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# Sol–gel synthesis highly porous titanium dioxide microspheres with cellulose nanofibrils-based aerogel templates

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ABSTRACT

Highly porous titanium dioxide microspheres had been prepared via a template-assisted sol–gel process with cellulose nanofibril aerogel microsphere template. The modified porous titanium dioxide microspheres showed a typical super-hydrophobic property. The method reported in this study may be applied to fabricate other inorganic materials with desired porous structure.



Titanium dioxide ($TiO_2$) is a well-known semiconducting material with many unique chemical and physical properties, such as a wide band gap, chemical stability, semiconductivity, photocatalytic activity and photosensitivity [1]. $TiO_2$ has attracted much interest due to its broad applications in the areas such as solar cells [2,3], fillers [4,5], photocatalysts [6,7], environmental purification, decomposition of carbonic acid gas, and generation of hydrogen gas [8,9]. It is well known that the properties and performance of $TiO_2$ strongly depend on the size, shape, surface properties, etc. Porous structure of $TiO_2$ is also a critical important property [10]. For instance, highly porous titanium dioxide with suitable pore size, porosity, and specific surface area could perform better than regular titanium dioxide nanoparticles in catalytic application because the pore system would provide high fluid contact and easy fluid transport through the pores [11]. Sol–gel method is commonly used to prepare different structured titanium dioxide nanoparticles. This method has a number of advantages over conventional synthetic procedures, such as low synthesis temperature, high purity and could be facilely utilized in a homogeneous process [12]. Template synthesis is a method usually used to fabricate titanium dioxide materials with a predetermined morphology and microstructure to meet the requirement of different applications. With this technique, the titanium dioxide structure strongly depends on the structure of the template used. Therefore, choosing an appropriate template is crucial to synthesize targeted porous nanostructures [13]. In this study, aerogel microspheres made from cellulose nanofibrils were used as the template. Because of extreme low density, high porous, high moisture absorption and good mechanical stability even in harsh environment of the cellulose aerogel microspheres, it is expected that the aerogel could be ideal template for synthesizing titanium dioxide materials with desired porous structure.

Titanium (IV) tetraisopropoxide (TTIP, 99%) was purchased from Aldrich (Germany). P25-$TiO_2$ (surface area of about 50 $m^2$ $g^{-1}$) was purchased from Degussa (Germany). 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS, 97%) used for surface hydrophobic modification was purchased from Alfa Aesar. Other reagents were all of analytical grade and received from local resources. The preparation of cellulose nanofibrils and their aerogel microspheres was the same as reported previously in our article [14]. 0.02 g of the aerogel microsphere template was soaked in 100 ml of 20 wt.% TTIP alcohol solution at 20 °C. The TTIP-saturated templates were rinsed 5 times with dehydrated ethanol to remove the residual titania precursors, and then soaked 2 h in water–alcohol solution for the hydrolysis and polycondensation of titanium precursors in templates. All samples were rinsed with large quantity of water, and freeze-dried followed by calcination at 500 °C for 3 h to obtain the porous titanium dioxide structure.

Different from aerogels made from regenerated cellulose derivatives, the aerogels made from native cellulose nanofibrils showed fibrous morphology [15]. The synthetic route of porous titanium dioxide was illustrated in Scheme 1. The cellulose nanofibril aerogel microspheres were soaked in titanium–alcohol solution, and then rinsed by dehydrated ethanol to get rid of the un-immobilized titanium precursor in the interstice. Then, the left titanium precursor was hydrolyzed in water alcohol solution to form amorphous titania. Because

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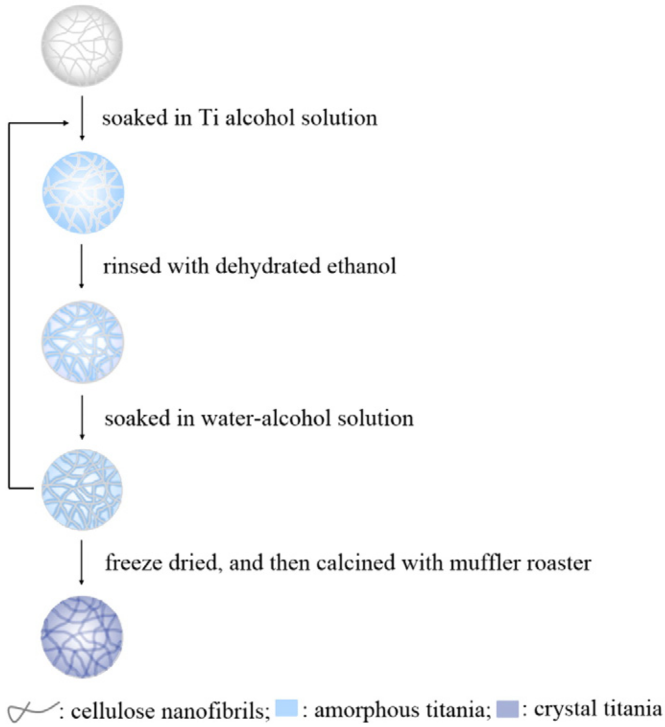


**Scheme 1.** Schematic illustration of fabrication process of porous titanium dioxide microspheres.

un-immobilized titanium precursors were removed, but only these immobilized on the nanofibrils left during the hydrolysis step, the porous structure of the aerogel microsphere template could be well maintained. After that, the hybridized microspheres could be freeze-dried and calcined directly at suitable condition, or soaked in the titanium alcohol solution to re-loading additional titanium precursors again. As shown here, external morphology and interior porous channels of the materials depend strongly upon the loading times under same template and sol–gel condition.

