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Simple Coating with pH-Responsive Polymer-Functionalized Silica Nanoparticles of Mixed Sizes for Controlled Surface Properties

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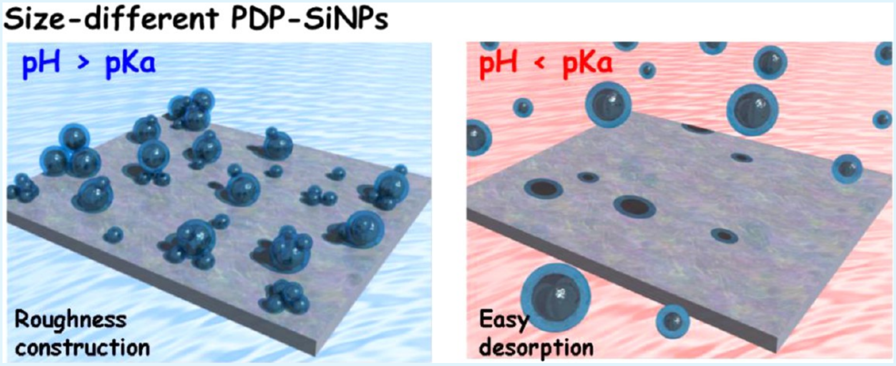
Supporting Information



ABSTRACT: Different-sized silica nanoparticles (SiNPs) were functionalized by pH-responsive poly(2-(diisopropylamino)ethyl methacrylate) (PDP) via surface-initiated atom transfer radical polymerization (ATRP). The functionalized PDP-SiNPs were used to coat glass surfaces, polymeric nanofibers, and paper via simple coating methods such as dip, cast, and spray coating. A PDP-SiNPs mixture having different sizes was found to change the surface properties of the substrates remarkably, compared to one containing PDP-SiNPs with uniform sizes. High surface roughness was achieved with very little coating materials, which is beneficial from an economical point of view. Moreover, adsorption/desorption of PDP-SiNPs onto/from the substrates could be controlled by changing solution pH due to the protonation/deprotonation of the PDP. The surface properties of the coated substrates were analyzed by contact angle (CA) measurement, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). This inexpensive system provides a simple, quick, and effective approach to changing the surface properties of substrates that could be exploited for large-scale surface modification.

KEYWORDS: *silica nanoparticles, 2-(diisopropylamino)ethyl methacrylate, atom transfer radical polymerization (ATRP), roughness, contact angle*

1. INTRODUCTION

Water-repellent surfaces are of great importance for a range of applications such as self-cleaning, anti-frost surface, resistance to water corrosion, and effective solution transport and its practical use will give economic benefits to our daily life. Generally, hydrophobic surfaces possessing high contact angle (CA > 150°) and low sliding angle (SA < 10°) for water droplets are called super-hydrophobic surfaces and are observed in nature. For example, the lotus leaf shows super-hydrophobicity known as the "lotus effect", because of their waxy and hierarchical nano/microstructure on the surface.[1,2] Butterfly wings are composed of terraced nano/microstructures, which show an anisotropic CA that effectively repels water drops toward the outside.[3] Water striders, on the other hand, can float on water due to their hierarchical and waxy legs.[4] The common features on these surfaces are the waxy materials (low surface energy) and hierarchical nano/microstructures (high roughness), and their relationship with the CA can be explained by theories of Wenzel[5] and Cassie and Baxter.[6]

On the basis of these theories, biomimetic surfaces for super-hydrophobicity have been actively reported. Lotus leaf-like surfaces were prepared using carbon nanotubes, and the surface showed super-hydrophobicity similar to that of the lotus leaf.[2] Poly(styrene) (PSt) nanofibers prepared by electrospinning, to mimic the silver ragwort leaf, was also observed to be super-hydrophobic with a CA of >150°.[7] Poly(dimethylsiloxane) film transcribed by grasshopper wings exhibited anisotropic CA behavior, because of the unique feature of the wing.[8] The slippery surface inspiring the inner surfaces of *Nepenthes* pitcher plant not only eliminates oils but also prevents ice formation.[9]

