Journal of Colloid and Interface Science 437 (2015) 24–27

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Short Communication

Controlling surface energy of glass substrates to prepare superhydrophobic and transparent films from silica nanoparticle suspensions

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ARTICLE INFO

Article history:
Received 19 June 2014
Accepted 10 September 2014

Keywords:
Superhydrophobicity
Transparency
Surface energy
Nanoparticles
Silica
Spraying

ABSTRACT

We fabricated superhydrophobic and transparent silica nanoparticle (SNP) films on glass plates *via* spray-coating technique. When suspensions containing 1-propanol and hydrophobic SNPs were sprayed over glass plates that were modified with dodecyl groups, superhydrophobic and transparent SNP films were formed on the substrates. Surface energy of the glass plates had a significant role to obtain superhydrophobic and transparent SNP films. SNP films did not show superhydrophobicity when bare glass plates were used as substrates, because water droplets tend to adhere the exposed part of the hydrophilic glass plate. Glass plates having extreme low surface energy were not also suitable because suspension solution was repelled from the substrates, which resulted in forming non-uniform SNP films.

1. Introduction

Exceptionally hydrophobic surface, on which water droplets easily roll off, is called superhydrophobic surface [1–3]. Superhydrophobic surface is often found in nature (e.g., lotus leaves, wings of cicada, and legs of water slider). Superhydrophobicity is observed when surface has both low surface energy and appropriate roughness. It has been reported that hierarchical nano- and micrometer sized roughness is effective for superhydrophobicity. Some kinds of leaves are typical examples: they have micrometer-sized projection on which nanometer-sized roughness is present [4].

To the best of our knowledge, artificial superhydrophobic surface was firstly fabricated by Cassie and Baxter in 1944 [5], but since the study, superhydrophobic surface had hardly been examined for a long period. After some pioneering researches in around 2000 [6–8], papers on superhydrophobic surface have remarkably increased. In my opinion, the rapid progress of superhydrophobic field would overlap the technological advance in material chemistry. Superhydrophobic surface requires complex hierarchical roughness that was not easy to fabricate; therefore, the technological advance (especially in nanotechnology) would boost the studies on superhydrophobicity. In the early stage of the study, complicated methods such as lithography and vapor deposition were often applied to prepare superhydrophobic surface, and then the preparation methods have become much simpler as wet-chemical techniques have been used in the field.

Transparency is an important property in superhydrophobic films; for example, when superhydrophobic films are coated on windows and solar cell panels, transparency of the films is the essential requirement. However, the preparation of superhydrophobic and transparent films is not straightforward because surface roughness brings about the decrease in transparency, which is known as Mie scattering [9]. Hence, to avoid the blurring in surface due to roughness, one should precisely control surface roughness that must be large enough to show superhydrophobicity but be as low as possible to keep transparency. In addition to surface roughness, constituents and thickness of the films could also be factors that determine transparency. These strict restrictions make it inevitably difficult to prepare superhydrophobic and transparent films on glass substrates. So far, sophisticated methods have been developed for the challenging objective [10–15]. For example, Deng et al. recently prepared superhydrophobic (and superoleophobic) structured silica coatings over glass using candle soots as a template [16].

Spray-coating is one of the simplest methods to form coatings and has been examined to readily prepare superhydrophobic films [17–23]. Here, we demonstrate that superhydrophobic and transparent films can be prepared on glass plates just by spraying silica

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http://dx.doi.org/10.1016/j.jcis.2014.09.021
0021-9797/

nanoparticle (SNP) suspensions. In this study, we mainly focused on the effect of surface energy of substrates on superhydrophobicity of the spray-coated SNP films. Surface energy of substrates has rarely been taken into consideration in superhydrophobic field, but as shown in this study, we clarified that surface energy of glass substrates has a significant effect on the properties of spray-coated SNP films.

2. Experimental section

2 g of SNPs (average diameter: 25 nm, C.I. Kasei Co. Ltd.) was refluxed in dehydrated toluene (40 mL) containing silane-coupling agents (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane; 1 mL). Through the treatment, hydrophilic SNPs turned into hydrophobic owing to the immobilization of hydrophobic moieties of the silane-coupling agents. The hydrophobic SNPs (0.05 g) were added into 1-propanol (5 mL), and the mixtures were stirred (30 min) and sonicated (20 min). The resulting suspensions were spray-coated on glass substrates and then dried at room temperature overnight to form SNP films [24,25].

We used four types of glass substrates: as-purchased glass plates (microscope slide made of soda-lime glass) and glass plates treated with silane-coupling agents (i.e., ethyltrichlorosilane, dodecyltrichlorosilane, and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane). Prior to treating glass plates with silane-coupling agents, glass plates were activated in 28.0–30.0% NH_3 solution (20 mL), 30.0–35.3% H_2O_2 solution (20 mL), and water (100 mL) at 353 K for 1 h. The glass plates were refluxed in dehydrated toluene (150 mL) containing the silane coupling agents (1.5 mL) for 1 h. Hereafter, the glass plates treated with ethyltrichlorosilane, dodecyltrichlorosilane, and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane will be denoted as C_2-, C_{12}-, and F-glass, respectively.

