Protocol

Protocol for preparation of highly durable superhydrophobic bulks with hierarchical porous structures

Step 1

PU foam → PU foam skeleton

PU foam

0.5 hr

Specification cutting
Tailoring the specifications of PU templates.

Step 2

Immersing in nanoparticles slurry → Drying in the oven

5 days

Inside filling
Filling nanoparticles inside PU foam.

Step 3

Nanoparticles slurry drop coating → Drying in the oven

12 hr

Surface dipping
Constructing surface accretion layer by slurry drop coating.

Step 4

Sintering in inert gas.

5 hr

Sintering
Thermal forming of hierarchal porous bulk.

Yunyun Meng, Binrui Wu, Chaoyi Peng, ..., Nan Wu, Manish K. Tiwari, Xian Yi

binruiwu@foxmail.com (B.W.)
lierenwn@nudt.edu.cn (N.W.)

Highlights

Steps to fabricate CNT/PTFE hierarchical porous nanocomposites by template method

Optimized impregnation strategy for controllable nanoparticle distribution

Quantify the density of impregnated preform and the thickness of surface accretion layer

Superhydrophobic surfaces face challenges in comprehensive durability when used in extreme outdoor environments. Here, we present a protocol for preparing nanocomposite bulks with hierarchical structures using the template technique. We describe steps for using hybrid nanoparticles of polytetrafluoroethylene and multi-walled carbon nanotube to fill inside and dip on the polyurethane (PU) foam. We then detail procedures for its removal by sintering treatment. The extra accretion layer on the PU foam surface was highlighted to construct hierarchical porous structures.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

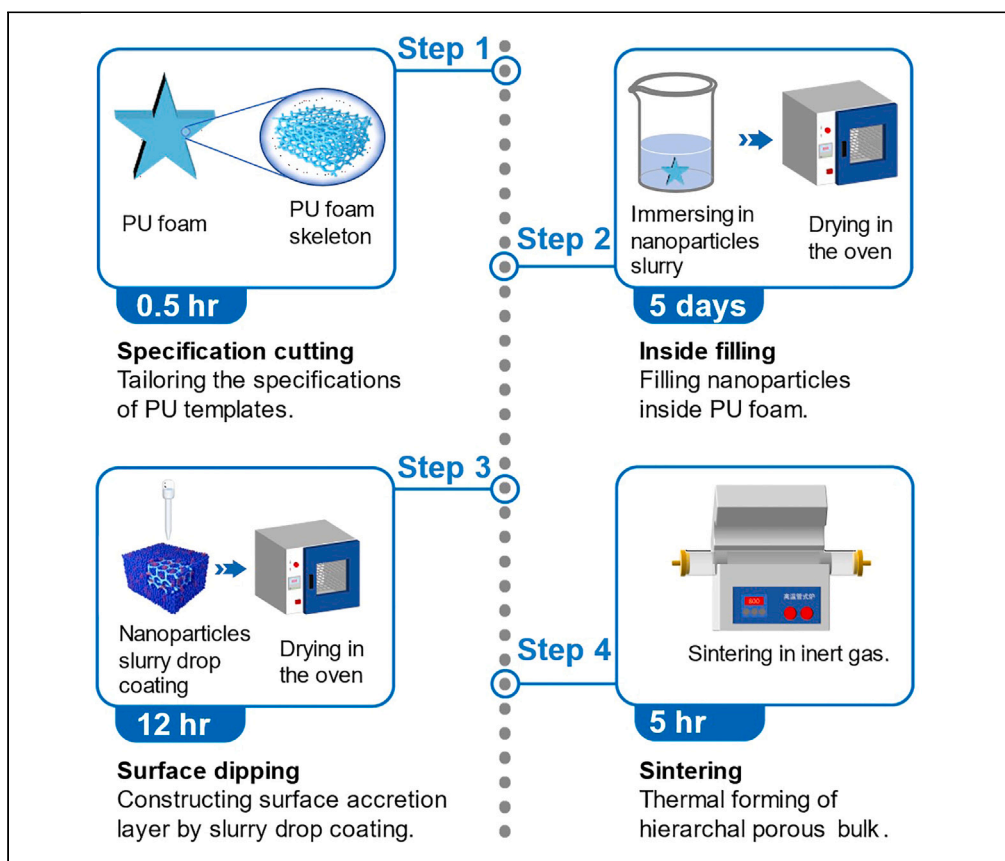## Protocol

Protocol for preparation of highly durable superhydrophobic bulks with hierarchical porous structures

Yunyun Meng,[1] Binrui Wu,[2,3,7,*] Chaoyi Peng,[4] Suli Xing,[1] Changping Yin,[1] Nan Wu,[1,8,*] Manish K. Tiwari,[5,6] and Xian Yi[3]

[1]Department of Materials Science and Engineering, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, Hunan 410073, P.R. China

[2]State Key Laboratory of NBC Protection for Civilian, Beijing 102205, P.R. China

[3]Key Laboratory of Icing and Anti/De-Icing, China Aerodynamics Research and Development Center, Mianyang Sichuan 621000, P.R. China

[4]Zhuzhou Times New Materials Technology CO., LTD, Zhuzhou, Hunan 412007, P.R. China

[5]Nanoengineered Systems Laboratory, UCL Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

[6]Wellcome/EPSRC Centre for Interventional and Surgical Sciences (WEISS), University College London, London W1W 7TS, UK

[7]Technical contact

[8]Lead contact

*Correspondence: binruiwu@foxmail.com (B.W.), lierenwn@nudt.edu.cn (N.W.)
https://doi.org/10.1016/j.xpro.2024.102853

SUMMARY

Superhydrophobic surfaces face challenges in comprehensive durability when used in extreme outdoor environments. Here, we present a protocol for preparing nanocomposite bulks with hierarchical structures using the template technique. We describe steps for using hybrid nanoparticles of polytetrafluoroethylene and multi-walled carbon nanotube to fill inside and dip on the polyurethane (PU) foam. We then detail procedures for its removal by sintering treatment. The extra accretion layer on the PU foam surface was highlighted to construct hierarchical porous structures.

