Journal of Colloid and Interface Science 408 (2013) 1–5

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Preparation of disk-like particles with micro/nano hierarchical structures

Zhen Meng, Wenbo Yang, Pengpeng Chen, Weina Wang, Xudong Jia *, Kai Xi *

State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China
Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, PR China
Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 4 January 2013
Accepted 11 July 2013
Available online 24 July 2013

Keywords:
Hybrid
Monodispersed
Self-assembly
Micro/nano hierarchical structure
Superhydrophobic

ABSTRACT

A facile, reproductive method has been successfully developed to produce disk-like microparticles self-assembled from monodispersed hybrid silica nanoparticles under certain circumstance. The disk-like microparticles with micro/nano hierarchical structures could be obtained in large amount under a mild condition and further used to biomimetic design of the superhydrophobic surface of lotus leaf. After traditional surface modification with dodecyltrichlorosiliane, the static contact angle of water on the surface with micro/nano hierarchical structure could reach 168.8°. The method of surface modification could be further simplified by click reaction with the introduction of thiol groups under mild condition. The present strategy for constructing the surface with micro/nano hierarchical structures offers the advantage of simple and large area fabrication, which enables a variety of superhydrophobic applications.

1. Introduction

More efforts have focused on the fabrication of long-range ordered 3D structures from colloids, as the photonic crystals, chemical and biochemical sensors, surface coating, optoelectronic device and other applications attract more attention [1,2]. Self-assembly of nanocolloids strongly depends on the interparticle interaction, particle shape, and narrow particle size distribution [3,4]. Several kinds of methods have been developed for assembling nanoparticles including capillary force, template directed patterning, and surface derivatization [5]. Silica has been widely used in the field of constructing micro/nano-architectures and surface functionalization due to its remarkable colloidal stability, controllable size distribution, and possibility of further functionalization [6–9]. After various kinds of silane coupling agents are used to functionalize the traditional silica particles by stöber procedure, new types of organic–inorganic hybrid silica materials are then obtained. Lee et al. reported the preparation of monodisperse hybrid silica particles with a range of sizes from one to several micrometers. The advantage of the method was a one-pot route, and size-selectivity of the particles could be controlled by the concentration of organosilane and the reaction temperature [10]. Lu et al. published their work on the formation mechanism and size control in one-pot synthesis of mercapto-silica colloidal spheres. They had also mentioned that it was much harder to produce monodisperse mercapto-silica spheres with small sizes (below 200 nm) [11].

Superhydrophobic surfaces have been the focus of considerable research, as they have exhibited great potentials not only for fundamental researches but also for industrial applications, such as the development of self-cleaning surfaces, microfluidics, water proof, anti-corrosion, and so on [12–14]. Surfaces with extreme water repellency are common in plant leaves, especially on lotus leaves [15,16]. The lotus leaf-effect (superhydrophobic and self-cleaning) has been proved to be the result of the surface chemical composition (wax layer) and the surface geometrical structures (micro/nano hierarchical structure) [17,18]. Wenzel's model and Cassie's model were proposed to explain the effect of roughness on hydrophobicity [19,20]. According to these models, the micro/nano hierarchical structures are essential for superhydrophobic surface fabrication. Many methods have been developed to fabricate the surfaces, such as etching (chemical, plasma, and laser), electrodeposition, anodic oxidation, sol–gel process, chemical vapor deposition, and solvent treatment of polymer [14,21–25]. However, due to either the complicated procedures or the high cost in fabrication, practical applications of most of these strategies are still very tough. There have also been some reports that focused on the micro/nano hierarchical structures using silica-based nanoparticles. Qian et al. developed a novel approach to synthesize raspberry-like particles as superhydrophobic materials [26]. Tsai et al.

* Corresponding authors. Address: Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, PR China. Fax: +86 25 83621337.
E-mail addresses: mengzhen@nju.edu.cn (Z. Meng), booksironline@gmail.com (P. Chen), monica0520@gmail.com (W. Wang), jiaxd@nju.edu.cn (X. Jia), xikai@nju.edu.cn (K. Xi).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.07.025

reported a facile method using layer-by-layer assemble of silica particles to fabricate raspberry-like superhydrophobic surfaces. The surface functionalization was also essential to the assembly of particles [27]. These reports have developed a method to synthesize spherical micro/nano hierarchical structures. We wonder if non-spherical micro/nano hierarchical particles assembled with just one kind of monodispersed nanoparticles could also show superhydrophobic properties. We tried to go further into the synthesis of such micro/nano structure with thiol groups, so the thiol-ene click reaction could be introduced to simplify the surface functionalization procedures under more mild reaction conditions.

Based on our previous work [28], herein, we report a facile, reproductive one-step approach for preparing micro/nano self-assembly hierarchical structures, which could be used to construct superhydrophobic surfaces. To the best of our knowledge, this is the first time to report the synthesis of disk-like microparticles in large amount through the self-assembly of monodispersed hybrid silica nanoparticles under a mild condition. And these disk-like micro/nano hierarchical structures could be used to biomimetic the superhydrophobic surface of lotus leaf.

