

Communication

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A General Strategy for Fabricating Thoroughly Mesoporous Nanofibers

Huilin Hou,^{†,*} Lin Wang,[†] Fengmei Gao,[†] Guodong Wei,[†] Bin Tang,[‡] Weiyou Yang,^{*,*†} and Tom Wu,^{*,§}

[†]Institute of Materials, Ningbo University of Technology, Ningbo, 315016, P.R. China

[‡]Research Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan, 030024, P.R. China

[§]Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

Supporting Information Placeholder

ABSTRACT: Recently, preparation of mesoporous fibers has attracted extensive attentions because of their unique and broad applications in photocatalysis, optoelectronics and biomaterials. However, it remains a great challenge to fabricate thoroughly mesoporous nanofibers with high purity and uniformity. Here, we report a general, simple and cost-effective strategy, namely foaming-assisted electrospinning, for producing mesoporous nanofibers with high purity and enhanced specific surface areas. As a proof of concept, the as-fabricated mesoporous TiO₂ fibers exhibit much higher photocatalytic activity and stability than both the conventional solid counterparts and the commercial available P25. The abundant vapors released from the introduced foaming agents are responsible for the creation of pores with uniform spatial distribution in the spun precursor fibers. The present work represents a critically important step in advancing the electrospinning technique for generating mesoporous fibers in a facile and universal manner.

Mesoporous materials are of great interest in the fields of catalysis, selective adsorption and host/guest supports, owing to their high specific surface areas as compared to their conventional solid counterparts.¹ Recently, preparation of mesoporous micro/nanofibers has particularly attracted extensive attentions because of their broad applications in photocatalysis, optoelectronics and biomaterials.² Besides the intrinsic porous characteristics, the 1D mesoporous nanofibers provide efficient paths for the electron transportation and possess a robust geometry to maintain the functionalities.³ Up to date, several methods have been invented to fabricate mesoporous nanofibers, such as hydrothermal route,⁴ template-assisted process,⁵ electrospinning technique,⁶ structure-selective synthesis⁷ and so on. However, it still remains a great challenge to fabricate thoroughly mesoporous nanofibers with satisfied purity and uniformity in a simple and universal manner.

Electrospinning is a versatile, simple and cost-effective strategy for producing 1D nanostructures of a wide range of materials with tunable diameters and morphologies.⁸ However, most of the reported works were focused on the fabrication of conventional solid fibers without any pores. Can we advance the facile technique of electrospinning to create mesoporous fiber structures? Such a breakthrough will lead to the fabrication of mesoporous fibers with enhanced specific surface areas in a controlled manner. This is the primary motivation behind the present work. Here,

we report a general strategy, namely foaming-assisted electrospinning, for the synthesis of mesoporous fibers. TiO₂ and TiO₂-based composites are chosen as the examples to demonstrate the versatile and general nature of our approach. The resultant mesoporous fibers exhibit much better performance compared to the conventional nanofibers and the commercially available P25 product, suggesting their very promising application prospect. The present work might open new doors for the exploration of mesoporous nanofibers with high photocatalytic activities.

TiO₂ mesoporous nanofibers were fabricated by calcination of precursor fibers, which were obtained by electrospinning the solution of polyvinylpyrrolidone (PVP), tetrabutyl titanate (TBOT), and foaming agent diisopropyl azodiformate (DIPA). The raw materials of TBOT (Aladdin, Shanghai, China), PVP (MW≈1300000, Aladdin, Shanghai, China) and DIPA (Adamas, Shanghai, China) were commercially available and directly used without further purification. Absolute ethyl alcohols and acetic acid were used as the solvents to homogenously mix TBOT, PVP and DIPA. In a typical experiment, PVP, TBOT and solvents were firstly mixed by vigorously stirring for 6 h. PVP is used here to tune the viscosity of the solution. DIPA of 10 wt% was then added into the above solution with further magnetic stirring for 2 h. The resultant solution was transferred into a plastic syringe with a stainless steel nozzle (anode, diameter: 0.22 mm). The tip of the stainless steel nozzle was placed in the front of a metal cathode (collector) with a typically fixed distance of 20 cm between the nozzle and the collector. An electrical potential of 18 kV was applied for electrospinning the precursor fibers, and then the products were dried in oven at 60 °C. Subsequently, the precursor fibers were positioned in a quartz crucible and annealed in a tube furnace at 550 °C in air for 2 h, before cooling to the ambient temperature. For comparison, a control experiment was also carried out without the foaming agent addition in the initial solutions, and the details are shown in Table S1 (Supporting Information). The resultant products were referred as Sample A1 and A2, respectively. To show the universality of this technique for generating mesoporous fibers, TiO₂-based hybrid mesoporous nanofibers were also synthesized with the similar experimental procedures. Zinc acetate (Zn(Ac)₂), copper acetate (Cu(Ac)₂) and ferric acetylacetonate (Fe(AcAc)₃) were used as the raw materials in the synthesis of TiO₂/ZnTiO₃, TiO₂/CuO and TiO₂/Fe₂O₃ hybrid nanofibers, respectively. Dimethylformamide (DMF) was added to improve the solubility of precursors during the preparation of the solutions. The detailed compositions of the initial solutions were