For complete details on the use and execution of this protocol, please refer to Wu et al.[1]

BEFORE YOU BEGIN

Many strategies have been reported to prepare highly robust superhydrophobic materials, which hardly support customized microstructure to deal with various environmental effects.[2,3] The interaction with dynamic water is considered a great challenge for superhydrophobic surfaces to emerge from the laboratory to an actual water environment,[4] which can be regarded as an evaluation criterion for the comprehensive durability of superhydrophobicity as it poses a serious threat to the stability of the microstructure and the trapped air layer. Two factors should be focused on preparing a superhydrophobic surface with resistance to high-speed water impact. Firstly, reduce the impact pressure by PTFE for its low acoustic impedance.[5] The prepared superhydrophobic coating can withstand a jet impact of 35 m/s; Secondly, efforts should be made to enhance the capillary pressure induced by the microstructure to resist wetting. Usually, this requires a sufficiently dense microstructure. However, these strategies are usually not enough for applying superhydrophobic surfaces in extreme environments. Therefore, a hierarchical porous structure should be useful to dissipate impacting pressure and self-eject the possible invaded water, as well as to deal with other extreme environments such as mechanochemistry, radiation, and corrosion.[1]
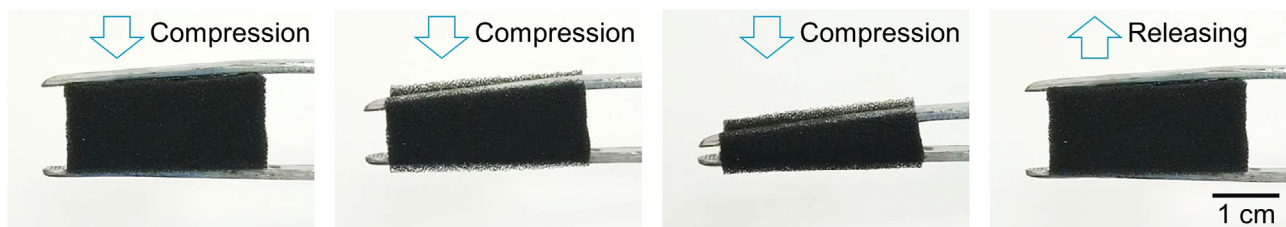
↓ Compression   ↓ Compression   ↓ Compression   ↑ Releasing

1 cm

Figure 1. Flexibility of pristine cuboid PU foam

Here, an immersion-sintering process was adopted to prepare hierarchical porous nanocomposite bulks. We constructed hierarchical porous structures by differing the distribution of nanoparticles, which was caused by immersion and drop coating to form inside fillings and surficial accretion layer of nanoparticles, respectively. The subsequent high-temperature treatment made the PU foam template completely decompose and the nanoparticles re-fuse to form a porous nanocomposite with a self-supporting skeleton. The obtained superhydrophobic bulks have been proven excellent tolerance to linear friction, water/particle impact, high temperature, corrosion, etc. The following section introduces the preparation work before the experiment.

Preparation of PU foam

⏲ Timing: 30 min

This preparation of hierarchical porous nanocomposites involves processing the PU foam with preset specifications, and then using them as templates to load nanoparticles. The porosity of the foam is usually described by PPI, and the larger the PPI value of the foam imply smaller the pores and tend to be blocked during impregnation. According to our experience, the porosity of PU foam should be limited to 200–350 PPI. Too dense foam is not suitable for the impregnation of mixed slurry, while foam with too large porosity is hard to shape. Here we choose PU foam with 300 PPI. The optical photos of PU foam released after compression show good flexibility (Figure 1), which facilitates the absorption of slurry in the impregnation operation.

Refer to the ''key resources table'' section for a list of materials needed for this protocol.

1. Cut the PU foam into a specific shape of a pentagram and cuboid with a cutter (Figure 2).

   Note: The cutting blade should be sharp enough to quickly cut the foam to form a regular surface. If necessary, automatic processing machines should be used to assist in preparation.

2. Weigh and record the shaped foam.

Preparation of nanoparticle slurry

⏲ Timing: 1 h

3. Weigh PTFE and MWCNT nanoparticles with a MWCNT proportion of 12 wt.%.

   ⚠ CRITICAL: Nanoparticles are easily suspended in the air; measurements should be taken to prevent inhalation and adhesion.

4. Add ethanol with a mass ratio of 100–10:1 between ethanol and the aforementioned mixed nanoparticles.

Figure 2. Pentagram cut from polyurethane foam

> ⚠ CRITICAL: Ethanol is hazardous because of its volatility and inflammability. Therefore, a face shield, glove, and protective clothing are needed, and the operation should be carried out in a fume cupboard for safety.

Alternative: Ethanol was chosen here because of its excellent wettability to these two highly hydrophobic nanoparticles, as well as its advantages of low cost and low toxicity. Other organic solvents that can wet these nanoparticles are also allowed.

5. Stir the hybrid aforementioned nanoparticles and ethanol in a high-speed shearing instrument (FA 25, Fluko) for 20 min.
6. Disperse the mixed nanoparticles further in an ultrasound emulsification instrument (VOSHIN-250W) for 20 min. Ensure the hybrid nanoparticles of MWCNT and PTFE are evenly mixed to obtain a uniform slurry (Figure 3).

Note: It is of great importance for nanoparticles to be completely dispersed into a slurry in ethanol. To evaluate the dispersion uniformity of nanoparticles, the fabricated nanocomposite bulk with an MWCNT content of 12 wt.% was used to conduct thermogravimetric testing in nitrogen gas. As shown in Figure 4, the PTFE melted at ~380°C and completely decomposed after 500°C while MWCNT remained, causing a residual mass of 12 wt.%, which is equivalent to the proportion of the MWCNT in the slurry. Therefore, the uniform in composition and concentration of nanoparticles in the slurry is believable after the dispersion treatment.

