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Water-Repellent Textile via Decorating Fibers with Amphiphilic Janus Particles

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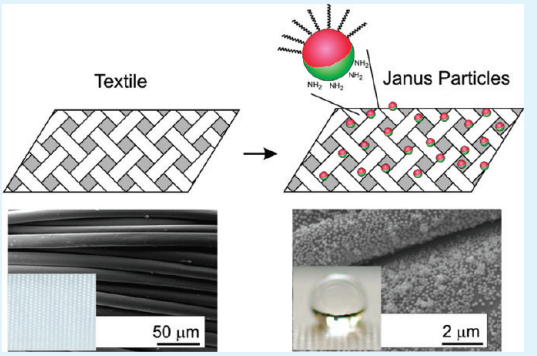
ABSTRACT: We investigated morphology and wetting properties of textiles modified by chemically immobilized amphiphilic micrometer and submicrometer large Janus particles. The Janus particles bind by their reactive side to the textile surface, while their hydrophobic side faces the environment. It was found that the character of immobilization of the Janus particles on textile depends on their size: larger particles bind between fibers, while smaller ones bind to the fiber surface. In both cases, immobilization of Janus particles results in the hydrophobization of the hydrophilic textile surface. Finally, we demonstrated that submicrometer large Janus particles are very efficient for the design of water-repellent textiles.



KEYWORDS: Janus particles, textile, ultrahydrophobic coatings, wetting

INTRODUCTION

Surface modification of textiles is a very important task and widely used to improve durability as well as water-repellent properties. The water-repellent textiles are typically prepared by adsorption of low-molecular weight compounds,[1−5] grafting of polymers,[6] impregnation with waxes and oils,[7−9] and growth of polymeric nanofilaments[10] or carbon nanotubes.[11,12] Colloidal particles are also very suitable for generation of materials with water-repellent[13−25] and switchable[16,26] properties. Recently, functional colloidal particles homogenously covered by polymers and silanes were successfully introduced for modification of textiles as well.[27−32] For example, Luzinov et al. demonstrated fabrication of water-repellent textiles with chemically attached colloidal nanoparticles.[33] The particles with reactive polymer shells were attached to the activated textile surface. The water-repellent properties were achieved by chemical immobilization of the hydrophobic polymer on the textile with particles. In particle-based and other approaches for the preparation of ultrahydrophobic textiles, a post-modification using a highly hydrophobic compound is required.

In this paper, we propose an alternative approach for the modification of textiles, which is based on the use of amphiphilic Janus particles. Janus particles are colloidal particles having different properties (such as charge, polarity, and optical and magnetic properties) at opposite sides.[34−41] The Janus particles can be considered as the colloid analogue of surfactants, which have different properties (charge, polarity) at their opposite sides.[34] We use Janus particles of different diameters with the sides modified by hydrophobic and hydrophilic reactive silanes. The Janus particles bind by their reactive side to the activated textile surface, and the hydrophobic side faces the environment (Figure 1). As a result, a hierarchically rough textile surface with water-repellent behavior can be fabricated. Moreover, no post-modification with hydrophobic compounds is required. To the best of our knowledge, this is the first example of the application of Janus particles for modification of textiles that has been reported to date.

EXPERIMENTAL SECTION

Materials. Tetraethyl orthosilicate (TEOS, Sigma), aminopropyltrimethoxy silane (APS, Gelest, Inc.), and octadecyltrichlorosilane (OTS, Gelest, Inc.) were used as received. Poly(glycidyl methacrylate) (PGMA) was prepared using free radical polymerization as described in ref 42. Poly(ethylene terephthalate) fabrics were woven at the Institute of Textile and Clothing Technology (ITB), Dresden, particularly for this study using multimicrofilament yarn. The basic types of weaves, plain (1/1) with warp density 720 yarn per 10 cm and weft density 301 yarn per 10 cm, were produced.

