a and b). Importantly, the trabecular-form scaffolds that consist of the TiO_2 nanonet create an excellent 3-D liquid percolation path as well as numerous interconnected pores with high surface area (Fig. 3c and d). This allows maximum contact between the nanonet and the reaction media, which makes these nanonets more advantageous than the typical electrospun 1-D TiO_2 fibers. Fine morphological details identified by TEM include the nanofiber network structure, which is presented in Fig. 3e. The selected area electron diffraction (SAED) pattern in Fig. 3f indicates discernible Debye–Scherrer rings of (101), (004), (200), (105), and (204) diffractions, which are characteristic of the anatase phase and are consistent with the XRD findings in Fig. 2.

The hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet were formed because of the following two main factors: (1) The relatively high viscosity of the precursor solution retards solvent evaporation, resulting in the exposure of the TiO_2 sol precursor to moisture during the electrospinning process. This precursor cannot fully convert into a gel; instead, it congeals and then solidifies into large trabecular-form scaffolds. (2) The SiO_2 template can be well dispersed in the precursor solution but not mutually dissolved; hence, the removal of the template from the fiber mats creates a porous nanofiber networks structure.

A typical pair of isotherms is shown in Fig. 4. The pair represents a type IV pore structure and a type H4 hysteresis loop according to IUPAC definition. The hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet yield a much higher BET specific surface area (225.9 m^2/g) than typical electrospun 1-D TiO_2 fibers [15]. The hysteresis loops remain nearly horizontal and parallel over a wide range of p/p° with no limiting adsorption at high p/p°. They are observed on aggregates of plate-like particles, giving rise to slit-shaped pores. However, BJH analysis of the isotherms shown in Fig. 4 (inset) indicates a broader pore size distribution, with larger pore diameters found from the adsorption branch (maximum peak at 6.45 nm) than from the desorption branch (maximum peak at 5.46 nm).

4. Conclusions

Hierarchical cancellous-bone-like microstructures composed of a TiO_2 nanonet were successfully fabricated by a facile process that combines the electrospinning technique with the template method. The resulting 3-D TiO_2 nano/micro porous network material had numerous excellent interconnected pores that enhanced the overall efficiency of the network due to an increase in the accessible surface area, which increases the contact with the reaction media. Results from XRD and TEM studies suggested an anatase crystalline structure. These trabecular-form scaffolds had thickness of roughly 0.5 to 2.5 μm and inner cavity size in 0.3–2.7 μm range, consisted of TiO_2 nanofiber networks, and exhibited a BET surface area of 225.9 m^2/g, as indicated by the nitrogen adsorption/desorption isotherm.

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