Preparation of drying and sintering equipment

⏱ Timing: 1 h

7. Use an oven to remove the ethanol carried by the slurry in the PU foam. When preparing the oven for operation, please check the following conditions:
   a. Blowing system with a controllable gas flow rate of 25~250 mL/min.
   b. Temperature control system with a control accuracy of $\pm 1°C$.
8. Prepare a furnace to sinter PU foam preform loaded with nanoparticles. Please check the following conditions before operation:
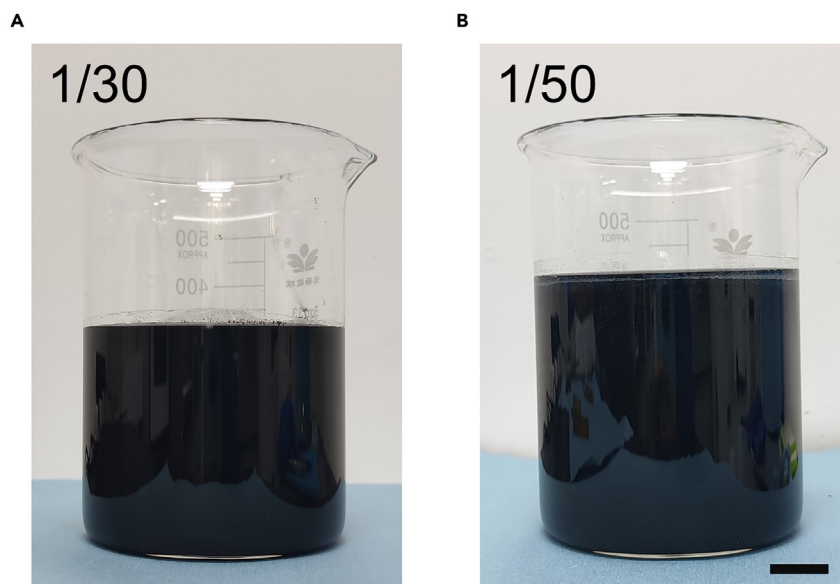
Figure 3. Optical photos of a slurry with uniformly dispersed nanoparticles
Scale bar: 20 cm.

a. Vacuum system under normal conditions which can maintain pressure at −0.1 Pa for more than 5 h.
b. Leak-free gas delivery system.
c. Temperature control system with a control accuracy of $\pm 1°C$.

KEY RESOURCES TABLE

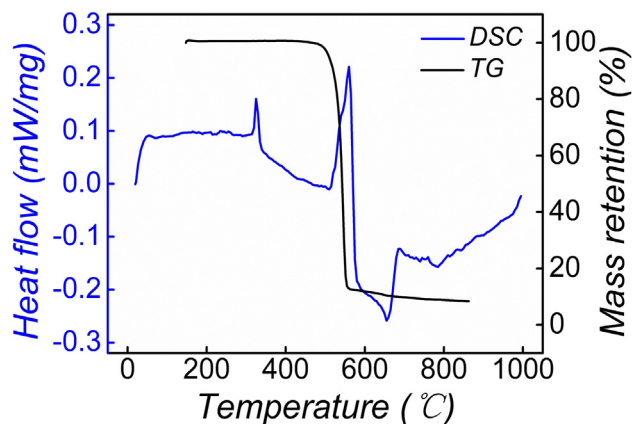| REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
MWCNT	Chengdu Organic Chemicals Co., Ltd.	TNM3 (timenano)
PTFE powder	Aladdin	CAS# 9002-84-0
Ethanol	Sigma-Aldrich	CAS# 64-17-5
PU foam	Shenzhen Jinkenuo Industrial Co., Ltd.	https://shop23ke3q1471942.1688.com/page/index.html?spm=0.0.wp_pc_common_header_companyName_undefined.0
High-purity N2	Shanghai TOMOE Gases Co., Ltd.	CAS# 7727-37-9
Software and algorithms		
Origin 2020	OriginLab	https://www.originlab.com/origin
Movie Maker	Microsoft	https://support.microsoft.com/
Other		
Ultrasound emulsification instrument	VOSHIN-250W	http://www.voshin17.com/pdshowtwo/productshow_11326006.html
High-speed shearing instrument	FA 25, Fluko	http://www.fluko.com/product-center/f862e667-4a6c-4b26-ad4f-a7c549495b65
Drying oven	DHG-9070 (A) (101-1)	http://www.yihengchina.com/
Scanning electron microscopy	Tescan Maia 3, Czech	http://www.tescan-china.com/zh-cn/technology/sem/mira3
High-speed camera	i-SPEED 3	http://www.test-inst.com/products/ix-i-speed-3.html
Vernier caliper	DL92150P	https://www.deli-tools.com/productinfo/info/55964.html
Analytical balances	XS105	https://www.mt.com/cn/zh/home/phased_out_products/Laboratory_Weighing_Solutions/Analytical/Excellence/XS_Analytical_Balance/XS105.html
Electronic scale	XPR5004SC	https://www.mt.com/cn/zh/home/products/Laboratory_Weighing_Solutions/precision-balances/XPR5004SC.html
Mercury porosimetry pore size analyzer	AutoPore V 9600	https://www.micromeritics.com.cn/autopore-v/
500 mL beaker	N/A	N/A
Tweezers	N/A	N/A

Figure 4. TG and DSC curve of prepared nanocomposite with MWCNT content of 12 wt.% in nitrogen gas
Data were adopted with changes from Wu et al., 2023.[1]

Alternatives: The PU foam is cheap and easily available but with poor workability. As a removable template, it is difficult to provide good mechanical properties for the final product. It can be replaced with metal foam,[6] which would be retained in the final product and serve as a mechanical super-stable microskeleton. When the mental foam is applied to our preparation strategy, the compromise of superhydrophobicity caused by the hydrophilic metal microskeleton should be weighed.

STEP-BY-STEP METHOD DETAILS
Immersion of nanoparticle slurry

⏱ Timing: 5 days

1. Immerse PU foam in the slurry with a ratio of nanoparticle and ethanol of 1:30.
2. Dry the PU foam with loaded slurry in the oven.

