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Original article

# Orientated-assembly of rod-like silica particles based on sandwich structure from the superhydrophobic template and the superhydrophilic substrates

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## ABSTRACT

The paper demonstrated a facile approach for the orientated assembly of the rod-like silica particles by sandwich structure from the combined effect of superhydrophobic template and the superhydrophilic substrates. The rod-like particles can be arranged in ring-like, square-like and etc from the confined effect of the template, which will produce an important insight for the orientated assembly of anisotropic particles and the development of the novel functional materials and devices.

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## 1. Introduction

Assembly of anisotropic particles have aroused wide research interest owing to the potential applications in various novel optic devices [1], catalysis [2], chemical biological sensing, field effect transistor [3], and *etc.* Typically, Wang *et al.* [4] reported the self-assembly of CdSe-CdS semiconductor nanorods by shape and structural anisotropy, producing multiple well-defined supercrystalline domains. Chen *et al.* [5] achieved the kagome lattice by designing a building block with the orthogonal self-adjusted coordination number on the particle's surface. Ding *et al.* [6] fabricated 3D colloidal crystals from ellipsoidal  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> core-shell particles by the convective self-assembly in an external magnetic field [7]. Ye *et al.* [8] investigated a class of highly faceted planar lanthanide fluoride nanocrystals nanoplates through interface design [9] induced particle orderly assembly. We developed an effective approach to achieve the well-ordered assembly based on the droplet template and interface assembly, which produces one-step formation of anisotropic assembly from

cake-shaped, and flower-shaped particles, the assemblies showed the special broad reflection signal and improved photo-limit behavior [10]. However, there is a challenge for the fabrication of pattern assembly from anisotropic particles. Recently, Su *et al.* [11] developed an effective approach for the pattern fabrication from small molecular, monodispersed particles based on groove-structured template by sandwich structure. Wang *et al.* optimized the approach for the pattern assembly of monodispersed particles by combined effect of superhydrophobic template and superhydrophilic substrate [12]. Which provides an important insight for the pattern anisotropic assembly. Herein, we extended the method for the fabrication of the pattern assembly from the anisotropic rod-like silica particles based on the sandwich structure consisting of the superhydrophobic template and superhydrophilic substrate, which resulted in the orientated arrangement of the anisotropic rod-like silica particles toward the template direction, producing an important insight for the creation of novel function materials from anisotropic particles.

## 2. Experimental

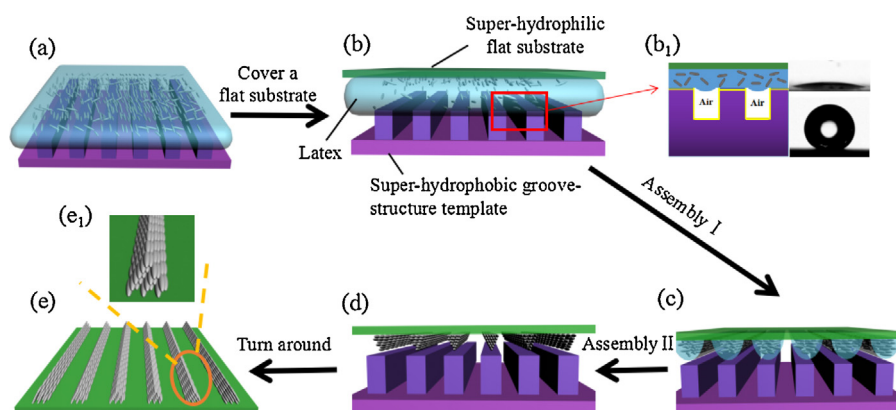
**Synthesis of rod-like silica:** Rod-like silica is synthesized by hydrolysis of tetraethylorthosilicate [13]. Firstly, 0.8 g hexadecyltrimethyl ammonium bromide is dissolved in 140 mL deionized

