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Ultrasonic Atomization Based Fabrication of Bio-inspired Micro-nano-binary Particles for Superhydrophobic Composite Coatings with Lotus/Petal Effect

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Abstract

To mimic a superhydrophobic surface as found in nature, micro-nano binary surface structures with specific chemical properties are required. This type of special binary structure was usually realized by introduction of hierarchical inorganic microparticles; however, existing preparation methods are usually complex and difficult for scalable manufacture. In order to solve this problem, a facile ultrasonic atomization-based spray drying method has been developed in the present study for producing hierarchical silica microparticles for eventual fabrication of superhydrophobic coatings with either a lotus or petal effect depending on the required application. 3-aminopropyl-triethoxysilane (APTES) was used as a modifier for enhancing the binding between the silica nanoparticles. The hierarchical silica microparticles exhibited an diameter of around 10μm and proper nano-roughness to realize a superhydrophobic effect. The prepared hierarchical silica microparticles/epoxy coating achieved a very high water contact angle up to 161° and a sliding angle as low as 5°. Both lotus and petal effects were achieved. Mechanical properties of the composite coating have also been enhanced by virtue of the modifiers. The interaction between –NH_2 group from the APTES modifier and –OH groups from the silica led to a strong adhesive force with water molecules, while the introduction –F groups to the silica could reduce this affinity and result in a smaller sliding angle.

Keywords: Ultrasonic atomization, superhydrophobic coating, lotus effect, petal effect, micro-nano-binary, Polymer composite

1. Introduction

Surfaces with a water contact angle greater than 150° are defined to be superhydrophobic [1-3]. A variety of superhydrophobic surfaces have been discovered in nature, such as plant leaves, insect wings and legs, among which two superhydrophobic states are observed in terms of lotus and petal effects [4-6]. These surface properties attribute to the combinational effect of both the micro-nano structure and the special chemical properties of the surfaces. The lotus effect, as observed in a lotus leaf, is characterized with a contact angle larger than 150° and a water sliding angle smaller than 10°, because water droplets are easily to roll off. Micro-sized papillae and cilium-like micro-nano structures with a mean diameter of ~7 μm are observed on the surfaces of lotus leaves, which are composed of wax like hydrophobic materials. The petal effect, as observed in the rose petal, is characterized with a contact angle greater than 150° and a high water sliding angle enabling water drops more likely to stick on its surface [6-10]. Hierarchical micropapillaes and nanorods with a mean diameter of ~10μm are also observed on the surfaces of rose petals, which endow them with superhydrophobicity, but with have high water adhesion as reflected from a higher water sliding angle due to deficiency of hydrophobic materials. Superhydrophobic coatings on different substrates, especially on metals, have attracted substantial attentions for various applications, including self-cleaning, antifogging and anti-bacterial and anti-corrosion by virtues of their advantageous surface properties [11-12].

As inspired by these properties as observed in natural, both micro-nano hierarchical structure and special chemical properties are required for designing a superhydrophobic surface. Micro-nano-binary particles have been promising candidates to offer the required roughness for this type of the surface, because of their micro-nano dual-scale rough hierarchical morphologies [10-11,13-14]. Many artificial superhydrophobic surfaces have been fabricated with micro-nano binary particles and polymers through various methods such as self-assembly, emulsion polymerization and layer-by-layer method [15-22]. The self-assembly method [15-16] is generally based on a sol-gel reaction, but an extra surface modification process is also necessary. The emulsion polymerization [15,17] is characterized by distribution of inorganic particles on the surfaces of monomer emulsion droplets. However, the secondary structures of these particles are difficult to control precisely, because of their special requirement for a continuous and dispersed phase. For the layer-by-layer technique [16,18-19], the inorganic particles are deposited on selected templates, and a number of deposition cycles are required to obtain desired superhydrophobic effects. EI-Maiss et al. [20] developed superhydrophobic surfaces with both low and high water adhesion properties utilizing a mixture of monomers. Ke et al. [21] fabricated micro-sized and nano-sized silica particles filled polydimethylsiloxane superhydrophobic coatings with a maximum contact angle of 155° on a glass substrate by a two-step drop coating method. However, the complex procedures of these existing fabrication methods, such as multiple time-consuming preparation steps and harsh processing conditions, make them difficult for scale-up manufacture.

