Protocol for growing silica nanowires on various substrates to enhance superwetting and self-jumping properties

The protocol outlines the steps for growing silica nanowires on various substrates such as glass and stainless-steel foil. Silica nanowires are grown by thermal chemical vapor deposition via a vapor-liquid-solid mechanism, in which silicon wafers are used as silicon sources and platinum films as catalysts. This protocol can be used to grow silica nanowires on other substrates such as quartz filter, quartz sphere, alumina plate, and silicon wafer, provided the substrate materials can tolerate the temperature during process heating.

Highlights
A simple, low-cost, and efficient approach for creating surface nanostructures
Protocol facilitates the growth of silica nanowires from silicon wafers
Promising for superwetting and self-jumping properties

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Protocol

Protocol for growing silica nanowires on various substrates to enhance superwetting and self-jumping properties

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SUMMARY
The protocol outlines the steps for growing silica nanowires on various substrates such as glass and stainless-steel foil. Silica nanowires are grown by thermal chemical vapor deposition via a vapor-liquid-solid mechanism, in which silicon wafers are used as silicon sources and platinum films as catalysts. This protocol can be used to grow silica nanowires on other substrates such as quartz filter, quartz sphere, alumina plate, and silicon wafer, provided the substrate materials can tolerate the temperature during process heating. For complete details on the use and execution of this profile, please refer to Lee et al. (2019), Tsai and Shieh (2019), and Tsai et al. (2021).

BEFORE YOU BEGIN
There are many ways to fabricate surface nanostructures on substrates. Several factors are to be considered, such as their applications, large-scale production, adhesion, stability, production cost, and safety. In this study, we adopt a simple yet effective method for fabricating abundant silica nanowires on various substrates. The nanowires adhere well to the substrate by in situ heating during the process (Tsai and Shieh, 2019), and their diameters can be reduced to sub-10 nm by dewetting the thin metal film (Lee et al., 2019). The following protocol describes the specific steps for growing silica nanowires on metal foils and meshes. Using this method, nanowires can be grown on substrates thinner than a human hair, which has led to the discovery of self-jumping metals (Tsai et al., 2021).

We grow silica nanowires using a vapor–liquid–solid (VLS) mechanism. In contrast to most studies, we use silicon (Si) wafers instead of silane gas as the silicon source. To generate silicon-containing vapor, we deposit a platinum (Pt) thin film on the silicon wafer for active oxidation, which facilitates the growth of the silica nanowires on another substrate. The following section describes the preparation process used before the growth experiments.

Pretreatment of silicon wafer and substrates
© Timing: 30 min

This protocol requires a clean pretreatment of the sample, followed by the deposition of a metal film to be used as a catalyst:

1. Before growing the nanowires, the silicon wafers and substrates (Cu foil, steel foil, steel mesh, quartz plate, quartz filter, and any other materials that can sustain the heating process
temperature) must all fit in the high-temperature furnace. For our furnace, we use the one-inch diameter dimensions with a 10 cm heating zone. The maximum sample size permitted is \(\frac{1}{24}\) cm; however, the size can be increased in larger furnaces.

2. Use silicon wafers as the silicon source for growing nanowires. In most cases, we adopt a single-crystal p-type silicon wafer with a resistivity of 1–100 ohm-cm. The wafer quality is not a critical parameter for growing nanowires. In our experience, cheaper polysilicon wafers also allow growth.

3. Deposit Pt thin film on both the Si wafer and the target substrates via a sputtering coater (SEM coater, SPI Supplies).
   a. For one-sided nanowire decorations, use a piece of Si wafer as the Si source. For double-sided nanowire decorations, place two pieces of Si wafer near the sample to simultaneously grow nanowires on both sides.
   b. Ultrasonically clean the samples with acetone, deionized water, and isopropanol for 9 min. Dry the samples using N\(_2\) purging prior to use.
   c. Deposit thin Pt films by sputtering on all samples (including silicon wafers and steel foils). The sputtering current is \(\approx 10\) mA, the pressure is \(\approx 0.2\) Torr, and duration is a few seconds (5–60 s) that determines the thickness of the thin metal film. For the silicon wafer, the deposition time is 10 s while that of metal foils is 30 s.
   d. To evaluate the thickness of the Pt film, we first deposit a correction fluid as a mask before Pt deposition and then remove it by ultrasonic acetone cleaning to create a step for tip scanning in atomic force microscopy (AFM). Compared to a previous study in which the film may break into droplets (Shakthivel et al., 2019), this method allows the creation of a step down to less than 2 nm (Lee et al., 2019). Pt has a fine grain size relative to Au, which is beneficial for thinner coatings. Figure 1 shows an AFM image with the corresponding depth profile obtained after 60 s of sputtering. An enlarged SEM image of the edge of the Pt film is shown in Figure 1C.