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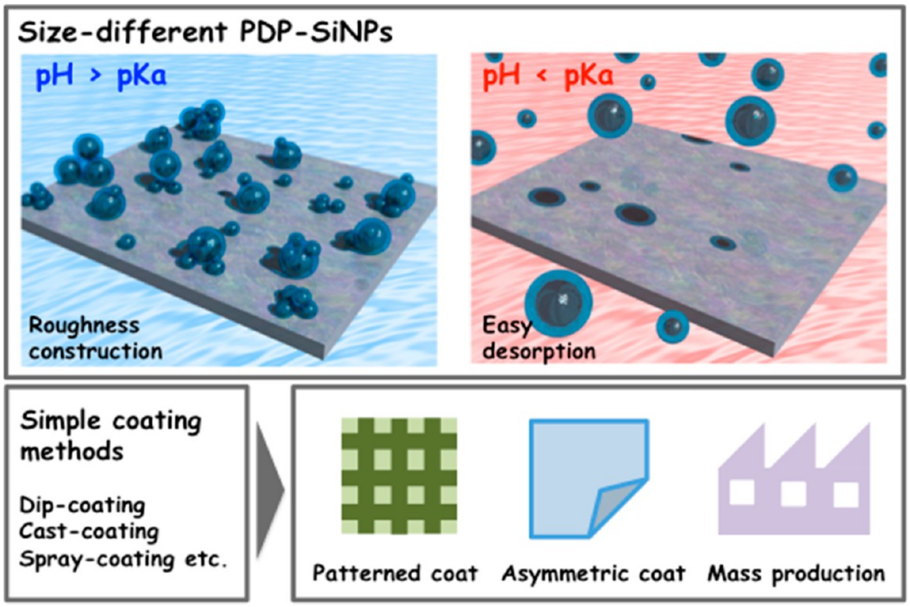

Figure 1. Schematic representation of different-sized PDP-SiNPs for controlled surface properties of substrates by simple coating methods.

Recently, surfaces with precisely controlled hierarchical nanostructures have been found to possess both the properties of super-hydrophobicity and transparency. Hierarchical structures are generally nontransparent and scatter light. To solve this problem, the size of the hierarchical structures must be less than the wavelengths of visible light. Park et al. achieved the preparation of super-hydrophobic and transparent silica materials through precisely arrayed nanoneedles on the surface.[10] However, these nanoneedle structures are usually prepared by top-down methods such as photoresist with multistep processes and, therefore, there is a need to improve the process for large production. Designing simple method is of great challenge for tunable surface properties of substrates when considering bottom-down approach. In the case of substrates with high surface roughness, super-hydrophobicity can be achieved simply by coating with hydrophobic chemical compounds or polymers. These modifications are often executed by treatment with silane coupling, dip coating, cast coating, spin coating, layer-by-layer (LBL) deposition, and surface-initiated polymerizations. On flat substrates with low roughness, however, it is difficult to construct surface with super-hydrophobicity properties by using low-molecular-weight compounds and flexible polymers. Even coating flat surfaces with trifluoromethyl groups with low surface energy resulted in CA ≈ 120°.[11]

Biocompatible silica nanoparticles (SiNPs) have attracted great attention as a simple material to construct high roughness on substrates, because of their easy control of size, shape, and surface modification. Recently, mixtures containing different sizes of SiNPs have been found useful in the fabrication of structures with efficient roughness, compared to those of uniform-sized particles. Ke et al. prepared high surface roughness using PDMS and octadecyltrichlorosilane (OTS)-modified SiNPs (500 and/or 100 nm) by drop-coating and heat treatment. The CAs of individual OTS-modified SiNPs of 500 and 100 nm were 125° ± 1° and 112° ± 1°, respectively. On the other hand, hierarchical structure composed of the mixed SiNPs reached super-hydrophobicity with CA = 155 ± 2° and SA ≈ 6°.[12] Zhou et al. coated polyester fabric using PDMS, fluorinated alkyl silane (FAS), and FAS-modified SiNPs (22 and 150 nm) by dip coating, followed by heat treatment. The CA of the coated polyester fabric was 171°, which showed excellent durability against laundry cycles, abrasion test, boiling treatment, dyeing, strong acid, and strong base.[13] Karunakaran et al. treated substrate surface with different-sized 3-aminopropyltrimethoxysilane (APTS)-modified SiNPs (20 and 100 nm) as two SiNPs layers for construction of efficient roughness. After hydrophobilization by (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane, the substrates showed super-hydrophobicity with high transparency.[14] In this way, high surface roughness can be achieved with mixed differently sized SiNPs, which can be of great importance, from an economic point of view.