Spray drying technique has been widely adopted to manufacture particles in food, pharmaceutical and other industries owing to its simple, rapid and reliable processes, making it to be suitable for scalable manufacture [22]. The entire spray drying processes can be divided into three units: atomization, drying and particles collection. In the atomization unit, liquid phase is transformed into tiny droplets. These droplets are then conveyed to a drying chamber for solvent evaporation, which is known as the drying unit. In the particle collection unit, the dried solid particles are separated from the conveying air through collectors. In a conventional spray drying process, pressure based nozzles are applied for the atomization. However, the generated droplets were found to be heterogeneous. In order to solve this problem, ultrasonic atomization technique was introduced so as to produce uniform droplets from liquid phases by virtues of the capillary and cavitation effects of ultrasound [22-25]. Compared with the above-mentioned fabrication processes of inorganic particles for superhydrophic coating, this ultrasonic atomization based spray dying is advantageous because it is a rapid and scalable process. However, this process has rarely been applied on fabrication of hierarchical inorganic particles for superhydrophobic coatings, because proper designs on the material formulations as well as fabrication procedures are required.

Therefore, the present work is amongst the first attempt to design and fabricate micro-nano-binary hierarchical silica particles for superhydrophobic composite coatings using a facile and scalable ultrasonic atomization-based spray drying method. The micro-nano-binary hierarchical silica particles were designed to microparticles with nano-roughness realized through aggregation of surface modified silica nanoparticles. Epoxy resin was selected to be the polymer matrix of the superhydrophobic composite coating due to its favorable characteristics, such as excellent adhesion to metals, rapid curing ability and chemical resistance [26-28]. Two modifiers were also applied for functionalization of the silica nanoparticles with 3-aminopropyl-triethoxysilane and 1H,1H,2H,2H-perfluorooctyltriethoxysilane. Influences of the functional groups of the modifiers on the morphologies of the hierarchical silica particles were investigated. Performances and mechanical properties of the superdrophobic composite coatings on the stainless steel substrates were also evaluated.

2. Experimental

2.1. Materials

Silica nanoparticles (mean diameter: ~15nm) were obtained from the Beijing DK nano technology Co., Ltd. 3-aminopropyl-triethoxysilane (APTES) and 1H,1H,2H,2Hperfluorooctyltriethoxysilane (PFTES), serving as the modifiers for adjusting the surface chemical property of the microparticles, were purchased from the Sigma-Aldrich. Hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), ethanol and acetone were supplied by the Merk & Co. Distilled water was used in all experiments. Potassium Bromide was acquired from the Sinopharm Chemical Reagent Shanghai Co., Ltd. The stainless steel with a grade of 304 was supplied from the Hip Yick Industrial Co. Ltd.