   ⚠ CRITICAL: The temperature of the oven should not be too high to avoid safety hazards caused by ethanol evaporation. Based on our experience, drying below 100°C is acceptable.

3. Weigh and record the dried PU foam.
4. Disperse the nanoparticle slurry for 5 min in a high-speed shear apparatus (20000 rpm), followed by repeating the operation above three steps for 20–30 cycles.

   Note: Before each repeated impregnation, the nanoparticle slurry should be stirred again to ensure the uniformity of slurry concentration. Considering that the PTFE and MWCNT nanoparticles have already been uniformly mixed (Figures 3 and 4), the operation can be simplified to 5 minutes of dispersion in a high-speed shear apparatus.

5. Repeat the operation of steps 1–4 for another 20–30 cycles but replace the slurry content with 1:50.

   Note: A low nanoparticle load will result in inadequate contact between particles, making it difficult to construct a self-supporting skeleton network during the PTFE melting process. Therefore, staged impregnation is necessary to ensure uniform distribution of nanoparticles and a stable increase of density of loaded PU foam, which is crucial for the mechanical
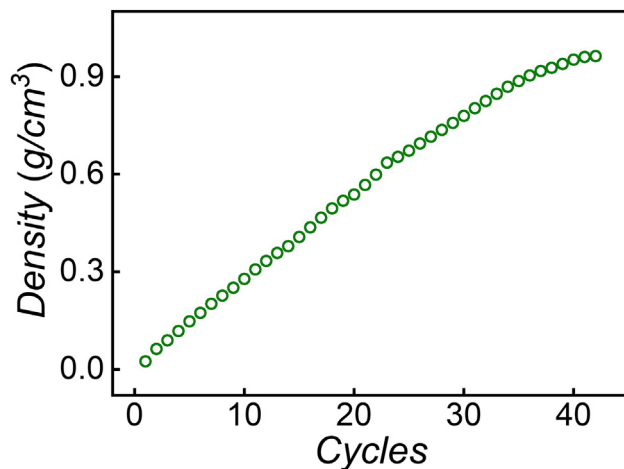
Figure 5. Variation of loaded PU foam density with immersion cycles

properties of the final product. As shown in Figure 5, the density of loaded PU foam increased with immersion cycles to 0.96 g/cm^3.

Dipping the accretion layer

⏱ Timing: 12 h

After filling the interior of PU foam with uniformly distributed nanoparticles, a subsequent drop coating operation is needed to form an extra accretion layer on the surface of loaded PU foam to construct the hierarchical porous structure. Notably, these precautions and safety regulations mentioned in the immersion process should also be followed during this process.

6. Drop coating with the slurry with a ratio of nanoparticle and ethanol of 1:50 on PU foam with loaded nanoparticles inside.
7. Dry the PU foam in the oven at 80°C for 1 h.
8. Weigh the dried PU foam and record.
9. Disperse the nanoparticle slurry for 5 min in a high-speed shear apparatus and followed by repeating the operation above until obtaining the expected thickness of the accretion layer.

   Note: The thickness of the accretion layer on the surface of the fabricated bulk is critical for its domination of the liquid behavior during high-speed water impact, which can be measured by the SEM image of the final product. However, this is a post-evaluation of the sample after thermal forming. Therefore, quantifying the thickness of the accretion layer before sintering is expected provided that the density of the accretion layer is clear, which will be confirmed in the "quantification and statistical analysis".

Sintering of PU preform

⏱ Timing: 5 h

The prepared PU foam preform with an accretion layer is sintered in a tubular furnace. The detailed sintering process is shown as follows.

10. Place the sample in the heating area of the tube furnace and seal the furnace chamber.
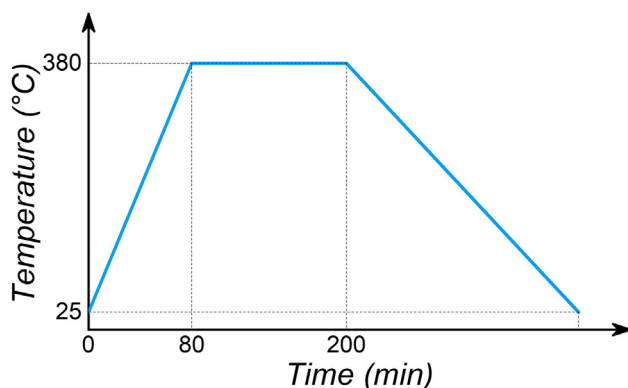
Figure 6. Schematic of the temperature-time profile for thermal forming of the nanocomposite bulk

Note: The sample should be mounted horizontally, maintaining good contact between the sample surface and the platform to avoid the deformation of melted PTFE caused by gravity.

11. Vacuum the furnace chamber and fill it with nitrogen gas. Repeat it to ensure the furnace chamber is in an inert atmosphere.

   Optional: Nitrogen gas was selected for its chemical inertness towards raw materials. Any inert gas was allowed.

12. Set up a heating program that raises the temperature from room temperature (25°C) to 380°C within 80 min, then remaining at 380°C for 2 h, followed by cooling down to room temperature with the furnace (Figure 6).

   ⚠ CRITICAL: The exhaust absorption devices such as liquid absorption or other methods should be set up before discharge emitting into the atmosphere.

EXPECTED OUTCOMES

The nanocomposite bulk with a hierarchical porous structure can be obtained by only a two-step operation of impregnation and high-temperature sintering. Due to the careful selection of raw materials and structural design, the fabricated porous nanocomposites have excellent comprehensive durability. The expected results of the fabricated sample will be consistent with our previous paper on Matter (Wu et al., 2023), and some criteria listed below.

