Robust Transparent Super Hydrophobic Coatings and Control of Interface Structure

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Abstract. Mechanically robust, transparent and superhydrophobic coatings on glass surface are critical for building and automotive self-cleaning function. In this paper, by using acidic SiO_2 sol as a binder and mixing two different sizes of hydrophilic SiO_2 nanoparticles with the binder, mechanically robust transparent coatings with micro/nano hierarchical structure were prepared. The influence of mixing process on interface structure was studied. Results show that abrasive resistance of micro/nano hierarchical structural coatings depends on the control of voids and holes on the interface. Water contact angle (WCA) of the micro/nano hierarchical structural coatings reaches $>150°$ when modified by fluoroalkylsilane. Under condition of load of 1 kg/cm^2, WCA can still maintain $>120°$ after 200 cycles of mechanical abrasion, showing excellent wear resistance and application prospect.

1. Introduction

Micro/nano hierarchical structure and low surface energy are two critical factors for superhydrophobic surfaces [1]. In recent years, applications of SiO_2 nanoparticles to prepare superhydrophobic surfaces have received widespread attention [2-4]. This is mainly because that aggregation of SiO_2 nanoparticles can provide multi-scale hierarchical structure -- nano-scale structure constructed by primary particle and micro-scale structure constructed by particle aggregation [5]. However, abrasive resistance and transparency of micro/nano hierarchical structure are still key issues [6-9].

Abrasive resistance of micro/nano hierarchical structure constructed by nanoparticle aggregation without binder is weak due to small contact area between hierarchical structure and substrate [10-11]. To improve abrasive resistance, Cai et al. [12] sprayed commercial hydrophobic SiO_2 nanoparticles (R974, 12 nm) onto glass substrate pre-coated with organic binder (epoxy resin) to fabricate a superhydrophobic surface with a WCA of 154.7°; Xu et al. [13] used inorganic SiO_2 sol as binder, dispersed 2500 nm/400 nm or 400 nm/50 nm dual-sized SiO_2 particles in acidic SiO_2 sol to construct micro/nano hierarchical structure, and prepared a superhydrophobic coating with a WCA of 160°. Though the abrasive resistance is improved, but the coating is not transparent because of the big

particle size of SiO_2, and the application is limited.

In this paper, we focused on the influence of mixing process of SiO_2 nanoparticles and binder on interface structure between micro/nano structure and glass. The voids and holes on the interface were controlled, and mechanically robust transparent superhydrophobic coatings were successfully prepared on glass.

2. Experimental

2.1. Preparation of micro/nano structural coatings

Reagents: tetraethoxysilane (TEOS), ethanol, coupling reagent (KH560), deionized water, dilute nitric acid, commercial hydrophilic SiO_2 nanopowder A380 (7 nm, Degussa) and A200 (25nm, Degussa), and fluoroalkylsilane (1H, 1H, 2H, 2H-perfluorodecyl three chlorinated silane) were used as received.

The preparation of acidic SiO_2 sol is based on our previous report [14]. TEOS was hydrolyzed in aqueous-ethanol solution of dilute nitric acid and KH560 was added as coupling reagent.

0.2 g of A380 SiO_2 nanopowder and 0.2 g of A200 SiO_2 nanopowder were added to 20 g of ethanol, stirred for 50 min, and sonicated for 1 h to prepare SiO_2 nanopowder dispersion sol (labeled as AA sol). 2.5 g of AA sol was mixed with 1.0 g of the prepared acidic SiO_2 sol and 4.0 g of isopropanol, sonicated for 1 h to prepare a mixed sol of SiO_2 nanopowder and acidic SiO_2 sol (labeled as AAS sol).

A commercial green glass of 50 mm x 50 mm x 3.2 mm pre-treated by polished and decontaminated was used as substrate. Before coating, glass substrate was chemically activated by ultraviolet ozone irradiation (UVO irradiation, 10 min) to form a highly active hydroxyl polar surface [15]. The sol was coated onto glass substrate by spin coating with a KW-4A homogenizer (speed 600 rpm, time 10 s), followed by pre-curing at 80 ℃ for 20 min and solidification at 180 ℃ for 1 h.