Scanning electron microscopy (the Zeiss LEO 1530 microscopy) was used to study the morphological characteristics of the products. From Fig. 1 it was observed that, with modified sol–gel procedure, the titania precursors were deposited mostly on the nanofibrils, rather than the interstice of the aerogel template. If the hybrid materials were dried at room temperature, the capillary pressure due to the meniscus curvature of liquid water could destroy the microsphere morphology and porous structure. Therefore, freeze-drying was adopted to dry these composite microspheres, which can keep the templates from collapsing. Finally, by calcination, the templates were removed and the amorphous titania was converted to crystal particles which were bonded together along the original cellulose to form pore network. As designed, the highly porous titanium dioxide microspheres were obtained. From the SEM results, it should be concluded that the cellulose nanofibril aerogel microspheres could be very suitable template for preparation of titanium dioxide microspheres with desired porous structure.

Before and after calcination, thermogravimetric analysis was performed on a PerkinElmer STA 6000 thermal analyzer at a heating rate of 10 °C $min^{-1}$ under an air flow of 100 ml $min^{-1}$ and the degrading process of the products as a function of temperature was shown in Fig. 2a. It can be seen from TGA curves that there were two major zones of weight losses between room temperature and 410 °C. The first weight loss below 210 °C was determined to be about 6% of total weight loss, which is attributed to the release of adsorbed water and residual organic solvent. The second weight loss was observed in the temperature range from 210 to 410 °C, which accounted for about 17% in

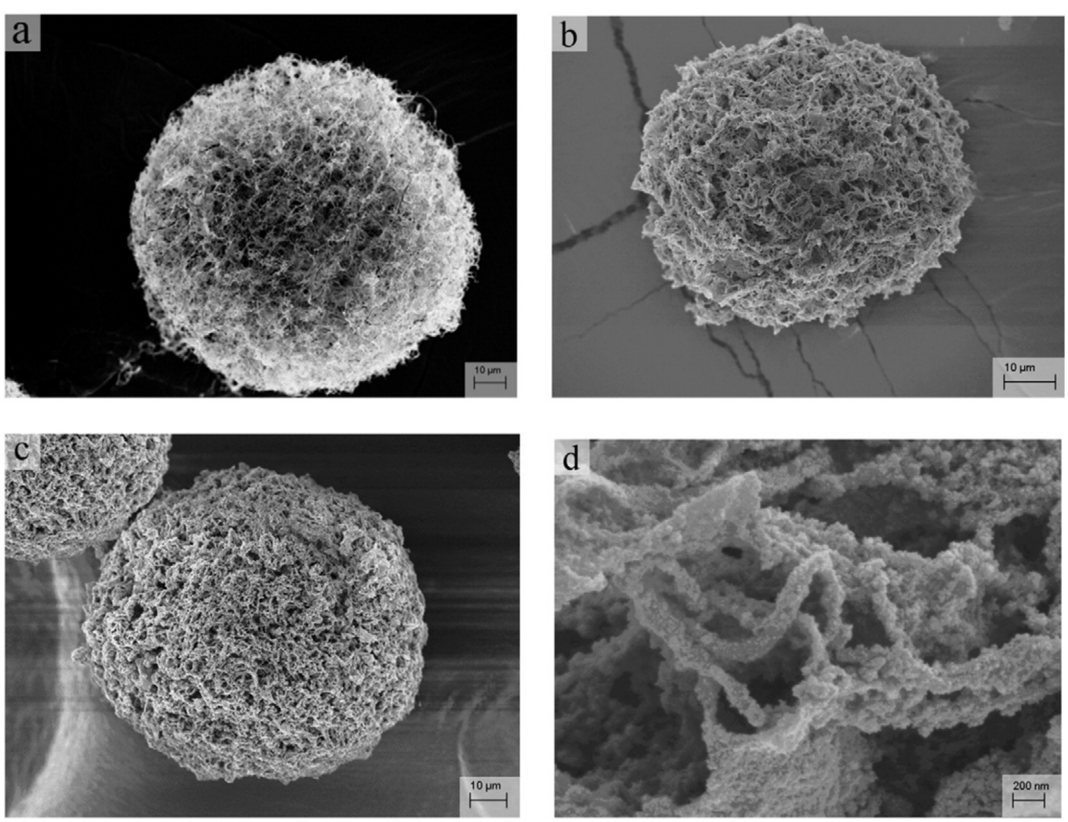


**Fig. 1.** SEM images of cellulose nanofibril aerogel microsphere and titanium dioxide porous microspheres. (a) cellulose nanofibril aerogel microsphere template; (b) titanium dioxide porous microsphere prepared by the hydrolysis and polycondensation of titanium precursors in templates loading 3 times; (c) titanium dioxide porous microsphere prepared by the hydrolysis and polycondensation of titanium precursors in templates loading 7 times; (d) porous titanium dioxide microsphere under larger magnification.