**Note:** Since the high roughness of metal foils is not suitable for the thickness evaluation by AFM, we use a silicon wafer as a flat substrate to evaluate the thickness in this step.

**Alternatives:** Pt thin films are used as catalysts to assist in growing nanowires. High uniformity and small grain size count as the advantages of Pt. Pt alternatives include Au (Shalav et al., 2011), Cu (Gomez-Martinez et al., 2016), and Ni (Shakthivel et al., 2019). The process temperature could be decreased further using Au, but the coating uniformity and dewetting behavior must be considered.
CRITICAL: Samples should be clean; otherwise, they affect the subsequent Pt deposition and nanowire growth.

Sample configuration for growing silica nanowires

4. Stack the silicon wafers and samples layer by layer and separate them with a curved quartz boat or using quartz spacers with a spacing of 5 mm in a high-temperature furnace (Figure 2). For the silicon wafers, place the platinum-coated side toward the sample.
   a. Using solid silicon wafer as a silicon source lowers the melting point of the alloy (Pt deposited on the silicon wafer), which ensures that the Si is easily etched by diluted oxygen to form SiO vapor.
   b. The fabrication process is easy and safe because silane gas is not required in this process.

Note: The distance between the silicon wafer and the sample is not crucial for growing nanowires. However, when the two are too close, there is a risk of disturbing the airflow and even bringing them into contact, which can be detrimental in growing nanowires.

5. We use a high-temperature furnace to grow nanowires. While preparing for the operation of the furnace, check the following conditions:
   a. the vacuum system under normal conditions (base pressure, leak rate, pumping time, and pump oil level)
   b. the cooling water system with standard pressure
   c. the gas delivery system without leakage

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | | |
| Acetone | Echo Chemical Co., Ltd | CAS#67-64-1 |
| Ethanol | Echo Chemical Co., Ltd | CAS#64-17-5 |
| Propanol | Echo Chemical Co., Ltd | CAS#67-63-0 |
| n-Hexane | Fisher Chemical | CAS#110-54-3 |
| Copper foil | Alfa Aesar | CAS#7440508 |
| Steel foil | Starek Scientific Co., Ltd | https://www.sciet.com/product/group/1163678 |
| Steel mesh | Homytech | http://homytech.com/ |

(Continued on next page)
STEP-BY-STEP METHOD DETAILS

Typical parameters are listed in the following table for growing silica nanowires by high-temperature tubular furnace equipment.

| Parameter          | Amount  |
|--------------------|---------|
| H₂ flow rate       | 0–200 sccm |
| Ar flow rate       | 0–100 sccm |
| Base pressure      | 10⁻¹⁻¹ torr |
| Working pressure   | 1–10 torr  |
| Temperature        | 830°C     |

**Critical:** Hydrogen is combustible. Hence, a gas sensor is required to monitor the hydrogen concentration in the environment.

**Alternatives:** A vacuum system with high-temperature heating capabilities is an alternative for furnaces. In addition, H₂ and Ar gases can be replaced by other gases (e.g., N₂) (Shalav et al., 2011) as long as traces of oxygen can be controlled for the active oxidation mechanism.

**Nanowire growth**

⊙ Timing: 2 h

Figure 3 shows a schematic and photograph of the system used for growing silica nanowires in a high-temperature furnace. The tubular quartz tube is 2.5 mm in diameter and 100 cm in length. The maximum temperature is ~1050°C.

1. After precleaning and Pt deposition, stack the samples layer by layer (Figure 2) and place them at the center of the furnace. The operating procedures are as follows:
   a. The reaction gases include H₂ and Ar. The flow rate ratio affects the growth rate of nanowires. Typically, set H₂ and Ar gases at flow rates of 70 and 40 sccm, respectively, on the metal foil samples.
b. Set the working pressure during the process at 5 Torr.

c. After pressure stabilization, heat the chamber to a growth temperature of 830°C. The heating duration, adjusted from 0 to 60 min, determines the length of the nanowires.

d. After growing the nanowires, cool the furnace system to 510°C under Ar and H₂ flow. Then, turn off H₂ for subsequent cooling. When the temperature reaches 200°C, stop Ar gas flow, and remove the samples. Figure 4 shows a schematic of the temperature-time profile with typical gas flow rates.

Surface treatment

© Timing: 2 h

2. The as-prepared nanowire samples have superhydrophilic properties, which offer substrates with antifogging properties (Tsai and Shieh, 2019). We use tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (F₁₃-TCS) to modify surfaces with a low-energy molecule, which makes the surfaces superhydrophobic (Beck et al., 2002). The chlorosilanes connect covalently to the silica substrates, providing a stable surface with low surface energy.

a. Figure 5 shows the surface modification experiment performed by injecting 5-µL F₁₃-TCS into the inverted Petri dish at 210°C.

b. Deposit a water drop on the surface of the sample to confirm the success of the F₁₃-TCS treatment. Successful treatments cause the water droplets to stand on the surface.