2.2. Fabrication of superhydrophobic composite coatings on metal substrates

Entire fabrication process of the superhydrophobic composite coating can be divided into two parts: preparation of micro-nano-binary silica particles and composite coatings. Preparation of the micro-nano binary silica particles were performed by the ultrasonic atomization based spray drying process. Briefly, 3.0g silica nanoparticles were ultrasonically dispersed into 100 ml ethanol for 30 minutes. Acidity of this silica suspensions were adjusted to a pH value of 2.5 using 1.0mol/L HCl solution. APTES (0.025mol) or a mixture of APTES (0.025mol)/PFTES (0.005mol) were added dropwise into the silica suspension under mild agitation for 24 hours at ambient temperature. No modifier was added for control samples. Before transferring to spray drying process, pH value of the suspension was adjusted to 7.0 using NH_4OH solution. Spray drying of the as prepared suspension was performed by a tailor-made spray drying system (Shanghai Shunyi Tech. Co., Ltd, China) equipped with a 50 KHz ultrasonic nozzle as an atomization unit and a cyclone as a powder collecting unit. The operating parameters were set as follow: inlet drying air temperature:100 °C drying air flow rate: 175-200 L/h, feed rate of suspension: 50ml/h. Hierarchical silica microparticles were obtained after the spray drying process, because the silica nanoparticles in each atomized droplets were agglomerated during evaporation of ethanol as shown in Fig.1. Three types of hierarchical silica microparticles were prepared by adopting different modifiers: APTES/PFTES-modified, APTES-modified and non-modified particles. The modification scheme is shown in Fig.2.

Preparation of the superhydrophobic composite coatings on stainless steel substrates was realized via a two-step coating process. The stainless steel substrates (4cm×4cm) were firstly polished by 240- and 400-grit sand papers, and then ultrasonically cleaned in distilled water and rinsed with ethanol. Epoxy resin (4.0mL) and epoxy hardener (2.0mL) were added into 16 mL acetone and stirred for 30 minutes to form a homogeneous polymer solution. The pretreated steel substrates were dipped into this polymer solution and dried for 30 minutes at 50 °C. Afterward, the epoxy coated steel substrates were further dipped coated by 2 wt. % of hierarchical silica particles/ethanol suspension. Superhydrophobic composite coatings were obtained after 24 hours drying at 50 °C.

2.3 Characterization

Compositional information of the hierarchical silica particles was examined on a Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Multiscope Spectrum 100T) with a wavenumber ranging from 400 to 4000 cm^{-1}.The components of the prepared silica particles were confirmed by thermogravimetric analysis (TGA, Netzch STA 449C, Jupiter), with a constant heating rate of 10 °C/min from 40 to 600 °C under Argon gas condition. Scanning electron microscopy (SEM) (JEOL JSM-6490) was used to characterize the surface morphology of the prepared particles. The optical surface profiler (Zygo Nexview) was employed to capture the topographies and roughness of the fabricated coatings. Static contact angles (CA) and sliding angles of the composite coatings were detected via a contact angle goniometer (Sindatek Model 100SB). Mechanical properties of the composite coatings were determined by using carrying out nano-indentation tests on the Triboindenter Testing System (Hysitron, Standard diamond Berkovich Conical tip) with an in-situ imaging mode at an applied force of 500 μN. Five indentations at different locations of the coatings were made for each sample. The reduced moduli of the samples were obtained by applying the Oliver and Pharr methodology [28].

3. Results and discussion

3.1 Morphologies of the prepared micro-nano-binary silica particles

As shown in Fig.3, all the prepared micro-nano-binary silica microparticles exhibit spherical morphologies with diameters around 10 μm and nano-roughness, proving the design concept of the resulted nano-roughness generated through agglomeration of the nanoparticles. The functionalized silica microparticles are more uniform in size as compared with non-modified silica hierarchical particles as shown in Fig.3 due to the introduction of the modifiers. The presence of APTES ensured the strong bonding between the silica nanoparticles during formation of the hierarchical microparticles, because –OH groups on the surface of the silica could react with $–NH_2$ groups of the APTES. This chemical bonding endowed the hierarchical micorparticles with strong mechanical properties, as confirmed in the nano-indentation test discussed in the following section. The un-modified silica nanoparticles just physically aggregated together during the spray drying process, making that the generated hierarchical microparticles became fragile and thus heterogeneous as observed in Fig.3(c).