shown in Table S2 (Supporting Information), and the resultant products were referred as Samples B-D, respectively. The details for structure characterization and photocatalytic performance measurement of the mesoporous fibers were shown in the Supporting Information.

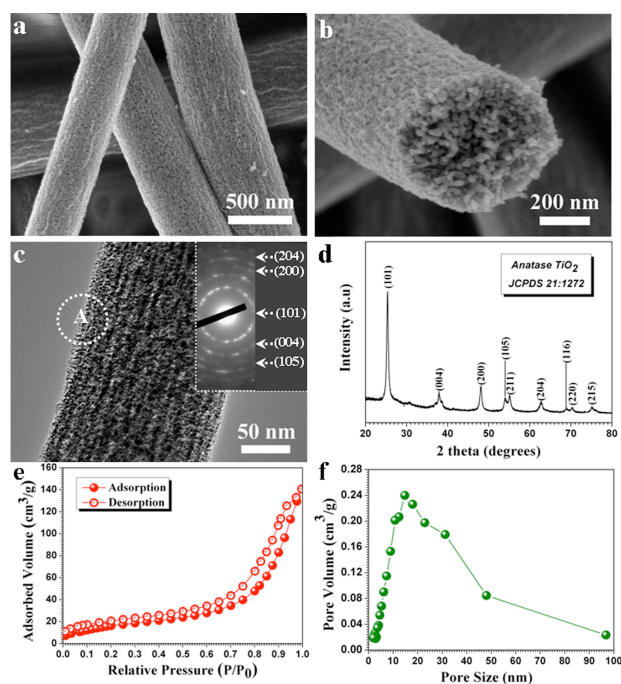


Figure 1. (a-b) Typical SEM images of the TiO₂ mesoporous nanofibers under different magnifications. (c) A representative TEM image of a single mesoporous TiO₂ nanofiber. The inset is the corresponding SAED pattern recorded from the marked area of A in (c). (d) A typical XRD pattern of Sample A1 after calcination. (e) Nitrogen adsorption-desorption isotherm of the TiO₂ mesoporous nanofibers. (f) Corresponding pore size distribution.

SEM was employed to characterize the spun precursor fibers and their corresponding calcined products. The as-spun precursor fibers of Sample A1 have smooth surfaces with average diameter of $\sim 1 \mu\text{m}$ and lengths up to several hundred of millimeters. The corresponding elemental mappings show uniform spatial distribution of Ti, N and O (Figure S1, Supporting Information). Figure 1(a) shows the typical SEM images of the calcined fibers (also see Figure S2(a-c), Supporting Information). All the precursor nanofibers have been completely converted into mesoporous nanofibers with a high purity. The fiber diameter is reduced to $\sim 600 \text{ nm}$, mainly owing to the elimination of PVP and the formation of crystalline TiO₂ after the high-temperature treatment. Figure 1(b) shows a representative cross-section SEM image of the TiO₂ mesoporous nanofibers, disclosing that the fibers possess a thoroughly porous structure with homogeneous pores.

Figure 1(c) provides a representative TEM image of a single TiO₂ nanofiber, further confirming that densely distributed pores exist throughout the fiber body. The SAED pattern (the inset in Figure 1(c)) recorded at the marked area in Figure 1(c) suggests that the obtained product is anatase TiO₂ (JCPDS, No. 21-1272) with a polycrystalline nature. Furthermore, the EDS spectrum discloses that the fibers possess only Ti and O (Figure S2(d), Supporting Information). Although the DIPA foamer contain N, we did not detect any N in the calcined fibers. We should also mention that many long mesoporous fibers survived the scratching and ultrasonic treatments during the TEM sample preparation

process, indicating their high structural robustness. Figure 1(d) presents the typical XRD pattern of the calcined products of Sample A1. All the peaks can be indexed to the anatase TiO₂ (JCPDS, No. 21-1272), suggesting the pure phase of the resultant fibers. The sharp diffraction peaks indicate that the products are highly crystalline.