Expected hierarchical porous structures

After the sintering treatment, the PU template completely decomposed, and PTFE melted and coated MWCNT to form a self-supporting skeleton (Figures 7 and 8A). As shown in Figure 8B, the
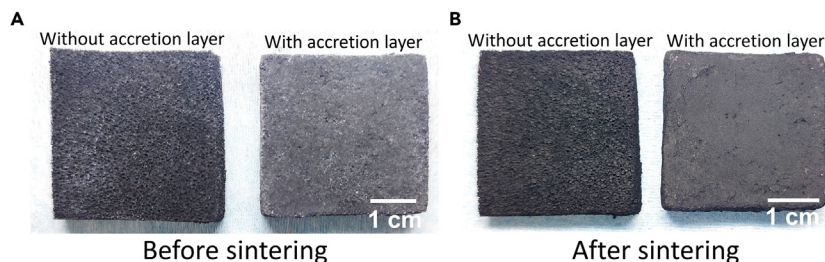

Figure 7. Optical photos of PU foam in immersion and sintering processes
Optical photos of PU foam performed without and with accretion layer (A) before and (B) after sintering. Data were adopted with changes from (Wu et al., 2023).[1]
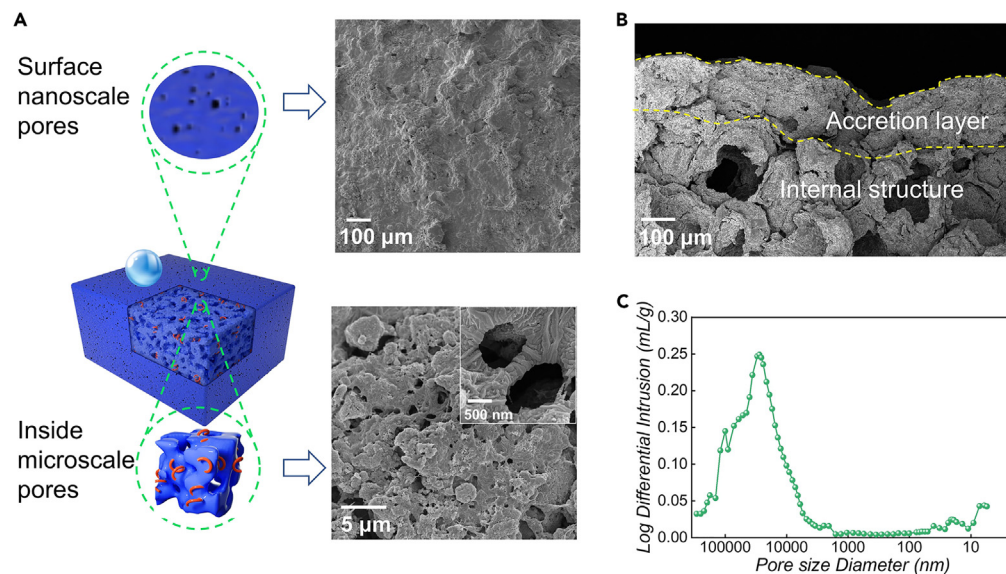
Figure 8. The hierarchical porous structure of the final nanocomposite material
(A) Schematic diagram and the corresponding SEM images of the hierarchical porous nanocomposite, indicating the differences in surface and internal pore characteristics. Data were adopted with changes from (Wu et al., 2023).[1]
(B) Cross-section SEM images of prepared hierarchical porous nanocomposite. The dense accumulation layer on the surface is approximately 100–200 μm, displaying a completely different morphology from the internal macropores.
(C) Pore size distribution of prepared hierarchical porous composite materials.

nanoparticles filled inside the foam form a microscale porous structure after PU removal, while the surface accretion layer forms a denser nanoscale porous structure. The pore size distribution can be clearly presented in the results of the mercury intrusion test (Figure 8C). The pore size is mainly distributed in two ranges, 10–100 μm and 5–50 nm. The sample has a porosity of 37.2%, a total pore volume of 0.26 mL/g, and a pore area of 7.8 m^2/g. This homogeneous material and hierarchical structure not only ensure good superhydrophobicity but also provide support for extreme environmental resistance.

Expected robust superhydrophobicity

After immersion and sintering, both the interior and surface of the porous nanocomposite bulk should have homogeneous superhydrophobicity. As shown in Figure 9A, the water drops are proved in the Cassie-Baxter state on the broken nanocomposite bulk. In addition, this unique hierarchical structure has a strong ability to entrap the air layer. When immersed in boiling water, the mirror reflection of the air layer can still be observed (Figure 9B). Importantly, when subjected to high-speed water jet impact, the surface of the porous bulk still maintains no water adhesion, which is attributed to the dense surface accretion layer and the regulatory effect of the hierarchical porous structure on the invaded water (Figure 9C).

Expected excellent sandpaper abrasion

Due to the inherent hydrophobicity of the raw materials and the micro/nano hierarchical rough structure (with homogeneous superhydrophobicity), the prepared superhydrophobic bulk should have excellent resistance to sandpaper abrasion. Under a pressure of 5 kPa by sandpaper of 80 grit, the surface of the nanocomposite bulk can still maintain good superhydrophobicity even after linear friction distance of 48 m (Figure 10). The porosity of nanocomposite bulk continuously provides micro/nano hierarchical structures, leading to an unchanged superhydrophobicity throughout the friction process.
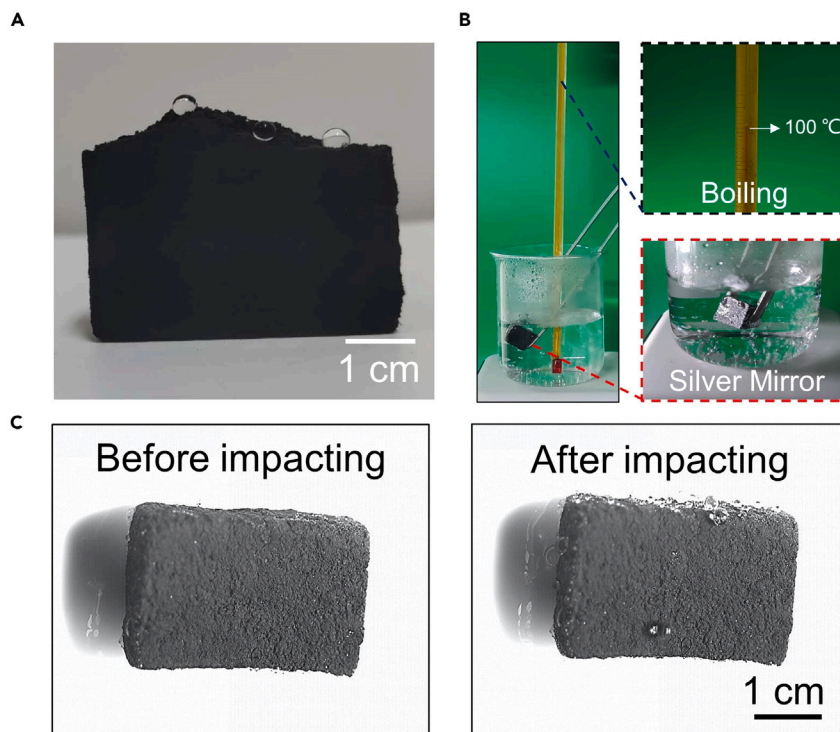
Figure 9. Robust superhydrophobicity of fabricated nanocomposite bulk