3.2 FT-IR analysis

From Fig.4, the strong peaks at 1116, 1095 and 1182 cm^{-1} are assigned to the stretching vibration of Si-O-Si [16, 19]. Broad bands at about 3400 cm^{-1} in Figs.3(a) & (b) were observed, indicating the stretching vibration of N-H from the APTES. The bands at 2934 cm^{-1}, around 1490 cm^{-1} and 1380 cm^{-1} in Figs.3(a) & (b) are ascribed to the stretching and bending vibration of $-CH_2-$ groups [18]. The N-H shearing of APTES [18] has been demonstrated by the peaks at 1568 cm^{-1}, 1490 cm^{-1} in Figs.3(a) & (b), further confirming the presence of the APTES on the surfaces of the silica particles. The peak at 1319 cm^{-1} in Fig.3(a) is assigned to the $-CF_3$ group, indicating the existence of the PFTES. Compared to the curve of the un-modified silica particles, all these results suggested that APTES and PFTES have been successfully grafted to the corresponding silica particles.

3.3 Thermal gravimetric analysis

The effective functionalization of the micro-nano-binary silica particles was further confirmed by thermal gravimetric analysis. As indicated from Fig.5(c), weight loss of the un-modified silica particles occurs at around 50 °C and ceases at around 150 °C, as resulted from evaporation of residue water in the particles. In contrast, the modified particles experienced a significant weight loss during the heating process. The modified silica particles as shown in Figs.5(a) & (b) suffers from a higher weight loss than the un-modified samples during 50-150 °C. This phenomenon can be explained by the fact that more water molecules were trapped by $-NH_2$ groups of the APTES through hydrogen bonding. Compared with the APTES modified silica particles in Fig.5(b), the APTES/PFTES modified silica particles in Fig.5(a) exhibits a lower weight loss at 50-150 °C, which could be attributed to the presence of hydrophobic –F groups from the PFTES that reduce bonded water molecules. Moreover, further weight loses occur at 320 °C and 400 °C for the APTES/PFTES modified and the APTES modified particles respectively as shown in Figs.5(a)&(b), because of decomposition behaviors of the grafted modifiers. As compared with the APTES, the decomposition of PFTES occurred at a lower temperature of 320 °C [30]. The presence of the PFTES has rendered the corresponding silica particles suffer from substantial weight losses. The final residual weight ratio of the APTES/PFTES-modified particles was 40%, which is consistent with the weight ratio of the added raw materials.

3.4 Wetting properties

Wettability of the coatings on the stainless steel samples, prepared with different hierarchical silica particles, are presented in Fig.6. Water contact angles of the coating with the APTES/PFTES-modified, APTES modified particles and un-modified micro-nano-binary particles are 161.5°, 144.1° and 150.5° as shown in Figs.6(a1), 6(a2) and 6(a3), respectively. The water sliding angle of the APTES/PFTES-modified particles incorporated coating was determined to be around 5°, which indicates a lotus effect state. In contrast, a petal effect state was observed on the samples with the APTES modified particles and un-modified particles, because the water droplets could remain to stay on the coating surface even the samples were turned upside down as shown in Figs.6(b3) & (c3). All these effects can be explained by the different chemical properties and the micro-nano binary structure of the incorporated hierarchical particles in the composite coatings. Taking the advantages of the mere hierarchical micro-nano-binary structures of the silica particles, a superhydrophobic effect can be achieved for the composite coating even without the introduction of the modifier as shown in Fig.6(c). The variation of the water sliding angles is caused by the different chemical properties of the particle surface. The presence of the -OH groups from neat silica particles and $–NH_2$ groups from the APTES made water more easily adhered to their surfaces, thus resulting in larger sliding angles as shown in Fig.6(b3) & (c3) due to the hydrogen bonding between these hydrophilic groups with the water molecules. On the other hand, this adhesive effect was reduced for the samples with the introduction of -F group from low surface energy agent of PFTES, leading to a much smaller sliding angle as shown in Fig.6(a3). The water repellent effect of the –F group has also been confirmed in the TGA analysis as discussed previously in Section 3.3.