Synthesis of Janus Particles (Jps). Amphiphilic Janus particles were prepared as described in refs 40 and 42. Briefly, 200 nm and 1 μm large silica particles were prepared using a multistep hydrolysis−condensation procedure of TEOS in an ammonia hydroxide−ethanol solution using the Stöber approach as described in refs 43 and 44. Silica particles were mixed with wax and water at elevated temperature (T = 60 °C). Obtained wax colloidosomes were collected and exposed to a 2 wt % methanol APS solution in order to modify one side of the silica particles.[40] The opposite side of silica particles was modified by 2 wt % toluene solution of OTS after removal of wax.

Modification of Textile Fabrics. Textile fabrics from poly(ethylene terephthalate) (PET) fabric were modified according to the procedure described in refs 33 and 45. Briefly, the textile was washed several times in acetone, ethanol, and finally water. The cleaned textile material was treated with 40% sodium hydroxide for 2 min in order to partially hydrolyze PET on the fiber surface and form additional carboxyl and hydroxyl groups. The fabric was then thoroughly rinsed in water to

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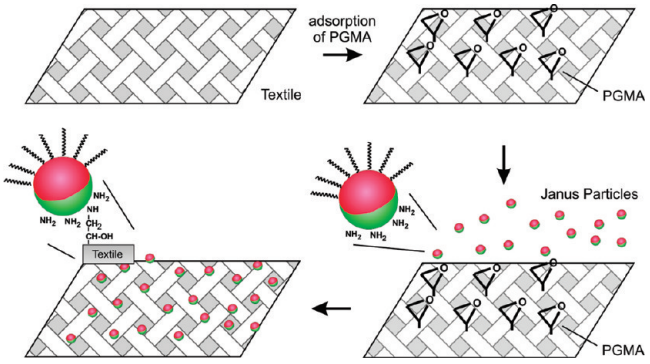

Figure 1. Scheme of modification of a textile surface using amphiphilic Janus particles. The textile is preliminary modified by poly(glycidyl methacrylate) (PGMA), which provides reactive epoxy groups. The Janus particles react with the epoxy groups by their amine sides, while their hydrophobic sides face the environment.

remove all the residuals and dried in an oven at 70 °C. Afterward, PGMA was absorbed on the textile surface from a 0.1% ethanol solution in order to produce enough of the reactive epoxy groups needed for immobilization of the Janus particles.

Contact Angle Measurements. Advancing water contact angles were measured by the sessile drop method using a conventional drop shape analysis technique (Krüss DSA 10, Hamburg, Germany). Deionized reagent grade water was used for contact angle measurements. Liquid droplets (15 μL) were dropped carefully onto the sample surface, and the average value of 5 measurements, made at different positions of the same sample, was adopted as the average values of contact angles of the substrates. The error of the mean contact angle values, calculated as the standard deviation, did not exceed 2−3°. Tilt angle was measured using a FibroDAT 1122HS dynamic contact angle tester (Fibro Systems AB, Sweden) equipped with a high-speed video camera. All contact angle measurements were carried out at 24 ± 0.5 °C and relative humidity of 40 ± 3%, which were kept constant.

Surface Topography. The surface topography was examined by using the optical imaging device MicroGlider (Fries Research & Technology GmbH, Bergisch Gladbach, Germany) and environmental scanning electron microscopy ESEM performed on DSM 982 Gemini (ZEISS, Germany). The roughness characteristics were obtained from 250 × 250 μm^2 (MicroGlider) scale images. The resolution of each MicroGlider image taken was 500 × 500 lines. The fractal dimension was calculated from MicroGlider data. The definition of a fractal is any point-set whose fractal dimension is strictly greater than its topological dimension. A fractal surface is a surface for which the lateral and vertical scaling behavior are not identical but determined by a scaling law. We applied the box counting method (MicroGlider Software FRT Mark III) to the cross section of the investigated films to find the fractal dimension of the prepared coatings.[13]

Deposition of Particles onto Different Substrates by Sedimentation. Janus particles dispersed in ethanol were adsorbed on the textile during 1 h. Then, the textile was dried and annealed at 70 °C in order to chemically bind Janus particles. Nongrafted particles were removed by ultrasonication and multiple rinsing in ethanol and water. Obtained particle-modified textiles demonstrated unchanged wetting properties after washing with ethanol.