(A) Optical photo of broken nanocomposite bulk with water drops, suggesting internally homogeneous superhydrophobicity.

(B) Optical photos of nanocomposite in boiling water. The silver mirror on the bulk surface indicates the robustness of the entrapped air layer.

(C) Optical photos of fabricated nanocomposite before and after water jet impact with a velocity of 84 m/s. Data were adopted with changes from (Wu et al., 2023).[1]

Expected significant mechanical properties

The hard and wear-resistant superhydrophobic nanocomposite bulk should have good mechanical properties. Compared with the flexible foam template, the prepared superhydrophobic porous nanocomposite bulks are strengthened and can bear the weight of 2 kg (Figure 11A). The prepared bulk exhibits excellent compressive strength (2.9 MPa) and modulus (8.4 GPa) due to the reinforcing effect of CNTs on PTFE. These mechanical properties can meet the general stress environment (Figure 11B).

QUANTIFICATION AND STATISTICAL ANALYSIS

Shape the nanocomposite

It is very important to obtain pre-sized nanocomposite products. Therefore, the changes in size and density of the initial PU foam template should be predictable in the impregnation and sintering process. We define the volume change rates after loading nanoparticles and sintering as η_1 and η_2.

$$\eta_1 = \frac{V_1}{V_0}, \eta_2 = \frac{V_2}{V_1}$$

Where V_0, V_1, and V_2 are the volume of the pristine PU foam template, the loaded PU foam preform, and the final product. After our measurement and calculation, the impregnation process leads to a slight expansion of the shape ($\eta_1 = 1.27$), and on this basis, subsequent sintering will lead to size shrinkage ($\eta_2 = 0.885$).
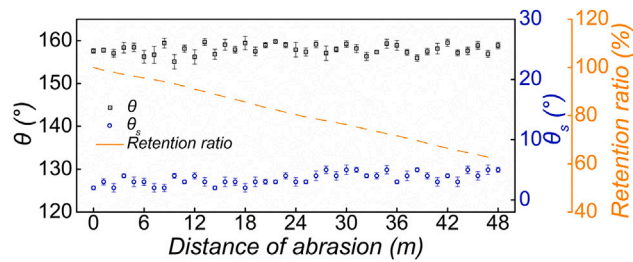
Figure 10. Variation of the wettability of the prepared nanocomposites with abrasion distance, tested with 80 grit sandpaper at pressure of ~5 kPa

Data were adopted with changes from (Wu et al., 2023).[1]

Regulation of nanocomposite bulk density

The density of the final product determines the pore characteristics and mechanical properties, which thus should be customizable. There is an exercisable scheme to regulate the density of nanocomposite bulk demonstrated below:

The density of pristine PU foam (ρ_0) was expressed as:

$$\rho_0 = \frac{m_0}{V_0}$$

After immersion treatment in nanoparticle slurry, the density of loaded PU foam (ρ_1) without accretion layer was:

$$\rho_1 = \frac{m_1}{V_1} = \frac{m_0 + M}{\eta_1 V_0}$$

After sintering, the density of the final product (ρ_2) can be expressed as:

$$\rho_2 = \frac{m_2}{V_2} = \frac{M}{\eta_2 V_1} = \frac{M + m_0 - m_0}{\eta_1 \eta_2 V_0} = \frac{\rho_1 \eta_1 V_0 - \rho_0 V_0}{\eta_1 \eta_2 V_0} = \frac{\rho_1 \eta_1 - \rho_0}{\eta_1 \eta_2}$$

Obviously, the density of the final nanocomposite is determined by ρ_1, which can be calculated by measuring the mass of loaded nanoparticles in the immersion process.

Tailoring the thickness of the accretion layer

After the initial impregnation process, the nanoparticles fill porous foam and are anchored by the foam frame. The subsequent drop coating will accumulate nanoparticles on the surface of loaded PU foam. Here, we quantify the density of the accretion layer as a reference value, whose thickness is dominated by drop coating.
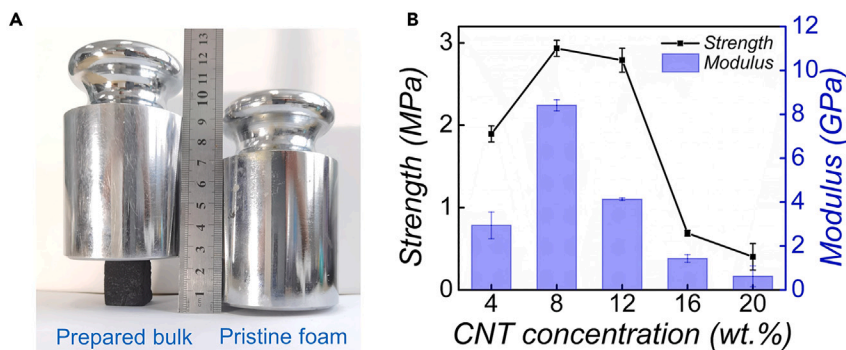

Figure 11. Mechanical properties of prepared nanocomposite bulk

(A) Optical photo of fabricated nanocomposite bulk and pristine PU foam templet with 2 kg loads on them.