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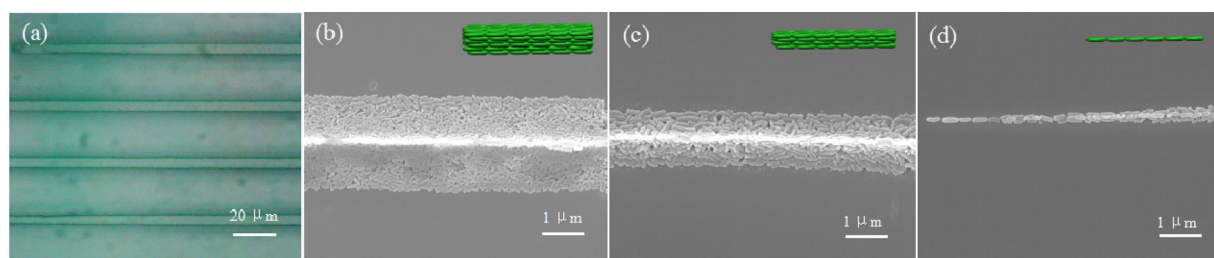
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**Fig. 1.** Schematic of process of pattern assembly based on sandwich approach. (a, b) rod-like Silica latex was carefully dropped onto the superhydrophobic groove-structured template and covered by a flat superhydrophilic transfer substrate, yielding a fixed-gap sandwich assembly system. The assembly system was put at constant template/humidity for 12 h. (b<sub>1</sub>) Schematic of the contact position for the silica particle latex between the superhydrophobic template and superhydrophilic transfer substrate, the inset is the shape of the water droplet on the transfer substrate and the template, respectively. (c, d) With the solvent evaporation, the groove wall array served as wetting defects to control the rupture of silica latex, yielding a micrometer-scale liquid film between the substrate and the top surface of the groove wall. Such a liquid bridge provides a gradually reducing confined space for latex aggregation. (e) Close-packed, linear assembly arrays of silica particle can be formed upon the substrate. After the removal of the groove-structured template by physical peeling, a precisely positioned assembly pattern with an orderly orientation can be generated, the rod-like particles are arranged based on the direction of line.



**Fig. 2.** (a) Optical image and (b-d) SEM images of the as-fabricated linear-assembly from rod-like silica particles. (a, b) 15 wt%, (c) 8 wt%, (d) 2 wt%, respectively. Inset schemes the possible assembly way of the rod-like silica particles.

water in 500 mL conical flask at room temperature (20 °C), and then 4.5 mL ammonium hydroxide was added into it after 15 min. Followed by the magnetic stirring of 15 min to make sure all the homogeneous mixing of the solution, 2.4 mL tetraethoxysilane was added in the system drop by drop with stirring speed at 600 r/min for 5 h. Finally, white power was obtained after the particles were separated by filter and calcinated at 550 °C. Different kinds of particles were obtained when controlling the amount of ammonium (Fig. S1 in Supporting information). The length/diameter ratio gradually changes as the different amount of ammonium added. The results of statistical are shown in Fig. S2 in Supporting information. The component of the sample is characterized by XRD in Fig. S3 in Supporting information.

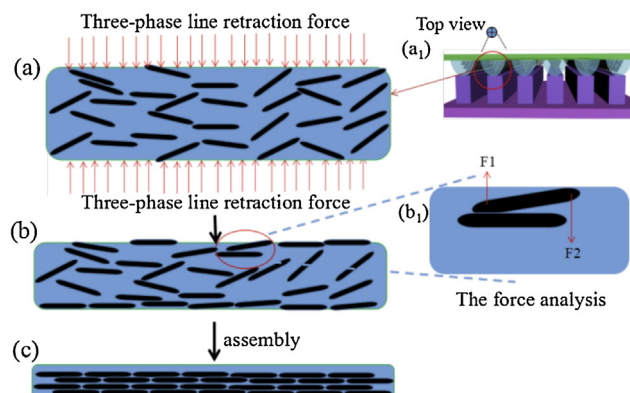
Orientated assembly of rod-like silica based on sandwich approach: A heptadecafluoro-1,1,2,2-tetradecyltrimethoxysilane modified groove-structured silicon substrate with width of 5 μm, gap of 20 μm, and height of 20 μm was held horizontally. Then rod-like silica suspension (5 wt% in water, with 20 μL SDBS (0.2 mg/mL)) was carefully dropped onto the template and covered by a flat substrate, yielding a sandwich assembly. After the assembly system was kept at 20 °C for 12 h, linear-like assemblies were achieved from rod-like silica. It is noted that controlling the gap between the chosen substrate and the groove-structured template at ca. 20 μm is crucial for obtaining a continuous liquid stripe. The process of other pattern assembly was similar except changing the kind of templates, the optic microscopy images of template are shown in Fig. S4 in Supporting information.

Characterization: SEM images were obtained from a Thermo-7500F high-resolution field emission scanning electron microscope.

The X-ray diffraction measurement was carried out on a Rigaku D/max-2500 X-ray diffractometer. The particles were separated from dispersion by HC-3518 centrifugal machine. The particles were calcined at 550 °C for 9 h. The optic photos were obtained by BX51 Upright Metallurgical Microscope.

### 3. Results and discussion

Fig. 1 schemes the whole formation process of linear-like pattern from rod-like silica particles based on sandwich approach. In this case, the liquid membrane containing nanoparticles can be confined in a fixed space, the designed silicon column template



**Fig. 3.** The force analysis of the assembly process.

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