RESULTS AND DISCUSSION

Amphiphilic Janus particles modified by hydrophobic OTS and reactive moderately hydrophilic APS were prepared according to the approach developed by Granik.[38] First, wax colloidosomes were prepared by mixing wax with silica particles in water.

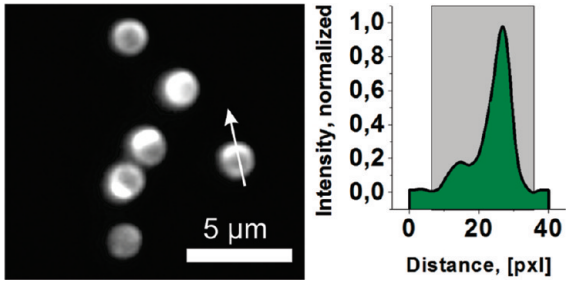

Figure 2. Fluorescence microscopy images for APS-OTS 1 μm large Janus particles after labeling with FITC (left) and intensity cross section (right).

The exposed sides of the silica particles were modified by APS. After removal of wax, hydrophobic OTS was adsorbed on the unoccupied side of the silica particles. We prepared large (d = 1 μm) and small (d = 200 nm) Janus particles using this approach. The ratio between perfluorinated and APS-modified sides was 3:1. The Janus character of the obtained particles was proved by labeling with fluorescent dye, fluorescein isothiocyanate (FITC), which selectively reacts with amino groups. We found that obtained particles are brighter on one side after labeling with FITC, which clearly indicates their Janus character (Figure 2).

In order to increase the amount of reactive carboxylic groups, the textile was treated with 40% sodium hydroxide. Then, the textile was rinsed in water and treated with a diluted PGMA solution. PGMA chains adsorb on the textile surface and, most probably, react with available carboxylic groups of poly(ethylene terephthalate), which constitutes the textile. As result, a thin layer of chemically attached PGMA is formed. Janus particles were deposited and chemically bound to the PGMA-modified textile (Figure 1). The formation of chemical bonds between textile and particles can hardly be directly proved because of the small contact area. On the other hand, particles are unable to bind to the textile without PGMA. Moreover, particles remain stable on the textile surface after sonication in an ultrasonic bath for several minutes. These two observations provide indirect evidence for the chemical binding of the particles.

We found that the character of distribution of the Janus particles on the textile surface depends on their size. In particular, the large (1 μm) Janus particles tend to assemble between individual fibers (Figure 3b), while smaller ones (200 nm) bind to the whole fiber surface (Figure 3c). Moreover, small Janus particles form raspberry-like aggregates, which bind to the textile as well. In fact, the deposition process depends on the structure of the textile and diameter of the fibers, so that the ratio diameter of particles/diameter of fibers is a key parameter. The reason for the different distribution of Janus particles on the textile surface could be gravity: larger particles, which are 2 orders of magnitude heavier than smaller ones, merely slide into the grooves between the fibers during adsorption. On the other hand, larger particles can be easier washed away from the fiber surface than the smaller ones. Immobilization of Janus particles results in an increase in the textile fractal dimension (Figure 3, lower panel). Moreover, different distributions of small and large Janus particles on the textile surface results in different fractal dimensions (FD): $FD_{\text{unmodified textile}}$ = 2.128, $FD_{1\mu m}$ = 2.161 and FD_{200nm} = 2.299.