3.5 Nano-indentation analysis

Nano-mechanical properties of the superhydrophobic coatings with modified and un-modified micro-nano-binary silica particles were characterized by nano-indentation tests. For this test, the reduced elastic modulus for each sample subjected to a maximum loading of 500 μN was recorded for comparisons. Both the composite coating samples separately modified with APTES/PFTES and APTES could sustain the loading of 500 μN; however, the coating with un-modified particles could only bear the loading of 70 μN as shown in Fig.7. Moreover, the reduced moduli of the samples with functionalized micro-nano-binary particles exhibits higher reduced modulus than those with un-modified particles. All these results have further proved effectiveness of the modifiers in enhancing the mechanical properties of the fabricated composite coatings.

Conclusions

Micro-nano-binary silica particles with a diameter of ~10μm and nano-roughness have been successfully fabricated by a facile and scalable-up ultrasonic atomization based spray drying process. Superhydrophobic effects have been achieved by virtue of the hierarchical structure of the generated micro-nano-binary silica particles. Both lotus and petal effects have been achieved by adopting different modifiers. With the functionalization through APTES as a chemical binding agent, the generated hierarchical silica microparticles, which were formed through aggregation of strongly bonded nanoparticles, have a more uniform size than the un-modified sample without APTES. With the help of a PFTES modifier, a small sliding angle (5°) was achieved to presenting a lotus effect state. The hierarchical silica microparticles without the PFTES exhibited a higher adhesion with water and thus achieved a petal effect owing to the interaction between the hydrophilic groups of -OH and –NH_2. In addition, the fabricated superhydrophobic coatings with the modified micro-nano-binary silica particles exhibited better mechanical properties than that with un-modified particles. All these results have proven the effectiveness of the ultrasonic atomization based spray drying as a promising technique for fabrication of hierarchical silica microparticles for superhydrophobic coatings. With the proposed method, the superhydrobic composite coatings with either a lotus or petal effect can be realized depending on the required application.

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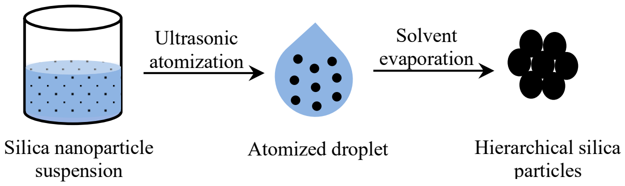

Fig.1 Schematic formation of micro-nano-binary silica particles through ultrasonic atomization based spray drying process