Monolayer coatings were prepared as follows. In order to study interface structure of monolayer coatings, (1) acidic SiO_2 sol, (2) AA sol and (3) AAS sol were coated on glass substrate to fabricate monolayer coatings of (1) SiO_2 gel (labeled as sample S), (2) SiO_2 nanoparticle aggregation (labeled as sample AA), and mixed SiO_2 nanoparticle with SiO_2 gel (labeled as sample AAS), respectively.

Bilayer coatings were prepared as follows. In order to study interface structure of bilayer coatings, at first, acidic SiO_2 sol was coated as under-layer. After air-dried and UVO irradiated, (4) AA sol and (5) AAS sol were coated as upper layer to fabricate bilayer coatings of (4) SiO_2 gel/SiO_2 nanoparticle aggregation (labeled as sample S/AA), and (5)SiO_2 gel/mixed SiO_2 nanoparticle with SiO_2 gel (labeled as sample S/AAS), respectively.

Fluoroalkylsilane modification was implemented by chemical vapor deposition according to reference [16]. The coated glass was placed in the reactor with polytetrafluoroethylene as inner tank, on the bottom of which was distributed three droplets of 1H, 1H, 2H, 2H-perfluorodecyl three chlorinated silane. There was no direct contact between the coated glass and the droplets. The reactor was heat treated at 120 ℃ for 2 h, after natural cooling, the coated glass was removed and heat treated at 150 ℃ for 1.5 h.

2.2. Characterizations

Abrasive resistance was conducted according to ISO 5470-1:2016 using a reciprocating linear wear-resistance instrument (x-5750-J, Shenzhen Xinhengsen Trading Co., Ltd.), under condition of load of 1 kg/cm^2 and reciprocating 200 times. Interface structure before and after abrasion was observed using a scanning electron microscope (SEM, SU-70, Hitachi) with an accelerating voltage of 5 kV. Since conductivity of glass sample was poor, sample surface was treated with gold spray

before SEM detection. Atomic force microscopy (AFM, Multimode 8, BRUKER) was used to characterize 3D topography and roughness of sample surface in tapping mode. An UV/VIS/NIR spectrometer (Lambda 750 S type, Perkin Elmer) was used to analyze optical transmittance. A contact angle measurement instrument (JCY-4, Shanghai Fangrui) was used to measure static water contact angle (water droplet 4 μl).

3. Results and discussion

The photos of as-prepared samples are shown in figure 1. The samples with monolayer coatings of sample S, sample AA and sample AAS are transparent, and the visible light transmittances (TLs) are 75.53%, 75.51% and 74.85%, respectively. The reason of sample AA with a coating constructed by aggregation of two types of SiO_2 nannoparticles of A380 (7 nm) and A200 (25 nm) being transparent is mainly because of the small nanosize of SiO_2 particles used. Compared with the superhydrophobic surface constructed with large nanosize of SiO_2 particles (2500 nm/400 nm or 400 nm/50 nm dual-sized SiO_2 particles) in Reference 13, the transparency is significantly improved.

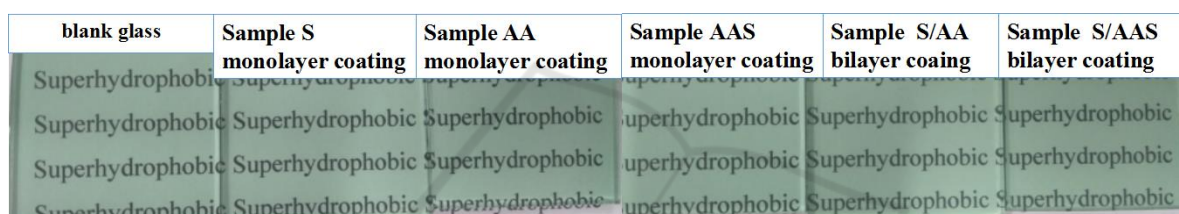| blank glass	Sample S monolayer coating	Sample AA monolayer coating	Sample AAS monolayer coating	Sample S/AA bilayer coaing	Sample S/AAS bilayer coating
Superhydrophobic	Superhydrophobic	Superhydrophobic	uperhydrophobic	Superhydrophobic	Superhydrophobic
Superhydrophobic	Superhydrophobic	Superhydrophobic	uperhydrophobic	Superhydrophobic	Superhydrophobic
Superhydrophobic	Superhydrophobic	Superhydrophobic	uperhydrophobic	Superhydrophobic	Superhydrophobic
Superhydrophobic	Superhydrophobic	Superhydrophobic	uperhydrophobic	Superhydrophobic	Superhydrophobic