Next, we investigated the wetting properties of native textile and textile with immobilized Janus particles. We found that, while the water contact angle on the native textile surface is very high in

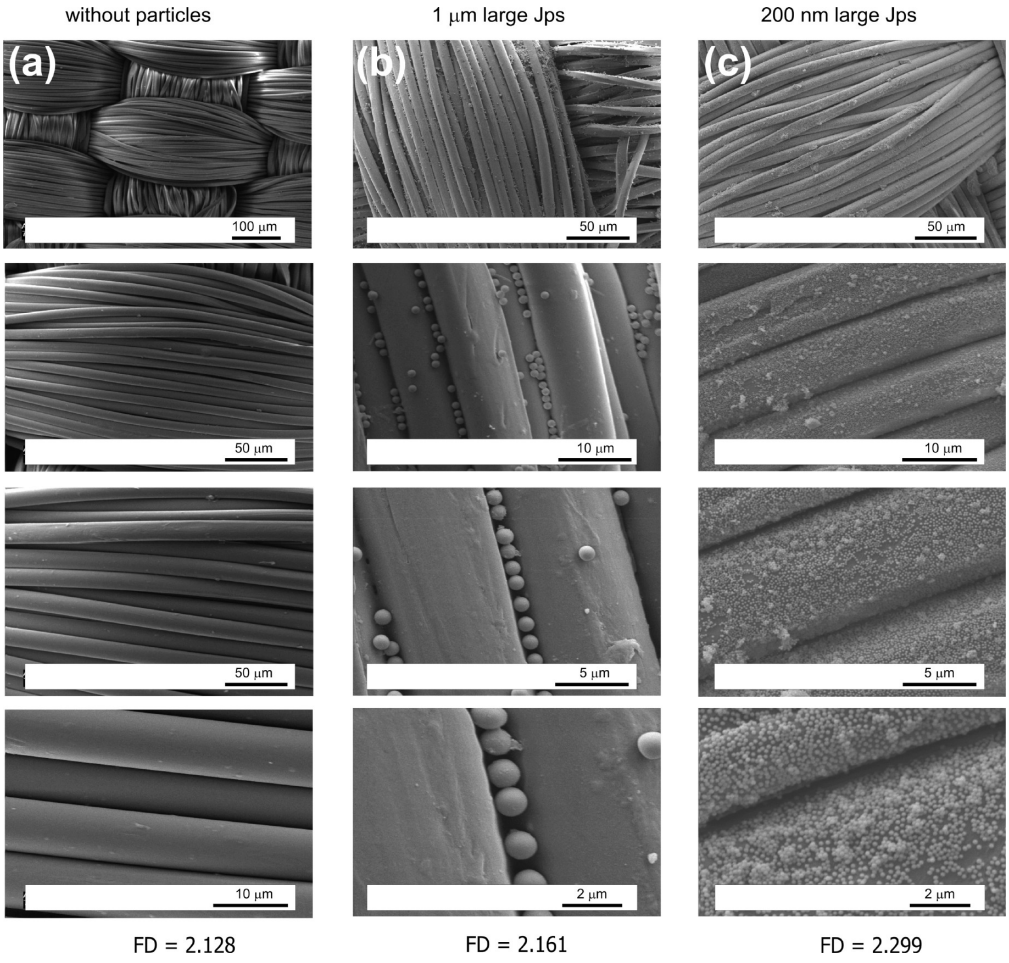

Figure 3. SEM images of textile: (a) before attachment of Janus particles, (b) with attached 1 μm large Janus particles, (c) with attached 200 nm large Janus particles. Fractal dimension (FD) for each system is given in the lower panel.