Note: F₁₃-TCS reacts with water. Hence, before injecting F₁₃-TCS into the Petri dish, the hot plate must be set above the boiling point of F₁₃-TCS (192°C) to keep the substrate surface dry.

EXPECTED OUTCOMES

Although appropriate conditions are required to grow the silicon oxide nanowires, the growth rate of the nanowires is remarkably high. Figure 6A shows the SEM image obtained after immediately stopping the heating when the temperature was increased to 830°C. This indicates that the nanowires could grow immediately without holding the temperature. Figures 6B and 6C show the SEM
images for heating times of 30 and 60 min, respectively, showing that the length of the nanowires can be controlled by the growth time.

Silica nanowires can be grown on many substrates that can sustain the process temperature (830°C). Figure 7A shows an SEM image of nanowires grown on a stainless-steel foil with a thickness of 10 μm, which is thinner than that of human hair. The structure and composition of the nanowires were obtained by transferring them to TEM grids with carbon films using ultrasonic vibration for imaging (Figure 7B). The inset in Figure 7B shows the selective diffraction pattern of the nanowire, which shows their amorphous structure. The nanowires were composed of silicon and oxide with an O/Si ratio of 1.73, as determined by EDS analysis (Figure 7C). The silicon-rich dioxide supports the hypothesis that the silicon source may originate from SiO vapor.

These nanowires provide substrate materials with unique properties. For example, as we treated the nanowires with F13-TCS, the surface exhibited superhydrophobic properties, creating an air layer underwater to repel water. Figure 8 shows the samples submerged in water under lighting from the right. Compared to the normal foil, the sample with superhydrophobic nanowires showed a shiny appearance, indicating that an air layer was created on the surface to enhance the reflection of light (Larmour et al., 2007).

Interestingly, we observed that these hydrophobic nanowires enable the metal foil to self-jump out of the surface (Methods video S1). This finding indicates that the water surface tension is sufficiently high to eject lightweight materials with hydrophobic surfaces (Tsai et al., 2021).

This protocol facilitates nanowire growth on several materials. Previous studies have deposited Si thin films on other substrates to grow silica nanowires (Shakthivel et al., 2019). In this protocol, the fabrication process does not require Si thin-film deposition. Instead, we used other Si wafers with a Pt coating to deliver the Si source. Figure 9 shows an example of a quartz plate (Tsai and Shieh, 2019). With tiny invisible nanowires, the plate demonstrated a highly transparent and superhydrophobic appearance. Notably, the transmittance can be further increased even when the plate surface is decorated with nanowires.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

The generation of SiO vapor is a key step in the active oxidation mechanism in growing silica nanowires. With the help of metals such as Pt, when SiO vapor is adsorbed into the metal, nanowires can be grown by the vapor—liquid—solid (VLS) mechanism. The SiO vapor is assumed to be generated by the
oxygen etching of the silicon substrate at a very low oxygen partial pressure. The corresponding critical partial pressure was influenced by the temperature, which increased as the temperature went up. Above the critical pressure, passive oxidation dominates rather than active oxidation, thereby inhibiting SiO formation. To prevent silicon dioxide formation, increasing the temperature to >900°C to raise the critical pressure is a common condition for generating active oxidation reactions. However, in our experiments, we found out that the process temperature in the Pt-Si system could be reduced to 830°C by controlling the amount of residual oxygen in the input gas. We used a stainless-steel mesh as a substrate to examine the length of the nanowires, which allowed us to observe the nanowires with SEM without either cutting or destroying the nanowires. Figure 10 shows SEM observation results of the growing silicon oxide nanowires for 30 min at a fixed hydrogen flow rate of 150 sccm. These results revealed that its growth rate increased with an increase in the argon flow rate and reached a maximum value at 25-sccm Ar. Since pure argon is an inert gas, it does not affect the partial pressure of hydrogen. Therefore, an increase in the growth rate indicates the presence of ultra-low levels of oxygen in argon, which provides the necessary source for the growth of the nanowires. However, when the argon flow rate is further increased, the growth rate decreases, indicating that excess argon gas brings excess oxygen, which is detrimental to the active oxidation process.
An alternative source of SiO production is the reaction of H₂ with SiO₂ (Shakthivel et al., 2019). The introduction of H₂ resulted in a small amount of oxygen and directly produced SiO to promote nanowires’ growth. Figure 11 shows the SEM results of varying the hydrogen flow rate at a fixed argon flow rate of 25 sccm, illustrating that the highest growth rate was achieved when the hydrogen flow rate was increased to 150 sccm. Similarly, the growth rate decreased when hydrogen gas was further increased. These results illustrate that the gas flow rate is crucial in controlling the growth of silica nanowires. The most favorable conditions for growing silica nanowires on the stainless-steel mesh in our system were: working pressure of 10 Torr and gas flow rate of 150/25 sccm for hydrogen and argon.