2. Experiment section

2.1. Materials

3-Mercaptopropyl triethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, and (anilinomethyl)triethoxysilane were acquired from Liyang Mingtian Chemical Co., Ltd., China. Ammonium hydroxide and sodium dodecylbenzene sulfonate (SDBS) were supplied by Jiangsu Yonghua Fine Chemistry Co., Ltd., China. Tetrahydrofuran and chloroform were supplied by Nanjing Chemical Reagent Co., Ltd., China. Polystyrene (PS, M_W = 200,000) was acquired from Zhenjiang Chimei Co., China. Dodecyltrichlorosilane, 1-Hexadecene, and Benzil Dimethyl Ketal were acquired from TCI Shanghai Chemical Industry Co., Ltd., China. All chemicals were used as received without further purification. Water was obtained from a Sartorius arium 611DI water purification system.

2.2. Synthesis

3-Mercaptopropyl triethoxysilane (23.8 g) and SDBS (0.026 g) were added to 300 mL of water under vigorous stirring until an emulsion formed. $NH_3{\cdot}H_2O$ (5 mL) was dropwise added to the emulsion (pH = 11.5), and the reaction mixture was allowed to stir (300 rpm) at 40 °C for 48 h. A homogeneous colloidal dispersion (sample A-1) was obtained. Followed by centrifuging, the precipitate was washed 3 times with 150 ml of water and dried under vacuum at 40 °C to get a white powder. Sample A-2 was prepared under the same condition except for the addition of SDBS in different amount (0.13 g). The concentration of SDBS used in the preparation of sample A-2 was the CMC (critical micelle concentration).

Sample B-1 was prepared in the same way as sample A-1 except for the different stirring speed (700 rpm). The white precipitate was formed when the reaction ended. The precipitate was then dried under vacuum at 40 °C to get a white powder.

Sample C-1, C-2, and C-3 were prepared in the same way as sample A-1 except at different temperatures (60 °C for sample C-1 and C-2, 80 °C for sample C-3). When these reactions ended, sample C-1 resulted in a homogeneous colloidal dispersion, while sample C-2 and sample C-3 resulted in a white precipitate. All the essential experimental parameters of these samples were listed in Table 1.

In the case of vinyltriethoxysilane, phenyltriethoxysilane and (anilinomethyl)triethoxysilane, the similar monodispersed nanoparticles with self-assembly hierarchical structures could be formed in the similar emulsion system.

Table 1
The essential experimental parameters for the samples.

Sample	Essential experimental parameters
A-1	SDBS 1/5 CMC, stirring 300 rpm, 40 °C, 2 days
A-2	SDBS 1 CMC, stirring 300 rpm, 40 °C, 2 days
B-1	SDBS 1/5 CMC, stirring 700 rpm, 40 °C, 2 days
C-1	SDBS 1/5 CMC, stirring 300 rpm, 60 °C, 2 days
C-2	SDBS 1/5 CMC, stirring 300 rpm, 60 °C, 3 days
C-3	SDBS 1/5 CMC, stirring 300 rpm, 80 °C, 2 days

Next, the white powders of sample A-1 and sample B-1 (1.0 wt%) were dispersed into a THF solution containing 0.5% (wt) of polystyrene to form a suspension. The suspensions were then coated onto a silicon wafer using a KW-4A spin coater. By directed self-assembly of particles, the regular structure surface was got for sample A-1, and a micro/nano hierarchical surface was obtained for sample B-1. Finally, the coated silicon wafer was chemically modified by dipping in the solution (1 wt% of dodecyltrichlorosilane in hexane) for 30 min to obtain a superhydrophobic surface.

To a 50 mL round bottom flask, 0.0265 g of 1-Hexadencene, 0.2 g sample B-1, 0.005 g benzildimethylketal (BDK) photoinitiator, and 20 mL of THF were added. The dispersion was then irradiated by a 220 W high-intensity ultraviolet lamp (Model SB-100P/F, manufactured by Spectronic Corporation Westbury New York, USA) under magnetic stirring for 30 min at room temperature. After that, the dispersion was centrifuged (at a speed of 5000 rpm) and re-dispersed thrice in THF to remove the unreacted 1-hexadencene and BDK. The obtained white precipitate was dried in vacuum at 40 °C for 24 h. The resulted white powder was smeared on an adhesive sheet to form a superhydrophobic surface.

2.3. Characterization

Transmission electron microscopy (TEM) was conducted on a JEM-1005 instrument (JEOL Co.) at 80 kV. One drop of the colloidal emulsion was placed on the sample grid, and the solvent was allowed to evaporate.

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 instrument. Samples were prepared by directly spin-coating the emulsion onto the silicon slice. An accelerating voltage of 10 kV with a Au coating of the sample was used to image these particles.

Dynamic light scattering (DLS) was conducted by using a BI-200SM light scattering analyzer (Brookhaven Inc.): temperature of 25.0 °C, aqueous suspension, angle of 90.00, and wavelength of 640.0 nm.

The static contact angles were measured by CAM 200 optical contact angle analyzer (KSV instruments Ltd.) at 25.0 °C with device server software (sigma 70X Cam 200 LB1000-LB5000 version 1.81). At least 5 different spots were chosen on each sample. For each spot, 7 data with internal time of 10 s were collect. Then, the CA of this spot was calculated by the software from these data. The 5 individual measurements were evaluated by the software to get the final CA of this sample.

3. Result and discussion

Scanning electron microscopy (SEM) was used to examine the morphology of these nanoparticles. The SEM images of Sample A-1 and Sample A-2 were shown in Fig. 1a and b. Clearly, these images showed that the hybrid silica particles were nanometer-sized and highly monodispersed. It could be found that the particle size was mainly controlled by adjusting the concentration of the