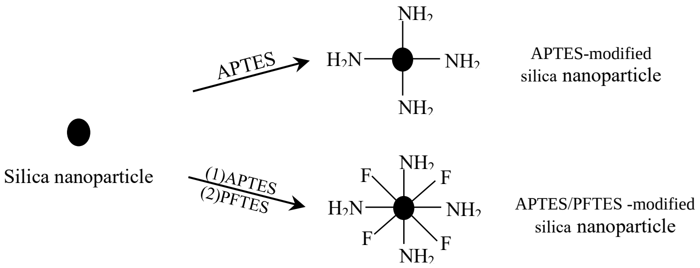

Fig.2 Modification scheme of silica nanoparticles

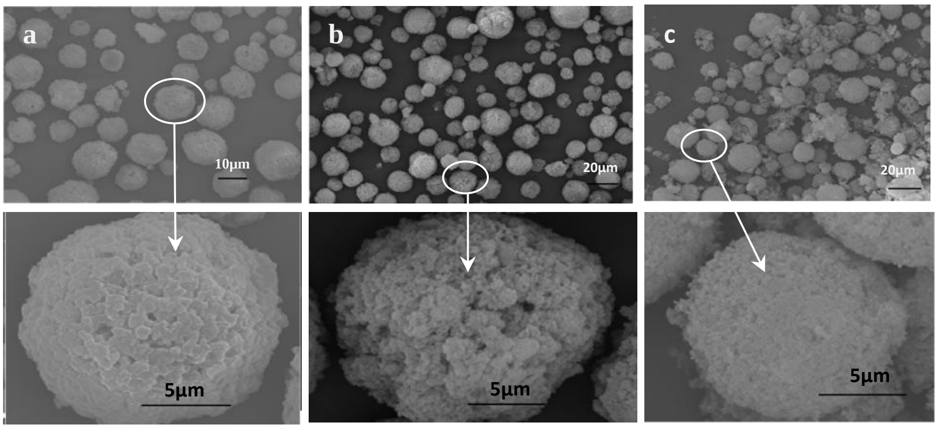

Fig.3. SEM images of micro-nano-binary silica particles, (a) APTES/PFTES-modified particles; (b) APTES-modified particles; and (c) un-modified particles

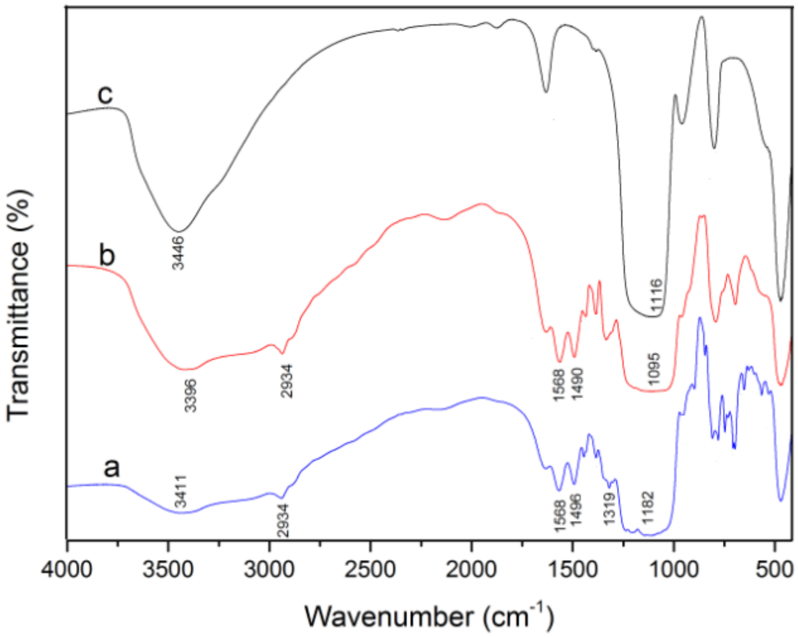

Fig.4. FTIR spectra of the prepared micro-nano-binary silica particles, (a) APTES/PFTES-modified particles; (b) APTES-modified particles; and (c) Un-modified silica particles

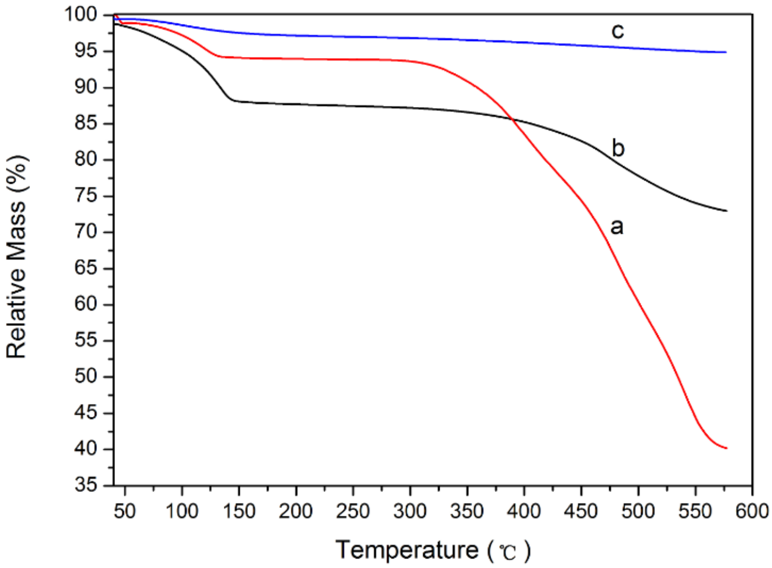

Fig.5. TGA curves of the prepared micro-nano-binary silica particles, (a) APTES/PFTES-modified particles; (b) APTES-modified particles; and (c) Un-modified silica particles