Moreover, SiNPs can easily incorporate various materials such as dyes, drugs, metal particles, and quantum dots (QDs).[15−20] Ogihara et al. prepared pigment-doped SiNPs with different colors (such as red, blue, yellow, green, and black). These bright SiNPs were coated onto substrates by simple spray coating, and the resulting coated surfaces showed super-hydrophobic properties.[21] Using the spray-coating method, SiNPs having dodecyltrichloro groups were also coated on paper and cotton to achieve both super-hydrophobicity and high transparency.[22] For their role, these coating materials basically remained on the surfaces of the substrates, strongly because of physicochemical interactions. Therefore, only a few reports focused on the active desorption of coating materials. Tunable adsorption/desorption of coated materials is a challenge to achieve controlled surface properties, reconstruction of roughness structures, and recycling of materials. In our previous study, SiNPs with pH-responsive poly(2-(diethylamino)ethyl methacrylate) (PDE) was prepared and used as a coating material. The different-sized PDE-SiNPs were successfully used in constructing surfaces with high roughness, and their adsorption/desorption behaviors, as a function of solution pH, were studied.[23]

In this study, poly(2-(diisopropylamino)ethyl methacrylate) (PDP) is polymerized from SiNPs by surface-initiated atom transfer radical polymerization (ATRP) and used as a pH-responsive coating material. PDP shows low pK_a (pK_a = 6.3) and high hydrophobicity (pH ≥ pK_a), compared to PDE, and

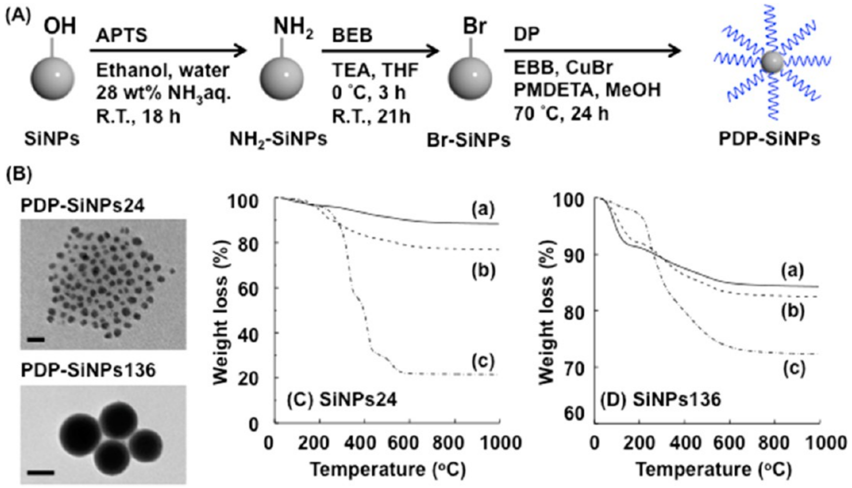

Figure 2. (A) Synthesis of different sizes of SiNPs with pH-responsive PDP by surface-initiated ATRP. (B) TEM images of PDP-SiNPs24 (scale bar 50 nm) and PDP-SiNPs136 (scale bar = 100 nm). (C) Weight loss of the modified SiNPs of 24 nm (NH$_2$-SiNPs24 (trace a), Br-SiNPs24 (trace b), and PDP-SiNPs24 (trace c). (D) Weight loss of the modified SiNPs of 136 nm (NH$_2$-SiNPs136 (trace a), Br-SiNPs136 (trace b), PDP-SiNPs136 (trace c)).

has been used as a biomaterial.[24,25] Suspension of a mixture of two different sizes of PDP-SiNPs is used to coat several substrates such as glass, poly(ε-caprolactone) (PCL) nanofiber, and paper by simple coating methods (Figure 1). These simple coating methods are expected to apply in patterned coat, asymmetric coat, and mass production. Surface properties of the coated substrates and adsorption/desorption behaviors of PDP-SiNPs are analyzed by CA measurement, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. EXPERIMENTAL SECTION

2.1. Materials. 2-(diisopropylamino)ethyl methacrylate (DP) was purchased from Sigma–Aldrich and purified by passing it through a basic alumina column. Tetraethoxysilane (TEOS), 3-aminopropyl triethoxysilane (APTS), triethylamine (TEA), 2-bromo-2-methylpropionyl bromide (BEB), ethyl α-bromoisobutyrate (EBB), copper(I) bromide (CuBr), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), and poly(ε-caprolactone) (PCL: M_n = 70–90 kDa) were obtained from Sigma–Aldrich and used as received. Bare SiNPs (20 nm) were provided from Nissan Chemical Industries, Ltd. Water used in this study was purified with a Millipore Milli-Q system. Other chemicals and solvents were used as received. PCL nanofiber was prepared by electrospinning (Imoto IMC-19F5, Japan). PCL was dissolved as 6 wt % in tetrafluoroethanol (TFE), and the viscous solution was used to fabricate nanofiber via the following conditions: DC voltage, 12 kV; pump rate, 0.5 mL/h; and distance, 17 cm.[26,27] Glass substrates (1 cm × 2.2 cm) were washed with a 36% HCl solution for 3 h at 70 °C and then were washed with a large amount of water before drying.