(B) Variation of compressive strength and compressive modulus of fabricated nanocomposite bulks with CNT content.
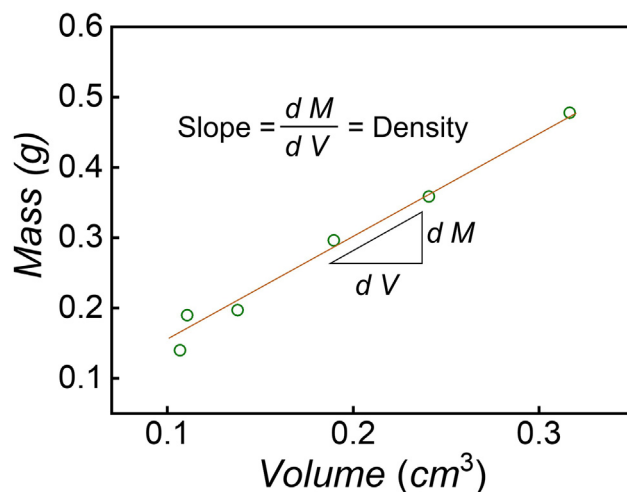
Data were adopted with changes from (Wu et al., 2023).[1]

Figure 12. Variation of mass of accretion layer with its volume

For a given surface, we recorded the thickness of the accretion layer under different impregnation masses and calculated the volume of the accretion layer. As shown in Figure 12, there is a significant linear relationship between mass and volume. And the density of the accretion layer is the slope of the fitting curve (1.5 g/cm^3). Therefore, the thickness of the accretion layer can be customized by monitoring the mass of the drop coating and the surface area it adheres to. This provides a reference value for preparing a customized accretion layer.

Selection of slurry concentration

The ratio of nanoparticles to ethanol in the slurry has a significant impact on the impregnation process. In our experience, too high nanoparticle proportion will result in the inadequate filling of foam. While the lower nanoparticle content may lead to slow impregnation and excessive organic solvent pollution. According to the above steps, we recommend a ratio of 1:10∼40 between the nanoparticles and ethanol in the initial impregnation stage, and a ratio of 1:40∼60 should be selected for later densification filling and surface dipping. It should be noted that when slurry with various concentrations was used, their settling characteristics should be first evaluated. As shown in Figure 13, the lower the content, the faster the settling speed of the slurry. Therefore, it is necessary to perform step-by-step impregnation.

LIMITATIONS

The mechanical properties and pore characteristics of porous nanocomposite bulk are very sensitive to the loading number of nanoparticles (density of the final product). Although multiple impregnations contribute to nanoparticle load, however, it is time-consuming and sensitive to the slurry characteristics. However, once the surface pores are blocked, the ideal loading of PU foam will not be formed. Therefore, any method for facilitating nanoparticle loading is feasible. If necessary, pressure-assisted impregnation can be used based on specially designed molds. This protocol only demonstrates a rationalized impregnation method to obtain PU performs with ideal nanoparticle loading.

TROUBLESHOOTING

Problem 1

Nanoparticles should fill inside the foam and stack on the surface, which is key to constructing hierarchical porous structures. However, improper impregnation operation from slurry/template selection will result in a low loading density of PU foam preform, failing to reach the set value. As shown in Figure 14A, when the 300-PPI foam is impregnated with slurry with 1:30 proportion of nanoparticle
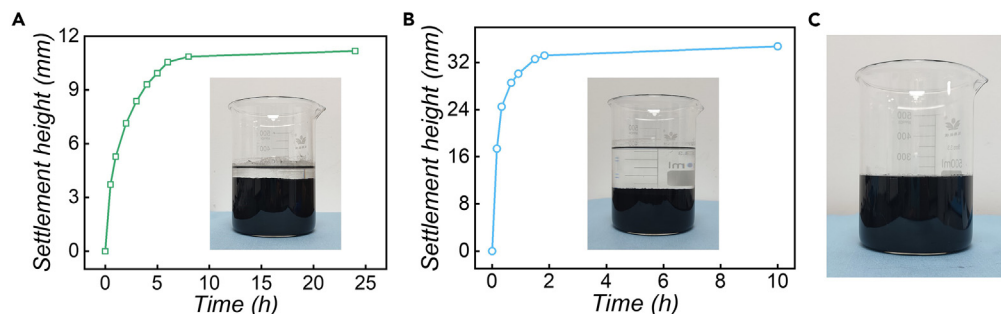
Figure 13. Sedimentation characteristics of nanoparticle slurries with different concentrations
Variation of normalized sedimentation height with time for slurry with ratios of nanoparticle with ethanol of (A) 1:30 and (B) 1:50. Inserted optical photos show the final state of slurry. (C) Optical photo of nanoparticle slurry with ratios of nanoparticle with ethanol of 1:15, suggesting the stability of the slurry.

and ethanol, the density of PU foam only reaches 0.33 g/cm^3 after 15 cycles of impregnation. The slurry with high nanoparticle content tends to have an excessive accumulation of nanoparticles near the surface in the later stage of impregnation, causing blocking and impeding the inside filling of nanoparticles. Similarly, when using 450-PPI foam for impregnation, the density growth is also stalled after 17 cycles of impregnation although the thinner slurry with 1:50 nanoparticle content is used (steps 1–5 in the "step-by-step method details").

Potential solution

The foam porosity and slurry concentration should be selected prudently to achieve the ideal load density. During the impregnation process, the staged impregnation strategy with different slurry concentrations should be followed. One feasible strategy can be adopted to gradually increase the loading of PU foam preform by gradually reducing the content of nanoparticles during the impregnation process.

Problem 2

When it comes to practical applications, cost affordability issues need to be considered. For our bulk materials, the MWCNTs play a critical role in enhancing PTFE in the final product but will inevitably increase the economic burden (steps 1–5 in the "step-by-step method details").