Figure 1. Photos of the prepared samples.

The samples with bilayer coatings of sample S/AA and sample S/AAS are also transparent, and the TLs are 75.76% and 74.77%, respectively. For comparison, blank glass is also shown in figure 1, and its TL is 74.81%. Results are that the samples prepared with monolayer and bilayer coaings have almost the same TL as blank glass, showing that as-prepared coatings are transparent.

3.1. Interface structures of monolayer coatings

For sample S, sample AA and sample AAS with monolayer coatings, the cross section SEM images before and after abrasive testing are shown in figure 2. The water contact angles (WCAs) detected before and after abrasive testing are also shown in figure 2.

For sample S with a monolayer coating constructed by acidic SiO_2 sol, the interfaces before (figure 2a) and after (figure 2a′) abrasive testing are compact with no voids and holes, showing strong abrasive resistance. The acidic SiO_2 sol was prepared by the hydrolyed TEOS under acidic condition, and abundant active hydroxyl groups were originated on the formed silica-based gel coating [12] and could reacted with hydroxyl groups on glass substrate surface, forming cross-linked Si-O-Si chemical bonding on the interface. In addition, the WCAs before and after abrasive testing are 113.34° and 111.07°, also indicating that high wear resistance of the coating constructed by acidic SiO_2 sol.

For sample AA with a monolayer coating constructed by aggregation of two types of SiO_2 nanoparticles, the interface before (figure 2b) abrasive testing is compact-less with abundant voids and holes, and after (figure 2b′) abrasive testing, there is no coating observed on glass substrate, showing poor abrasive resistance. The WCA before abrasive testing is 151.53°, and it is significantly reduced to 101.19° after abrasive testing.
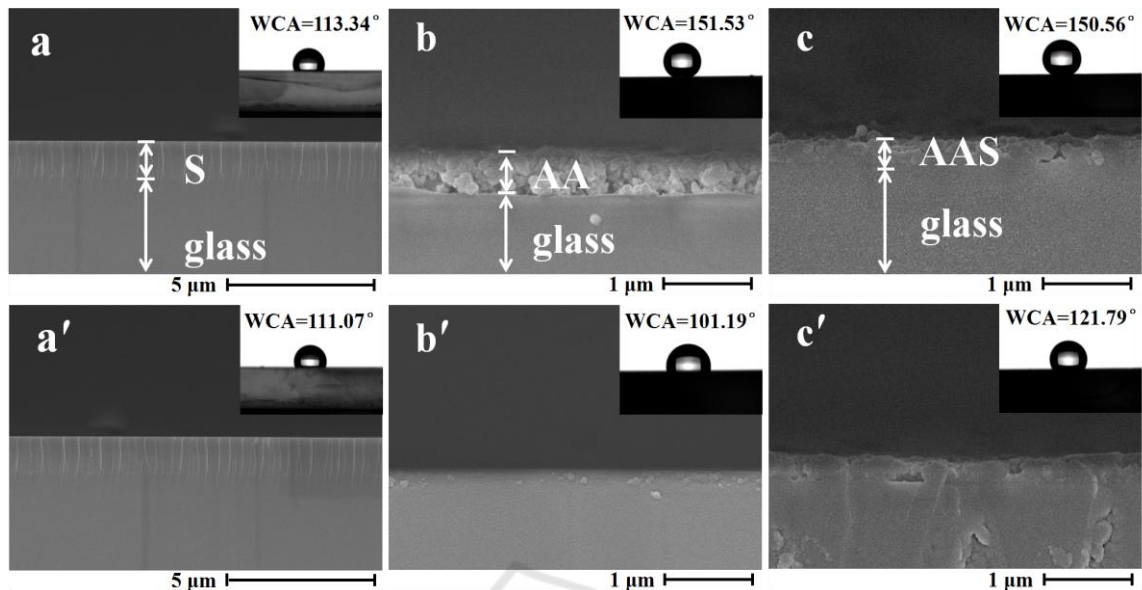
Figure 2. Cross section SEM observations before and after abrasive testing: sample S before (a) and after (a′), sample AA before (b) and after (b′), sample AAS before (c) and after (c′).