2.2. Preparation of Different-Sized PDP Functionalized Silica Nanoparticles (PDP-SiNPs). PDP-SiNPs were prepared via surface-initiated atom transfer radical polymerization (ATRP). As the ATRP initiator, bromo groups were modified on the SiNPs (Br-SiNPs: 24 and 136 nm), according to previously reported protocol.[23] The Br-SiNPs136 (0.15 g), with ethyl α-bromoisobutyrate (EBB) (8.4 mg, 0.044 mmol) as a free initiator and DP (3.71 g, 17.4 mmol), were dispersed in methanol (6 mL). A methanol (3 mL) solution of CuBr (112.3 mg, 0.78 mmol) and PMDETA (159.3 mg, 0.78 mmol) was added to the dispersion. After degassing with nitrogen gas for 30 min, the mixture was allowed to polymerize for 24 h at 70 °C. The resulting PDP-SiNPs136 was purified by centrifugation (14 000 rpm, 10 min) and washing with ethanol and acetone. The supernatant liquid was purified by dialysis against methanol after passing it through an alumina column, and dried under reduced pressure to measure the molecular weight and molecular weight distribution of the PDP polymerized from the free initiator.

2.3. Characterization. The molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) with Waters Ultrahydogel linear WAT011545 columns and Viscotek model 270 dual detectors. Sodium acetate/acetic acid buffer (0.50 M) was used as an eluent at a flow rate of 1.0 mL/min.

Thermogravimetric analysis (TGA) were carried out using a SDTQ600 (TA Instruments) analyzer between 25 and 1000 °C in air at a heating rate of 10 °C/min. The organic content was calculated by their weight loss between 115 and 700 °C.

Transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (Morgagni 268, FEI Company) with an accelerating voltage of 80 kV. The samples were prepared by adding a drop of PDP-SiNPs suspension on carbon-coated copper grids and were allowed to dry before analysis.

Contact angles (CAs) were measured at room temperature using a water drop. The substrates were coated with PDP-SiNPs dispersion (ethanol or acidic water) by dip-, cast-, and spray-coating methods. With dip coating, glass substrates were dipped into the PDP-SiNPs dispersion for 1 min as one step, and then were dried. The coating process was repeated by the objective step numbers (1, 3, 5, and 10 steps). The coated substrates were washed with a large amount of water. With cast coating, the dispersion of PDP-SiNPs was dropped on the glass substrates, and then was dried. The coating process was repeated by the objective step numbers and washed using a large amount of water. A paper sheet was coated with a dispersion of mixed PDP-SiNPs by spray coating. These dried samples were measured more than three times at different locations to obtain the average CA value.

The transmittance of glass substrates coated with functionalized SiNPs was measured via an irradiation of light (wavelength of 500 nm) using an ultraviolet-visible (UV-Vis) spectrometer (Model V-630, Jasco).

Scanning electron microscopy (SEM) (FEI Company) was used for observation of the coated PDP-SiNPs on substrates. The substrates were coated with PDP-SiNPs dispersion (ethanol or acidic water) and then were washed by a large amount of water. These samples were coated with gold, using a magnetron sputtering system.

Dynamic light scattering (DLS) was performed with a ZetaPlus-Zeta Potential Analyzer (Brookhaven Instruments Corporation) at a scattering angle of θ = 90°.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Different-Sized PDP-Coated Silica Nanoparticles (PDP-SiNPs). The size of silica nanoparticles (SiNPs) is a very important factor in the construction of rough surfaces. Karunakaran et al. reported the use of mixed SiNPs suspensions of 20, 50, and 100 nm for the creation of rough structures, and they showed that the combination of 20 and 100 nm SiNPs are ideal for the creation of high roughness on flat substrates.[14] Therefore, SiNPs 24 and 136 nm in size were selected for the construction of tunable surfaces with high surface roughness.