Nitrogen adsorption measurements (Figure 1(e)) revealed that the products exhibit the type IV isotherm behavior with H3 hysteresis, implying that the obtained fibers are mesoporous with a BET surface area of $\sim 64.9 \text{ m}^2/\text{g}$. The distribution of Barrett-Joyner-Halenda (BJH) pore sizes (Figure 1(f)) determined from the adsorption branches are peaked at $\sim 16 \text{ nm}$.

A control experiment without the foaming agent added in the initial solutions (see Sample A2 in Table S1, Supporting Information) was carried out to isolate the effect of the foaming agent of DIPA on the formation of the porous fibers. The as-spun polymer fibers are similar to those of Sample A1 (Figure S3(a-b), Supporting Information). However, their calcined products present the ordinary solid nanofibers (Figure S3(c-d), Supporting Information), which are quite different from the mesoporous structures synthesized with the 10 wt% foaming agents, suggesting that the introduced foaming agents are critical for the formation of the mesoporous structures. The XRD pattern (Figure S3(e), Supporting Information) discloses that the as-prepared Sample A2 is also pure anatase TiO₂, implying that the foaming agent has no effect on the compositions of the resultant products. However, the calcined fibers of Sample A2 shows a BET surface area of ca. $11.9 \text{ m}^2/\text{g}$ (Figure S3(f), Supporting Information), which is about 6 times lower than that of Sample A1 ($64.9 \text{ m}^2/\text{g}$). Table S3 in Supporting Information summarizes the surface properties of the Samples A1 and A2. Sample A1 possesses much higher pore volume than A2, implying that the foaming agent of DIPA is responsible for the formation of the mesopores within the fibers. This comparison unambiguously suggests: i) the foaming agents play a critically important role on the formation of the mesoporous fibers, which helps create the pores throughout the entire body of fibers with uniform spatial distribution; ii) the foaming agents significantly enhance the BET Surface area of the resultant fibers.

The formation mechanism of the mesoporous fibers could be explained as follows (schematically shown in Figure S4(a), Supporting Information). First, the DIPA, the foaming agent, is assembled into the precursor fibers (Step I). Since the DIPA is dissolved in the solutions before electrospinning, the foamer is distributed homogeneously within the fibers. The homogeneous distribution of DIPA is consistent with elemental mapping data and the formation of uniform porous structure throughout the fiber body. During the calcination process under air at 550°C (Step II), the DIPA foamer, with the chemical formula of $\text{C}_8\text{H}_{14}\text{N}_2\text{O}_4$, is completely decomposed into vapor phases (e.g. CO_2 , NO_2 and H_2O), which cause the formation of the pores within the fibers. This is confirmed by the thermal analysis of the as-spun PVP/TBOT/DIPA fibers of Sample A1 (Figure S4(b), Supporting Information). The initial slight weight loss in the low temperature range ($35\text{--}130^\circ\text{C}$) is owing to the residual solvent decomposition and volatilization. The 10 % weight loss between 130°C and 180°C is caused by the decomposition of DIPA (DSC exothermic peak at $\sim 160^\circ\text{C}$), which results in the formation of mesoporous precursor nanofibers. The 40% weight loss at the higher temperatures ($300\text{--}480^\circ\text{C}$) should be attributed to the decomposition of PVP (DSC endothermic peak at 420°C). Finally, the DSC exothermic peak at 500°C is attributed to the TiO₂ crystallization. In contrast, as shown in Figure S4(b), there are only two exothermic peaks observed for Sample A2, which are related to PVP decomposition and TiO₂ crystallization. These data suggest

that the introduction of the DIPA foaming agents notably affects the thermal behaviors of as-spun fibers.