For sample AAS with a monolayer coating constructed by a mixture of SiO_2 nanoparticles and acidic SiO_2 sol, the compactness of interface before (figure 2c) abrasive testing is improved and there is less voids and holes on the interface, comparing with the coating constructed only by aggregation of SiO_2 nanoparticles (sample AA, figure 2b). After abrasive testing (figure 2c′), the coating of sample AAS is only slightly damaged, indicating that the coating has better wear resistance. In addition, the WCAs before and after abrasive testing are 150.56° and 121.79°, showing mechanical robustness.

The experimental results of samples with monolayer coatings show that: ①superhydrophobicity can not be obtained if there is no micro/nano structure (eg. sample S); ②superhydrophobicity can be achieved when there is micro/nano structure, but if there are abundant voids and holes on interface of micro/nano structure layer, wear resistance is poor (eg. sample AA); ③reduction of voids and holes on interface can effectively improve wear resistance and thus maintain good hydrophobicity (eg. sample AAS). Compactness of interface is vital, and voids and holes on interface of micro/nano structural coating layer can be controlled by mixing SiO_2 nanoparticles with acid SiO_2 sol, and mechanically abrasive resistance of micro/nano structure can be enhanced.

3.2. Interface structures of bilayer coatings

For sample S/AA and sample S/AAS with bilayer coatings, the cross section SEM images before and after abrasive testing are shown in figure 3. The water contact angles (WCAs) detected before and after abrasive testing are also shown in figure 3.
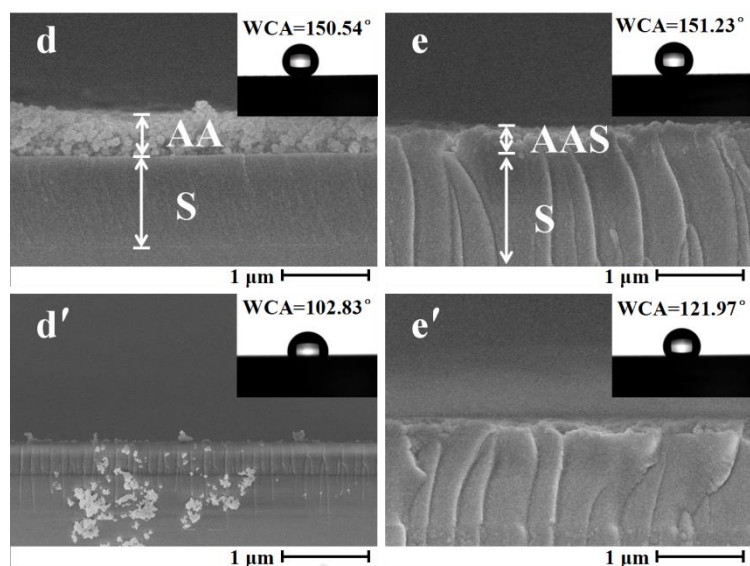
Figure 3. Cross section SEM observations before and after abrasive testing: sample S/AA before (d) and after (d′), sample S/AAS before (e) and after (e′).

For sample S/AA with an upper coating constructed by aggregation of two type SiO_2 nanoparticles on an under coating of acidic SiO_2 sol, the upper coating is micro/nano structure before abrasive testing (figure 3d) but cannot be observed after abrasive testing (figure 3d′), showing poor wear resistance of the upper coating. The WCAs before and after abrasive testing are 150.54° and 102.83°, indicating that the micro/nano structure has poor wear resistance.