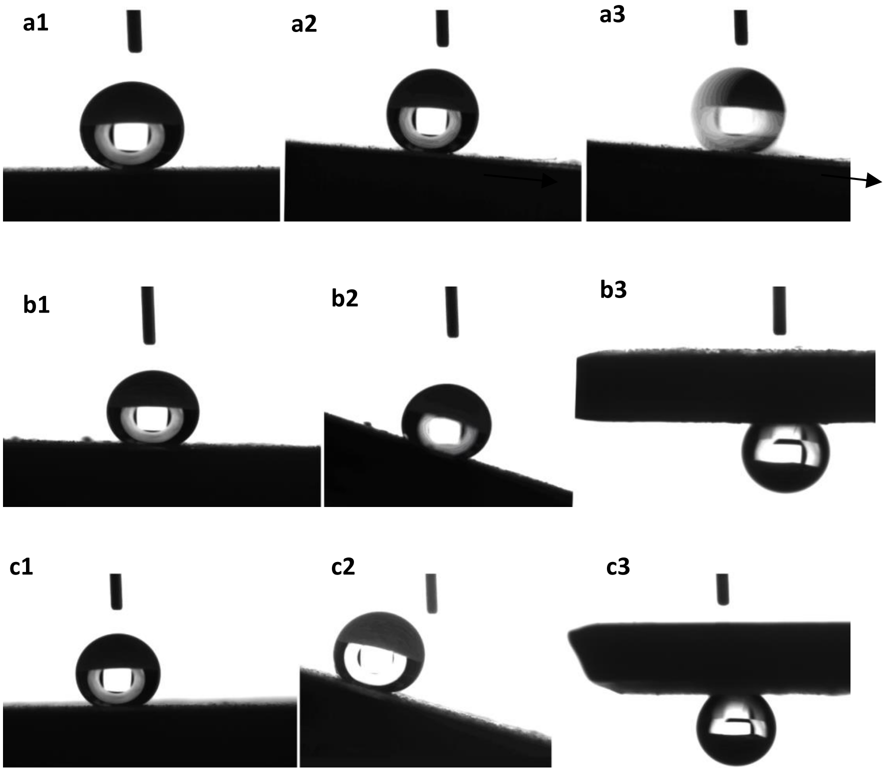

Fig.6. Images of water contact angles and slide angles for (a) APTES/PFTES-modified micro-nano-binary particles/epoxy coating; (b) APTES-modified micro-nano-binary particles/epoxy coating; and (c) Un-modified particles/epoxy coating

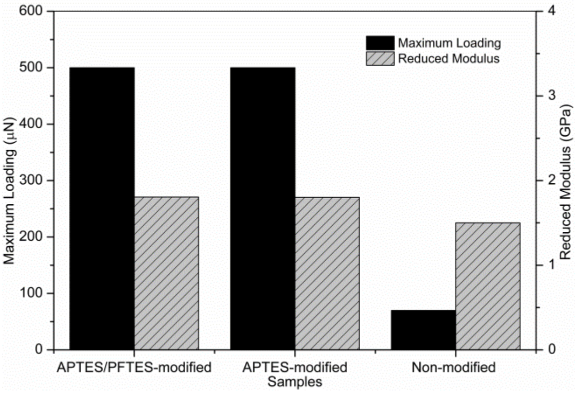

Fig.7 Comparison of maximum loading and reduced modulus of different samples