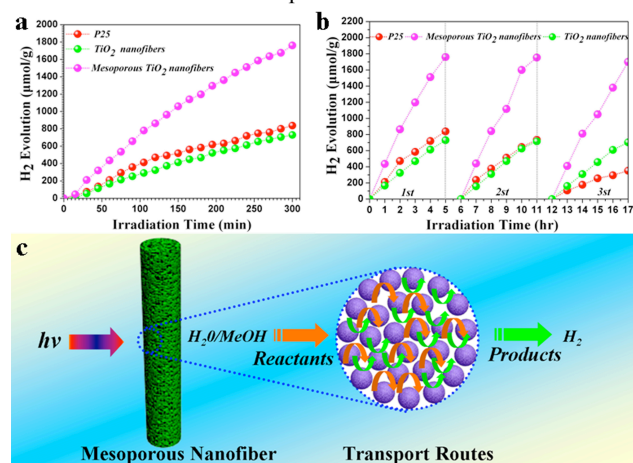


Figure 2. (a) The hydrogen production photocatalyzed by the as-fabricated mesoporous TiO₂ nanofibers, solid TiO₂ nanofibers and P25 under different irradiation time. (b) Results of reusability experiments for photocatalytic H₂ generation using the present three photocatalysts. (c) Schematic illustration of mesoporous fibers with enhanced photocatalytic activities.

The as-fabricated TiO₂ mesoporous nanofibers (Sample A1) and solid TiO₂ nanofibers (Sample A2), as well as the commercial P25, were used as the photocatalysts for evaluation of their photocatalytic properties. The surface properties of P25 are shown in Table S3, Supporting Information. Figure 2(a) plots the evolution of hydrogen produced from the aqueous suspensions of the three photocatalysts (their average hydrogen production rates are shown in Figure S5, Supporting Information). It is clear that the hydrogen evolution rate of the TiO₂ mesoporous nanofibers (ca. 399.2 μmol g⁻¹h⁻¹) is much higher than those of solid counterpart (ca. 156.9 μmol g⁻¹h⁻¹) and P25 (ca. 197.8 μmol g⁻¹h⁻¹), suggesting that the creation of pores in/on the fibers by the foaming agents significantly improves the photocatalytic activity of TiO₂. More interestingly, the hydrogen production rate of thoroughly mesoporous TiO₂ nanofibers is higher than most values reported for solid and porous TiO₂ nanofibers (see Table S4, Supporting Information). To further investigate their reusability and stability, these three photocatalysts were recovered and reused for photocatalytic H₂ production under the similar conditions. As shown in Figure 3(b), there is nearly no loss of H₂ evolution rate for both mesoporous and solid TiO₂ fibers photocatalysts, whereas the activity of P25 evidently declined after 3 cycles. This confirms that the obtained mesoporous TiO₂ fibers are much more stable with a higher photocatalytic activity than the commercial product of P25. To account for the high performance of mesoporous TiO₂ fibers, a schematic diagram is illustrated in Figure 3(c). First, the one-dimensional (1D) fibers could remarkably inhibit the agglomeration of nanoparticles, which contributes to the stable photocatalytic performance.⁹ Second, the columnar mesoporous architecture possesses the interconnected channels, which offers more active sites to adsorb reactants, e.g. water and MeOH groups. Finally, the mesoporous channels existing throughout the fibers allow the effective transportation of gaseous products.¹⁰ In other words, the morphology of the 1D mesoporous fibers is beneficial to the participation materials moving easily into/out of the framework, yielding a high reaction rate. These synergetic effects as mentioned above are responsible for the much improved photocatalytic properties of the mesoporous fibers with high activity and stability.