LIMITATIONS
Growth conditions were sensitive to oxygen concentration. However, oxygen gas was not intentionally introduced during this process. Therefore, the optimal conditions vary depending on the operating system. The parameters of this method are used as references. The optimal conditions for the other systems should be established. In addition, since silica nanowires were also grown on the silicon wafer, if necessary, they must be removed before reusing the wafer.

TROUBLESHOOTING
Problem 1
No nanowires were observed on the substrates (step 1 in “step-by-step method details”).
Potential solution
Check if the temperature is above the set point, and whether the position of the sample is close to the heating zone.

Check the Pt film coating. After deposition, the surfaces of the samples exhibited some metal brightness.

Verify that the gas source is supplied correctly to the system. Figure 12 shows the successful and failed growth of nanowires on the metal mesh. The failed growth was caused by insufficient gas supply.

Problem 2
Nanowires’ growth rate slowed with time (step 1 in “step-by-step method details”).

Potential solution
Silica nanowires grown on the silicon wafer may inhibit the supply of SiO vapor necessary for growing nanowires on other substrates. To grow longer nanowires, the used silicon wafer should be renewed.

Problem 3
Unsuccessful surface treatment by F_{13}-TCS (step 2 in “step-by-step method details”).

Potential solution
F_{13}-TCS is sensitive to humidity. After injecting the F_{13}-TCS into the Petri dish, the dish should be closed as soon as possible. Using a glove box helps reduce the effect of humidity on the performance of the F_{13}-TCS.

Problem 4
The nanowire diameter was determined by the size of the Pt nanoparticles formed after dewetting the Pt thin film. The driving force for dewetting is to decrease the interface energy between the thin film and substrate by heating the film (Thompson, 2012), which results in the agglomeration of the
thin film to form nanoparticles for subsequent nanowire growth. In general, the size of nanoparticles by thermal dewetting decreases with film thickness. Therefore, the nanowire diameter depends on the thickness of the Pt thin film. However, it is difficult to reduce the particle size to as small as the thickness of the thin film by thermal dewetting. (step 1 in “step-by-step method details”)

**Potential solution**
To reduce the particle size by thermal dewetting, the interface energy between the thin films and the substrates should be considered. We proposed two methods to reduce particle size (Lee et al., 2019):

Cleaning the surface with HF, which can remove the native oxide and reduce the surface energy by forming Si-F on the surface.

Using plasma pretreatment before growing nanowires: the plasma bombardment enables further reduction of nanoparticle size.

**Problem 5**
Although our method provides an operating temperature lower than that of silica nanowires typically grown by the VLS mechanism in previous research, the working temperature (830°C) is still high (step 1 in “step-by-step method details”).

Figure 9. Silica nanowires make quartz plate superhydrophobic without the decline of transparency

Figure 10. SEM images of silica nanowires grown on stain steel mesh at various Ar flow rates and a constant hydrogen gas flow rate (150 sccm) (A) 10, (B) 15, (C) 20, (D) 25, and (E) 40 sccm of Ar. Scale bar: 5 μm.
Potential solution

We propose the use of rapid thermal annealing (RTA) as a potential solution. As shown in Figure 6A, nanowires formed even when the heating terminated immediately as the temperature reached 830°C. Therefore, RTA could be useful for substrates that require a small thermal budget. In addition, using plasma may also provide an additional driving force to lower the growth temperature.

Figure 11. SEM images of silica nanowires grown on stain steel mesh at various H₂ flow rates and a constant argon gas flow rate (25 sccm) (A) Bare mesh before nanowire growth, (B) 50, (C) 70, (D) 100, (E) 120, (F) 150, (G) 180, and (H) 200 sccm of H₂. Scale bar: 5 μm.

Figure 12. Silica nanowires that were grown on steel mesh (A) Successful and (B) failed growth. Scale bar represents 10 μm.
RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Jiann Shieh (jshieh@nuu.edu.tw).

Materials availability
This study did not generate any unique reagents.

Data and code availability
This study did not generate any datasets and code.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.xpro.2021.101066.

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AUTHOR CONTRIBUTIONS
Conceptualization, J.S.; methodology, J.S.; validation, G.F.H., J.Y.T., B.W.H., and Y.F.H.; writing – original draft, J.S.; writing – review & editing, J.S.; investigation, J.S., G.F.H., J.Y.T., B.W.H., and Y.F.H.; funding acquisition, J.Y.T. and J.S; resources, J.S; supervision, J.S.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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