Two different sizes of SiNPs functionalized by poly(2-(diisopropylamino)ethyl methacrylate) (PDP-SiNPs) were synthesized by surface-initiated atom transfer radical polymerization (ATRP), as shown Figure 2A. EBB was also added to the polymerization system, as a free initiator, to allow the formation of free polymer chain in solution for the determination of the molecular weight and molecular weight distribution of the polymer on SiNPs. The polymer produced in solution from the free initiator and that on SiNPs were expected to have similar molecular weight and molecular weight distribution, as reported previously.[28,29] After polymerization, PDP-SiNPs and PDP were separated by centrifugation (14000 rpm, 10 min). The number-average molecular weights of PDP were M_n = 8600 g/mol (for PDP-SiNPs24: M_w/M_n = 1.34) and M_n = 6000 g/mol (for PDP-SiNPs136: M_w/M_n = 1.22), respectively. The PDP coated on SiNPs were synthesized to have molecular weights that were similar to that of poly(2-(diethylamino)ethyl methacrylate) (PDE) in our previous report (PDE-SiNPs20: M_n = 9200 g/mol, M_w/M_n = 1.34, PDE-SiNPs128: M_n = 6300 g/mol, M_w/M_n = 1.29).[23] We believed the chain length of the polymers on the silica nanoparticles surface played an important role in the pH-responsive properties, as well as in the construction of high surface roughness. Figure 2B shows the corresponding transmission electron microscopy (TEM) images of those functionalized PDP-SiNPs. Figure 2C shows the percent weight loss of PDP-SiNPs as a function of temperature as analyzed by thermogravimetric analysis (TGA). The weight losses between 115 °C and 700 °C in air were used to calculate the organic content on the SiNPs. The organic contents of NH_2-SiNPs24, Br-SiNPs24, and PDP-SiNPs24 were 9.0%, 21.6%, and 77.9 %, respectively. On the other hand, the organic contents recorded for NH_2-SiNP136, Br-SiNPs136, and PDP-SiNPs136 were 9.2%, 13.2%, and 26.0 %, respectively. A higher organic content was observed for PDP-SiNPs24, as compared to that of PDP-SiNP136, probably because of their larger surface area. In addition, grafting-from methods such as surface-initiated ATRP generally allowed higher polymer density, compared to grafting-to methods.[29−32] The calculated polymer density of PDP-SiNPs136 was 0.77 chain/nm^2, which suggested that the SiNPs were coated with high polymer density. These data are shown in Table 1. Chemical compositions of the functionalized SiNPs were also analyzed by Fourier transform infrared (FT-IR) spectroscopy (see Figure S1 in the Supporting Information). These results suggested that the desired PDP-SiNPs were successfully prepared.

3.2. Controlled Surface Properties of Substrates by Simple Coating of Mixed PDP-SiNPs. High surface roughness on substrates was achieved by using a small quantity of a mixture of two different sizes of the synthesized PDP-SiNPs. Based on our previous data, mixed sizes of SiNPs functionalized with poly(2-(diethylamino)ethyl methacrylate) (PDE-SiNPs) were prepared, and a mixed suspension was coated on flat glass substrates by cast coating and dip coating. Surface treatment with a mixture of two different sizes of PDE-SiNPs was found to create surface roughness with a contact angle of CA ≈ 120° when the mixture weight ratio was 1:3 for PDE-SiNPs20/PDE-SiNPs128. Moreover, the deposited PDE-SiNPs could be removed from the surface simply by acid solution treatment.[23]

Table 1. Characterization of PDP-SiNPs

	SiNPs24	SiNPs136
organic content[a] NH_2-SiNPs	9.0%	9.2%
Br-SiNPs (%)	21.6%	13.2%
PDP-SiNPs (%)	77.9%	26.0%
M_n[b]	8600 g mol^{-1}	6000 g mol^{-1}
M_w/M_n[b]	1.34	1.22

[a] The weight losses between 115 and 700 °C, as determined by TGA, were used to calculate the organic amount of the SiNPs. [b] As determined by GPC.

Stratakis et al. polymerized PDE and PDP from rough substrates by surface-initiated ATRP. Interestingly, the roughness of the surface modified by PDP showed higher CA (154.1° ± 1°: super-hydrophobicity), compared to that of PDE (~126° ± 1°) under alkaline conditions, because of their more hydrophobic isopropyl groups.[24] Therefore, we selected PDP to modify SiNPs for controlled surface properties of substrates. Moreover, simple coating methods such as cast, dip, spin, and spray coating are also important for bottom-up type mass production. PDP-SiNPs can be applied to these coating methods, because they can be easily dispersed in solvents of low toxicity, such as an acidic solution (pH < pK_a = 6.3), ethanol, or a mixture.