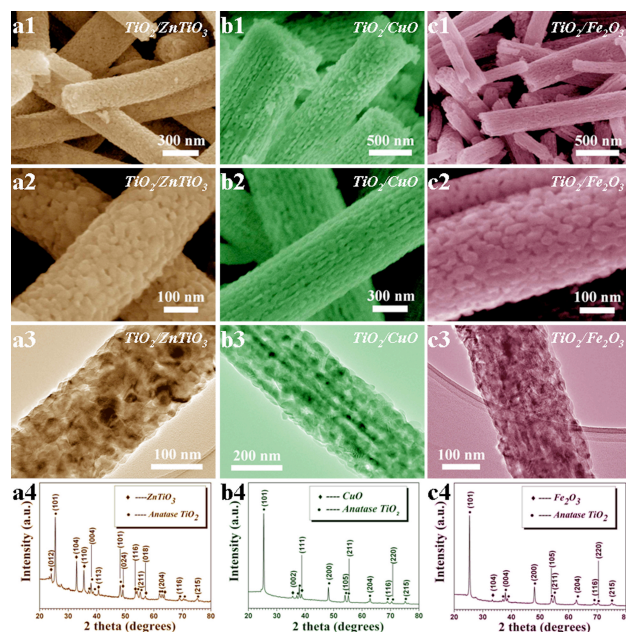


Figure 3. (a1-c2) Typical SEM images of the hybrid mesoporous nanofibers of TiO₂/ZnTiO₃ (a1-a2), TiO₂/CuO (b1-b2) and TiO₂/Fe₂O₃. (a3-c3) Typical TEM images of individual mesoporous nanofibers from Samples B, C and D, respectively. (a4-c4) Representative XRD patterns recorded from the calcined products of Samples B, C and D.

Now we come to the point on the versatile and universal characteristics of the present foaming-assisted electrospinning technique for producing mesoporous nanofibers. Three TiO₂-based hybrid materials are chosen as the examples (see Table S2, Supporting Information). Figure 3(a1-c2) displays the representative SEM images of the calcination products corresponding to the as-spun precursor fibers of Sample B, C and D (i.e., using zinc acetate, copper acetate and ferric acetylacetonate as the precursors, respectively) (Figure S6, Supporting Information), suggesting that the precursor fibers have been completely converted to mesoporous fibers (Figure S7, Supporting Information). Close observations on the cross sections (Figure S7, Supporting Information) indicate that all the fibers are thoroughly mesoporous. Figure 3(a3, b3 and c3) depict the typical TEM images of Sample B, C and D, respectively, further confirming their thoroughly mesoporous nature (also see Figure S8-10(a), Supporting Information). Figure 3(a4, b4 and c4) displays the typical XRD patterns corresponding to Sample B, C and D. These experimental results suggest that the obtained three samples are TiO₂/ZnTiO₃, TiO₂/CuO and TiO₂/Fe₂O₃ hybrid fibers, respectively, which are consistent with the SAED analyses (Figure S8(b), Figure S9(b) and Figure S10(b), Supporting Information). The EDS analyses (Figure S8(c), Figure S9(c) and Figure S10(c), Supporting Information) disclose the presence of Zn, Cu, and Fe elements, respectively, besides Ti and O, consistent with the expected compositions. The HRTEM images (Figure S8(d-f), Figure S9(d-f) and Figure S10(d-f), Supporting Information) further confirm that the synthesis products are TiO₂/ZnTiO₃, TiO₂/CuO and TiO₂/Fe₂O₃ hybrid fibers. The results of BET surface areas and the pore sizes distribution measurements (Figure S11, Supporting Information) indicate that these three products also display the type IV-like isotherm with H3 hysteresis, and the BET surface areas are ~37.8, 50.7 and 35.9 m²/g for TiO₂/ZnTiO₃, TiO₂/CuO and TiO₂/Fe₂O₃ hybrid fibers with average pore sizes of 17.1, 16.2 and 38.3 nm, respectively. The surface properties of the three hybrid products are summarized in Table S5, Supporting Information. These re-

sults demonstrate that diverse materials can be fabricated simply by using the corresponding raw materials, suggesting the versatility and universality of the present foaming-assisted electrospinning technique for the fabrication of mesoporous fibers.

In summary, we have demonstrated a novel and general strategy, namely foaming-assisted electrospinning, for producing mesoporous nanofibers. This universal method is effective for generating thoroughly mesoporous fibers with high purity and remarkably enhanced specific surface areas. As a proof of concept, the as-fabricated mesoporous TiO₂ fibers exhibit a much higher photocatalytic activity and stability than both the conventional solid counterparts and the commercial available P25. The release of vapor phases from the introduced foaming agents is responsible for the creation of pores in/on the polymeric precursor fibers, leading to the formation of mesoporous structures. Our work opens new doors for the exploration of thoroughly mesoporous fibers, and the novel synthesis will advance such materials towards the high-performance applications as photocatalysts and catalyst supports.

ASSOCIATED CONTENT

Supporting Information

Supplementary to the section of experimental procedure, additional data including SEM, TEM, XRD, TG-DCS and BET of the example products, and schematic illustration for the formation of mesoporous nanofibers. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Email : weiyouyang@tsinghua.org.cn (W. Yang);
tao.wu@kaust.edu.sa (T. Wu)

Notes

The authors declare no competing financial interests.

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Graphical Table of Contents (TOC)