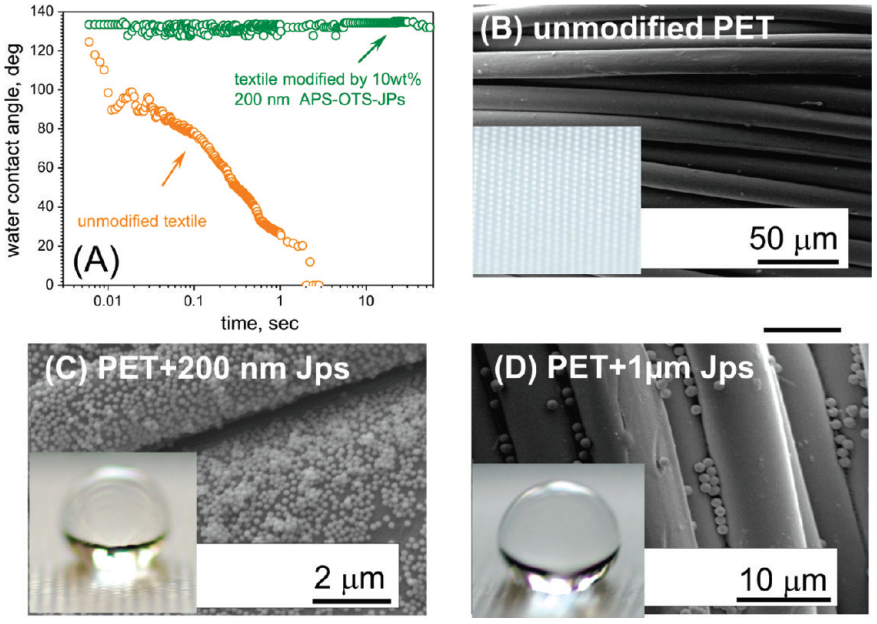

Figure 4. Wetting properties of textiles modified with Janus particles (Jps). (A) Time-resolved water contact angle on native textile (red) and textile modified by Janus particles (green). (B,C,D) Morphology images and optical images of water droplets on the native textile, textile modified by 200 nm, and 1 μm large Janus particles.