Potential solution

The ratio of additional MWCNT has a significant impact on the mechanical properties and density of the product (Figure 11B). Fortunately, as a higher nanoparticle concentration will lead to aggregation and may be inadvisable, the optimal addition of MWCNT of only 12 wt.% can make a trade-off between comprehensive consideration, especially the mechanical properties.

Problem 3

Although the density of loaded PU preforms and accretion layer have been quantified, accurately controlling of final product size is difficult, whose error can be limited to only $\pm$ 0.5 mm. Any error from foam templet cutting and deformation during the impregnation and sintering process will lead to uncontrollable final size (steps 1–5 in the "step-by-step method details").

Potential solution

The good flexibility of the original foam template makes it difficult to shape accurately, which can be avoided by cutting the foam preform that has been hardened after impregnation. At the same time, the errors caused by deformation can also be effectively reduced.
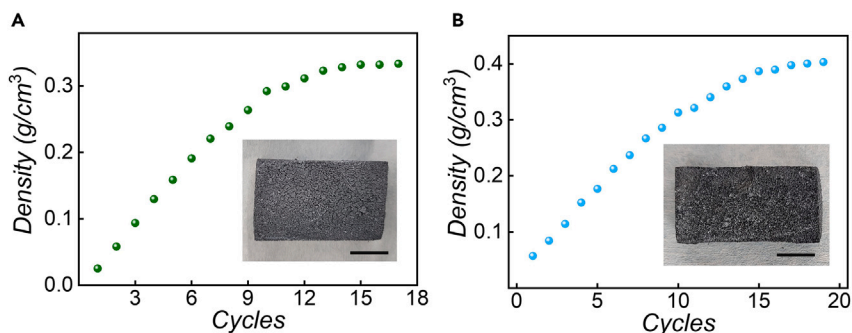
Figure 14. The density of loaded PU foam preforms in improper impregnation operation
Effect of immersion-drying cycles on the density of loaded PU foam preform with (A) 300 PPI using slurry with 1:30 proportion of nanoparticle and ethanol and (B) 450 PPI using slurry with 1:50 proportion of nanoparticle and ethanol. Scale bar: 2 cm.

Problem 4

The selection of PTFE and PU is deliberate because the construction of porous structures depends on the complete decomposition of PU foam before the melting of PTFE. Therefore, the sintering temperature must be above 380°C to melt PTFE. Although our method supports the preparation of 3D hard bulks and endows them with hierarchical porous structures, large-scale preparation is still limited by the templates and sintering equipment (step 10–12 in the "step-by-step method details").

Potential solution

3D printing may work to obtain the ideal large-scale product. When considering implementing this plan, it is necessary to optimize the template to blend it into the slurry. Commercially available nanoparticles such as PS and PP, have a wider range of decomposition temperatures and size selectivity and should be able to meet demand.

Problem 5

The crystalline morphology of PTFE after melting is related to the cooling rate after sintering. Excessive cooling rate results in insufficient movement of PTFE chain segments and an inability to form sufficient hierarchical structures,[7] which leads to a compromise in superhydrophobicity (step 12 in the "step-by-step method details").

Potential solution

Although the melting of PTFE and the decomposition of PU during the sintering process are predictable, careful examination of the sintering procedure is still necessary, especially the cooling rate. To form an expected hierarchical structure, too rapid and too slow cooling should be avoided. Cooling in the furnace to room temperature (15–30°C) is feasible.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Nan Wu (lierenwn@nudt.edu.cn).

Technical contact

Technical questions about this protocol should be directed to the technical contact, Binrui Wu, (binruiwu@foxmail.com).

Materials availability

This study did not generate any unique reagents.

Data and code availability

This study did not generate any datasets and code.

AUTHOR CONTRIBUTIONS

Conceptualization, Y.M., B.W., and M.K.T.; methodology, Y.M., B.W., and N.W.; validation, B.W., N.W., S.X., C.Y., and X.Y.; writing – original draft, Y.M.; writing – review and editing, Y.M., N.W., and B.W.; investigation, Y.M., N.W., and C.P.; funding acquisition, N.W., C.P., and M.K.T.; resources, N.W., S.X., C.Y., and X.Y.; supervision, N.W., C.P., and X.Y.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Wu, B., Meng, Y., Peng, C., Yang, J., Xing, S., Wu, N., Yin, C., Yang, J., Bai, S., and Tiwari, M.K. (2023). Porous bulk superhydrophobic nanocomposites for extreme environments. Matter 6, 1992–2004.

2. Luo, H., Yang, M., Li, D., Wang, Q., Zou, W., Xu, J., and Zhao, N. (2021). Transparent Super-Repellent Surfaces with Low Haze and High Jet Impact Resistance. ACS Appl. Mater. Interfaces 13, 13813–13821.

3. Donati, M., Lam, C.W.E., Milionis, A., Sharma, C.S., Tripathy, A., Zendeli, A., and Poulikakos, D. (2020). Sprayable Thin and Robust Carbon Nanofiber Composite Coating for Extreme Jumping Dropwise Condensation Performance. Adv. Mater. Interfaces 8, 2001176.

4. Kim, S., Wu, Z., Esmaili, E., Dombroskie, J.J., and Jung, S. (2020). How a raindrop gets shattered on biological surfaces. Proc. Natl. Acad. Sci. USA 117, 13901–13907.

5. Peng, C., Chen, Z., and Tiwari, M.K. (2018). All-organic superhydrophobic coatings with mechanochemical robustness and liquid impalement resistance. Nat. Mater. 17, 355–360.

6. Qing, Y., Shi, S., Lv, C., and Zheng, Q. (2020). Microskeleton-Nanofiller Composite with Mechanical Super-Robust Superhydrophobicity against Abrasion and Impact. Adv. Funct. Mater. 30, 1910665.

7. Meng, Y., Xing, S., Tang, J., Liu, H., Lyu, J., Wang, S., Yin, C., Yi, X., and Wu, N. (2023). Robust interface-free superhydrophobic polymer-based composites with recoverable and anti-icing properties. Prog. Org. Coat. 174, 107224.