Figure 3A shows the CAs of coated glass substrates with a mixture suspension PDP-SiNPs24/PDP-SiNPs136 at a weight ratio of 1:3 by dip coating with different coating steps (1, 3, 5, and 10 steps). The CA of the hydrophilic glass substrate (CA = 9.3° ± 0.1°) was gradually increased with increasing coating steps as more and more PDP-SiNPs were deposited on the surface. After 10 steps, the CA changed to 88.6° ± 2.6°. On the other hand, transparency of the glass substrate was gradually decreased with increasing coating steps (10 steps: 55.4%). A mixture of two different sizes of PDP-SiNPs (PDP-SiNPs24/PDP-SiNPs136) at a weight ratio of 1:3 was also used to coat glass substrate by cast coating for high coverage with PDP-SiNPs. Figure 3B shows the CAs of the coated glass substrates using cast coating with 10, 20, and 30 steps. The CAs were found to be similar to the values obtained from the cast-coating method with 10 steps (118.5° ± 1.8°), 20 steps (119.8° ± 1.5°), and 30 steps (116.4° ± 0.3°), respectively, despite the fact that the transmittances were gradually decreased as the number of coating steps increased. Therefore, there was no significant difference in the CA values after high surface coverage of the substrates. These results suggest that the roughness of the top side of silica constructions is similar, which means we need only the top layer of the constructions to add maximum change for surface properties of substrates. The CAs of a treated surface with another mixture of weight ratio 1:1 (PDP-SiNPs24/PDP-SiNPs136) was found to be ~104°, regardless of the number of coating steps (see Figure S2 in the Supporting Information). High coverage with PDP-SiNPs24

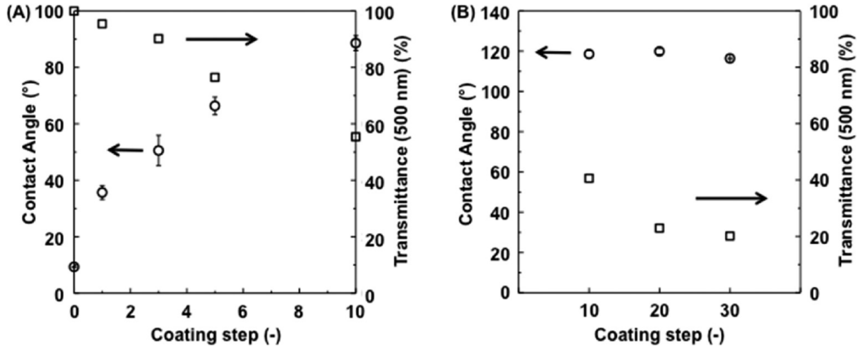

Figure 3. (A) Contact angle (CA) of flat glass substrates (1 cm × 2.2 cm) coated with a mixture suspension (ethanol, 0.05 wt %, PDP-SiNPs24/PDP-SiNPs136 ratio = 1:3 (wt/wt)) by dip coating. The glass substrates were dipped into the dispersion for 1 min as one step and were dried. This coating process was repeated by objective step numbers. The coated substrates were washed with water. (B) Contact angle of flat glass substrates (1 cm × 2.2 cm) coated with mixture suspension (ethanol, 0.05 wt %, PDP-SiNPs24/PDP-SiNPs136 ratio = 1:3 (wt/wt)) by cast coating. The dispersion (100 μL = 1 step) was depoisted dropwise onto the glass substrates and was dried. This coating process was repeated by objective step numbers. The coated substrates were washed with water. Transmittance of the coated glass substrates were measured by irradiation of light (wavelength 500 nm). A water drop (2 μL, pH 10) was used for CA measurement.