For sample S/AAS with an upper coating constructed by a mixture of SiO_2 nanoparticles and acidic SiO_2 sol on an under coating of acidic SiO_2 sol, the upper coating shows micro/nano structure before abrasive testing (figure 3e), and the upper micro/nano structural coating is slightly damaged and still remains observed after abrasive testing (figure 3e′). The WCAs before and after abrasive testing are 151.23° and 121.97°. The reduction of voids and holes on interface of micro/nano structural coating (figure 3e) results in the improvement of wear resistance of micro/nano structural coating, which is the same results as samples with monolayer coatings.

3.3. Micro/nano hierarchical surface

Micro/nano hierarchical structure can reduce the contact area between water droplets and solid surface [1] and is benefit to construct superhydrophobic surface. The surface of sample S/AAS was characterized by SEM and AFM. figure 4 (a) and (c) are SEM and AFM surface images before abrasive testing, and figure 4 (b) and (d) are SEM and AFM surface images after abrasive testing, respectively.

Before abrasive testing, the surface of sample S/AAS is micro/nano hierarchical structure formed by aggregation of SiO_2 nanoparticles, confirmed by SEM (figure 4a). After abrasive testing, the micro/nano hierarchical structural surface is damaged to some extent, but the micro/nano structure still exists (figure 4b). From AFM characterization, the maximum fluctuation and roughness are 340 nm and 40.3 nm before abrasive testing (figure 4c), and decrease to be 158 nm and 20.8 nm (figure 4d), respectively. SEM results well correspond to AFM results.
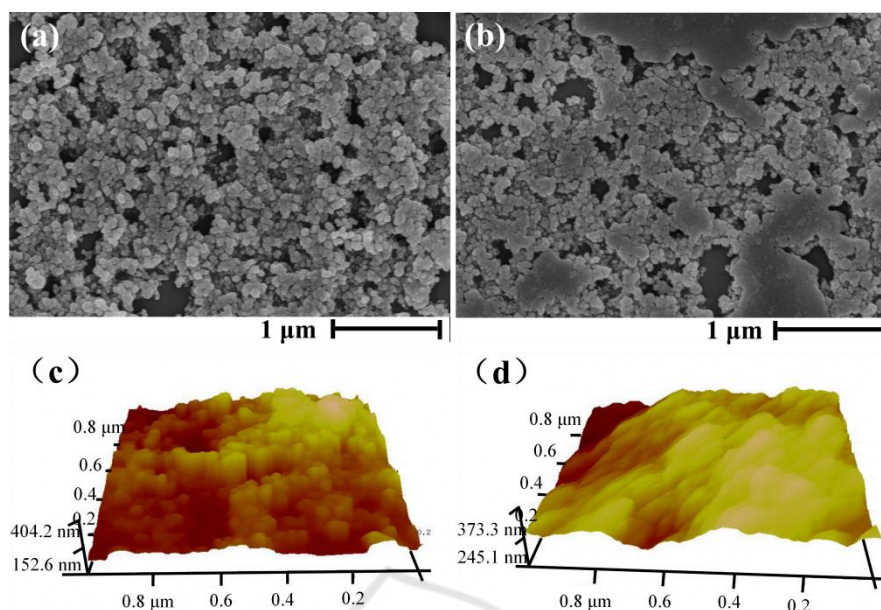
Figure 4. The surface morphology of sample S/AAS. SEM (a) and AFM (c) before abrasive testing; SEM (b) and AFM (d)after abrasive testing.

4. Conclusions

Abrasive resistance of micro/nano structural coating depends on control of voids and holes on interface. In this paper, acidic SiO_2 sol was used as a binder, and the interface structure of micro/nano structural coatings was effectively controlled by mixing process of SiO_2 nanoparticles and the binder. The voids and holes on the interface were reduced, and mechanically robust transparent superhydrophobic coating was successfully prepared, showing pratical application prospect.

Acknowledgement

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