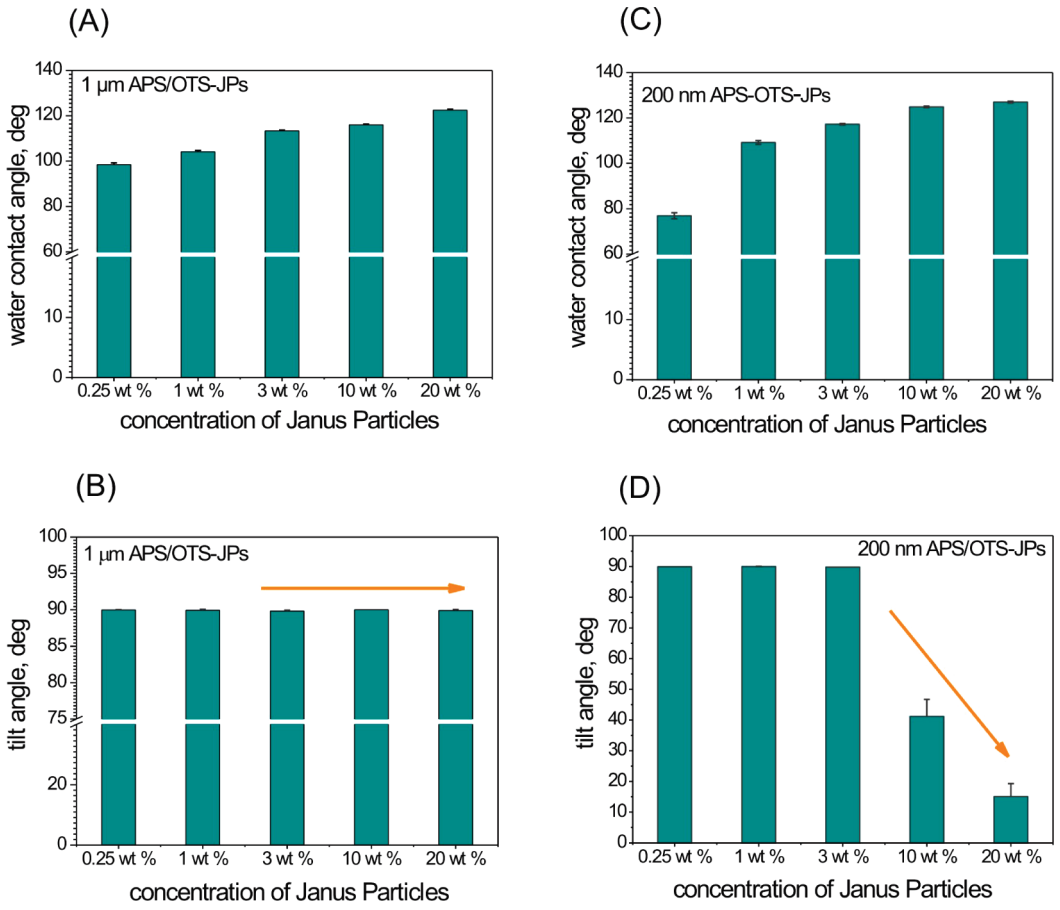

Figure 5. Wetting properties of textiles modified with Janus particles. Advancing water contact angle (upper panel) and tilt angle of water droplet (lower panel) on the textile grafted with 1 μm large (A,B) and 200 nm large (C,D) Janus particles.

the very first moment after deposition of the droplet, water rapidly penetrates into textile (Figure 4a,b). The native textile surface can, therefore, be considered as very hydrophilic: the water contact angle after 10 s is 0°. On the other hand, water droplets on the surface of the textile modified by Janus particles remain stable and do not penetrate into textile pores (Figure 4 c,d). Moreover, higher concentration of Janus particles in dispersion (up to 20 wt %) during deposition leads to an increase in the advancing water contact angle up to 120−140° in the case of both small (200 nm) and large (1 μm) Janus particles (Figure 5a,c). An increase in particle concentration in suspension during deposition has, on the other hand, an opposite effect on the value of the tilt angle of the water droplets in the cases of larger and smaller particles. In particular, the value of the tilt angle remains high (θ_{TILT} = 90°) and almost constant with increasing concentration in the case of large particles (Figure 5b). As a result, the water droplet is pinned to the textile surface. On the other hand, an increase in concentration of small particles results in a dramatic decrease in the tilt angle down to θ_{TILT} = 10° (Figure 5d). A low value for the tilt angle indicates that the water is not in the contact with the hydrophilic side of the Janus particles and that the hydrophilic side faces the textile surface. Thus, a high value for the advancing contact angle ($\theta_{ADV} \approx 140°$) and a low value for the tilt angle (θ_{TILT} = 10°) allows us to consider the surface of the textile modified by small Janus particles to be water repellent. In order to explain the difference in the wetting properties of the textile modified by small (200 nm) and large (1 μm) Janus particles, we suggest the following scenario. Large particles fill the pores between the individual textile fibers and, thus, prevent penetration of water. On the other hand, smaller particles form hierarchical rough hydrophobic structures on the surface of the textile, which have the highest value of fractal dimension, and provide water-repellent properties.

CONCLUSIONS

In conclusion, we investigated the morphology and wetting properties of textiles modified by chemically immobilized amphiphilic Janus particles of different sizes. It was found that the character of immobilization of Janus particles on the textile surface depends on their size: 1 μm large particles are deposited between fibers, while 200 nm large particles are deposited on the surface of fibers. We also found that small Janus particles form raspberry-like aggregates, which bind to the textile as well. In both cases, immobilization of Janus particles results in the hydrophobization of the hydrophilic textile surface. Finally, we demonstrated that 200 nm large Janus particles are very efficient for the design of water-repellent textiles. We believe that obtained results are of high importance for the engineering of novel multifunctional materials based on amphiphilic Janus particles.

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