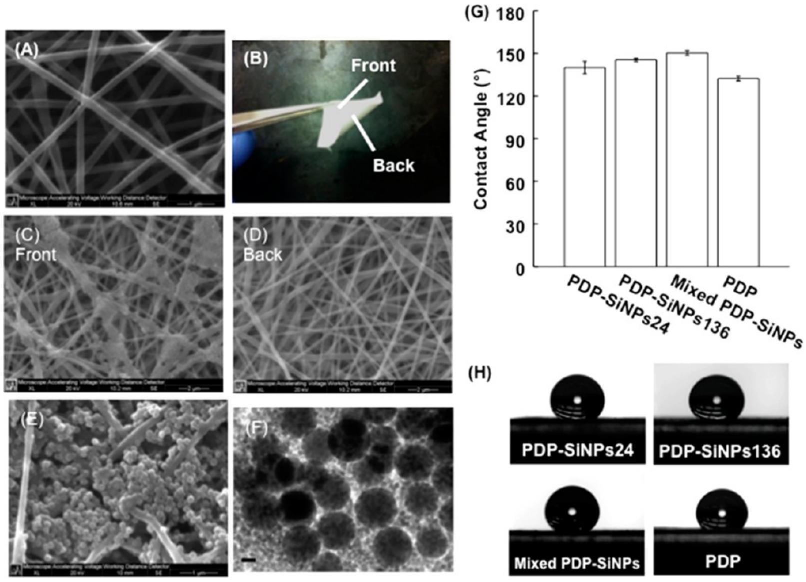

Figure 4. (A) SEM image of PCL nanofiber. (B) Picture of PCL nanofiber coated with PDP-SiNPs136. SEM images of the (C) front and (D) back surfaces of PCL nanofiber coated with PDP-SiNPs136. (E) SEM image of PCL nanofiber coated with mixed PDP-SiNPs24/PDP-SiNPs136. (F) TEM image of mixed PDP-SiNPs24/PDP-SiNPs136. (Scale bar = 50 nm for SEM micrographs.) (G) Contact angle of PCL nanofiber coated with PDP-SiNPs24, PDP-SiNPs136, mixture (PDP-SiNPs24/PDP-SiNPs136 ratio = 1:3 (wt/wt)), and PDP (the suspensions (HCl_{aq} (pH 2.5), 0.5 wt %, 200 μL) were deposited dropwise onto the nanofibers as cast coating; the coated nanofibers were immersed in pH 8.5 solution for 10 min and were dried). (H) Photographs of the water drop (Milli-Q, 8 μL) on the coated PCL nanofibers.

may have very well reduced the surface roughness, as shown previously.[23]

Cast coating can also be used to easily prepare asymmetric surface properties on substrates. Figure 4A shows poly(ε-caprolactone) (PCL) nanofibers fabricated by electrospinning. Only one side of the nanofiber was coated with a suspension of PDP-SiNPs136 in acidic solution by cast coating for asymmetric coating. There was no difference between the front and back surface of the coated PCL nanofibers upon visual inspection, as shown in Figure 4B. SEM images, however, showed the deposition of the PDP-SiNPs136 only on the treated surface (see Figures 4C and 4D). Mixed suspension of PDP-SiNPs was also coated on PCL nanofibers, and the resulting nanofibers were characterized by SEM, as shown in Figure 4E. PDP-SiNPs24 was however not seen on the PCL nanofibers, because of their small sizes. Therefore, the mixed suspension was deposited dropwise onto a TEM grid to investigate their hierarchy construction. It was observed that the PDP-SiNPs24 and PDP-SiNPs136 were randomly deposited to form hierarchical structures (see Figure 4F).

Figures 4G and 4H shows CAs of PCL nanofibers coated with single or mixed PDP-SiNPs and PDP polymer. The CA of the original PCL nanofibers was found to be 135.2° ± 0.8°, in agreement with the literature.[11] On the other hand, the CAs of PCL nanofibers coated with PDP-SiNPs24 and PDP-SiNPs136 were 140.1° ± 4.4° and 145.6° ± 1.2°, respectively. Interestingly a mixture of the two sizes of the PDP-SiNPs revealed a CA of 150.5° ± 1.7°, which exceeded that of the single size of SiNPs coating. In our previous report, in fact, silicon wafers coated with a mixture of PDE-SiNPs20 and PDE-SiNPs128 showed large surface roughness, as determined by AFM, in comparison to an individual SiNPs coating.[23]