In this study, the wettability of surface was evaluated based on the values of contact angle (CA) and sliding angle (SA). It is noted that superhydrophobic surface is defined as the surface with CA > 150° and SA < 10°. The CAs of water droplets (3 μL) on the samples were measured using a contact angle meter (Kyowa Interfacial Science Japan, CA-D). The angle at which a water droplet rolled off when a sample was tilted at 0.5°/s was measured as SA. Scanning electron microscopy (SEM) images were obtained using S-4700 (Hitachi) instruments. UV–vis spectra of SNP films were measured with a UV/VIS spectrophotometer V-560 (JASCO) by subtracting UV–vis spectra of glass plates as background.

3. Results and discussion

In order to obtain glass substrates with different surface energy, we modified the glass plates by using three types of silane-coupling agents. The effect of the silane-coupling treatments on the surface energy of the glass substrates was estimated by measuring water and 1-propanol CAs of the glass surface (Table 1). The order of water and 1-propanol CAs was as follows: no-treated glass < C_2-glass < C_{12}-glass < F-glass. The no-treated glass showed the lowest CAs because hydroxyl groups on the no-treated glass surface have strong affinity with liquids. The hydroxyl groups are disappeared after the silane-coupling treatment; the elimination reaction between H atom in the hydroxyl groups and Cl atom in the silane-coupling agents occurs, producing HCl, and the functional group of the silane-coupling agents is attached onto glass surface. Table 1 shows that CAs of the silane-coupled glass were ordered with hydrophobicity of the attached functional groups (i.e., ethyl < dodecyl < fluorine). We can see that 1-propanol CAs were smaller than water CAs, which is because 1-propanol has lower surface tension than water.

Table 1
Contact angles (CAs) of glass substrates for water and 1-propanol.

Substrates	Water CA/°	1-Propanol CA/°
No-treated glass	12	2
C_2-glass	84	3
C_{12}-glass	100	7
F-glass	103	23

Fig. 1 shows CAs and SAs of SNP films spray-coated over no-treated, C_2-, C_{12}-, and F-glass. Hydrophobicity of all the SNPs/glass samples increased as the amount of SNP films became larger, and how CAs and SAs changed with the amount of SNPs depended on the types of glass substrates. In the case of no-treated glass and F-glass as substrates, superhydrophobicity was not observed in the range of this work (note that no SA data in Fig. 1 mean that water droplets did not roll off from the samples, i.e., the water repellency was extremely low). In contrast, SNPs/C_2-glass and SNPs/C_{12}-glass showed superhydrophobicity when efficient amounts of SNPs were present. Comparing SAs of the samples, we can order the water repellency of SNPs/glass as follows: SNPs/no-treated glass < SNPs/F-glass < SNPs/C_2-glass < SNPs/C_{12}-glass. Fig. 2 shows a photograph and transmittance spectrum of superhydrophobic SNPs/C_{12}-glass. From the results, we can confirm that the SNP films have both superhydrophobicity and high transparency.

Fig. 3 shows SEM images of superhydrophobic SNPs/C_{12}-glass. In the measurement of the SEM image (a), the sample was tilted at 45° to observe surface roughness structure more clearly. The tilted SEM image shows that the SNP films have undulated structure which produces micrometer-sized roughness (a few ~ several tens micrometer). It was reported that such micrometer-sized roughness amplifies surface hydrophobicity to exhibit superhydrophobicity [26]. Hence, the undulated structure would allow the SNP films to be superhydrophobic. At the present moment, it is difficult to explain why the undulated roughness is formed on the spray-coated SNP films. Probably, drying of 1-propanol would be the key process to form the micrometer-sized roughness. Fig. 3(b) shows a surface SEM image with higher magnification. We can see the SNPs are aggregated, in which a large number of nanometer-sized vacancy and roughness are present. As previous works reported, such nanometer-sized roughness could enhance surface hydrophobicity [27]. From the SEM images, it could be concluded that the SNP films possessed superhydrophobicity owing to the presence of the micro- and nanometer sized roughness. Fig. 3(c) shows a cross-sectional SEM image of the SNP film. We can see that the film has porous structure and submicron thickness.

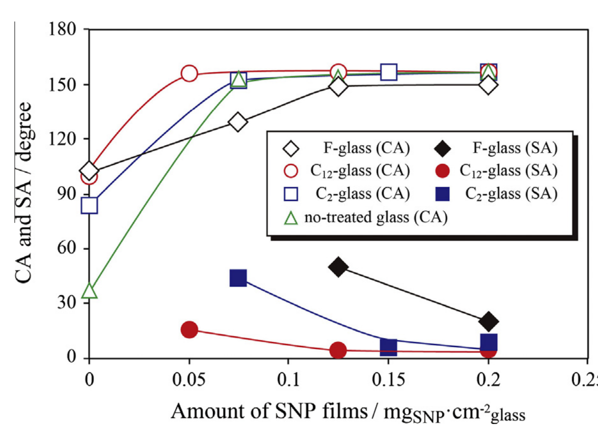

Fig. 1. CAs and SAs of SNPs/no-treated glass, SNPs/C_2-glass, SNPs/C_{12}-glass, and SNPs/F-glass with different amounts of SNP films.