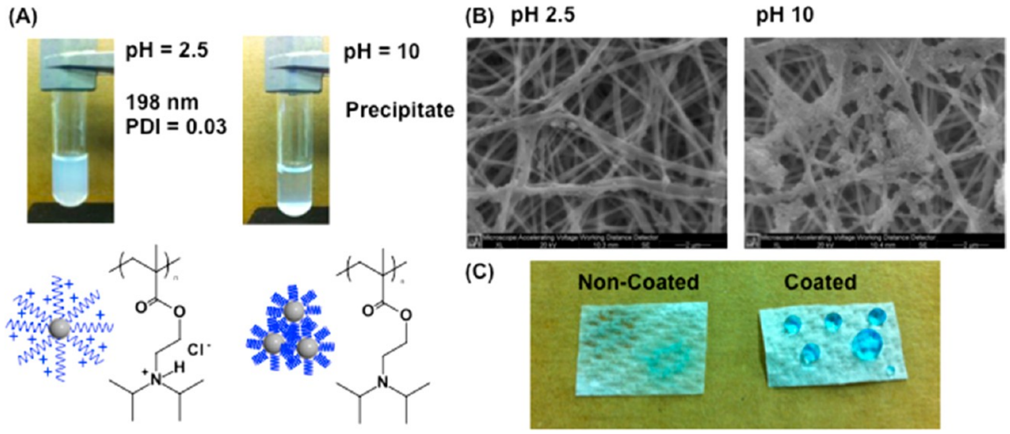

Figure 5. (A) Diameters of PDP-SiNPs136 in 0.1 wt % pH 2.5 and pH 10 aqueous solutions measured by dynamic light scattering (DLS). (B) Adsorption/desorption properties of PDP-SiNPs136 (HCl_{aq} (pH 2.5), 0.5 wt %, 200 μL) on PCL nanofibers coated by cast coating. The coated PCL nanofibers were washed with water after immersed in pH 2.5 or 10 aqueous solution for 24 h. (C) Paper sheet coated with mixed PDP-SiNPs (PDP-SiNPs24/PDP-SiNPs136 ratio = 1:3 (wt/wt)).

Moreover, the CA of PCL nanofiber coated with the polymer PDP (the same concentration as PDP-SiNPs136) was found to be 132.4° ± 1.6°, which is close to that of the noncoated nanofiber. These results suggest that the use of mixed PDP-SiNPs was essential to generate high surface roughness on both flat and fiber substrates, and the simple coating methods has led to the creation of a unique surface morphology on substrates including asymmetric coated surfaces.

The pH-responsiveness property of PDP-SiNPs136 was subsequently determined by dynamic light scattering (DLS) at pH 2.5 and 10. At pH 2.5, PDP became highly protonated and hydrophilic, and the diameter of the PDP-SiNPs136 was 198 nm (PDI ≈ 0.03). The larger diameter (as compared to TEM data) may be explained by the expanded PDP polymer chains. On the other hand, at pH 10, PDP-SiNPs136 was aggregated to each other and was precipitated out due to the hydrophobic deprotonated PDP chains (Figure 5A). PCL nanofibers coated with PDP-SiNPs136 were immersed in different pH solutions and were characterized by SEM for their surface morphologies. Most of the PDP-SiNPs136 was found to desorb from the PCL nanofibers immersed in pH 2.5 solution. As expected, at pH 10 solution, the PDP-SiNPs136 were mostly located on the surface, because of their hydrophobic interaction (Figure 5B). These results suggest that PDP-SiNPs can be easily controlled for their adsorption/desorption by solution pH. Treatment of paper sheets with mixed PDP-SiNPs by spray coating was found to change their surface properties. As shown in Figure 5C, the coated paper sheet successfully repelled the water drops. These results showed that we have successfully transformed a high water absorbency and hydrophilic surface to a hydrophobic one via a simple treatment with nanoparticles. Moreover, the paper sheet coated by PDP-SiNPs floated on water, compared to a treated paper sheet that can quickly soak up water (see Movie S1, proivded with the Supporting Information). This result showed that the PDP-SiNPs on the surface of the paper sheet prevented water molecules from penetrating through the paper.

Therefore, simple treatment of PDP-SiNPs can control surface properties of substrates by changing the surface morphology and can also transform a hydrophilic surface to a hydrophobic one. Moreover, the coated PDP-SiNPs can be easily washed away from the substrates by changing the solution pH.

4. CONCLUSIONS

Two different sizes of PDP-SiNPs were successfully prepared by surface-initiated ATRP, and treatment of different surfaces with the functionalized SiNPs such as glass, polymeric nanofibers, and paper sheet was achieved by inexpensive and simple coating methods such as dip coating, cast coating, and spray coating. A mixture of the PDP-SiNPs of distinct sizes was found to change the surface roughness and the hydrophilicity/hydrophobicity of the substrate surface. Moreover, adsorption/desorption of PDP-SiNPs on the substrates could be achieved simply by changing the solution pH due to protonation/deprotonation of PDP. The effective roughness construction for controlled surface properties and simple coating methods lead to an inexpensive system, which is promising for bottom-up surface modification.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FT-IR spectra of modified SiNPs. CAs of glass substrates coated with mixed SiNPs (PDP-SiNPs24/PDP-SiNPs136 ratio = 1:1 (wt/wt)). Movie of paper sheet coated with PDP-SiNPs24/PDP-SiNPs136. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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