Nanoporous Organic Network Coating of Nanostructured Polymer Films with Enhanced Adsorption Performance toward Particulate Matter

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ABSTRACT: This work shows that the surface properties of polyurethane acrylate (PUA) films can be controlled by the coating of nanoporous organic networks (NONs). By the NON coating, the hydrophilic nature of nanostructured PUA (N-PUA) film was converted to superhydrophobic surface. The NON-coated N-PUA films (N-PUA-NONs) were applied as stationary adsorbents for the capture of particulate matter (PM) in air. Compared with the original PUA films, the N-PUA-NON films showed much enhanced capture performance toward PM and recyclability through water washing, indicating the potential of outdoor application as stationary self-cleaning adsorbents under natural surroundings.

KEYWORDS: porous organic network, Sonogashira coupling, particulate matter, adsorption, film

N ature uses surfaces for tailored purposes.1 For example, because plants are stationary, they have utilized surfaces for various purposes. Especially, various new functions of leaves have been elucidated.2 In addition to photosynthesis, leaves can act as stationary adsorbents. It can be rationalized that nutrients suspended in air are captured through the adsorption action of leaves. Rain then induces water washing of the adsorbed chemicals, transferring the nutrients to routes. Moreover, the well-recognized lotus effect originates from the superhydrophobic microstructures of leaves.3 On the surface of lotus leaves, adsorbed dust can be removed by water washing. The adsorptive function of leaves can be utilized for artificial purposes. For example, trees diminish unpleasant smells in livestock and poultry production areas.4 In addition, there have been studies on the use of natural leaves for the adsorptive removal of pollutants.5

Recently, particulate matter (PM) in air has become a serious problem in East Asia.6 Various methods have been devised to remove or reduce PM.7−14 For example, electric-field-induced aggregation, physical filtration, and water scrubbers have been developed. However, these methods are energy consuming. In addition to these methods, stationary adsorbents can be developed. It is noteworthy that trees have been utilized for the reduction of PM in air.15 However, because PM is mostly problematic in urban and industrialized regions, the area for tree planting is limited. Thus, stationary adsorbent materials with functional surfaces, which can be called artificial adsorptive leaves, should be studied. Especially, the chemical engineering of surface and the understanding of adsorption performance should be explored.

Polymers are versatile engineering materials. Many polymer films including polyurethane acrylate (PUA) films have been engineered for various purposes.16 The physical properties of polymer surface have been controlled via a morphology engineering.16 In addition, the chemical properties of polymer films can be further tuned by the coating of secondary material. In this regard, more exploration is required for the efficient coating of polymer films.

Recently, various nanoporous organic network (NON) materials have been prepared by the coupling of rigid building blocks.17 Because of their high chemical stability, nanoporosity (main pore sizes <2 nm), and high surface areas, the NON materials have been applied for adsorption purposes.18−25 While the NON materials have been prepared mostly in powder form, the coating methods of NON materials onto other solid materials should be studied to extend their application fields.26 In this work, we report the coating of nanostructured PUA (N-PUA) polymer films with NON materials and their surface functions for the adsorption of PM.

Figure 1 shows the engineering schemes for the NON-coated PUA (PUA-NON) film and NON-coated nanostructured PUA (N-PUA-NON) films.

Received: October 19, 2018
Accepted: November 27, 2018
Published: November 27, 2018
A PUA film with even surface was coated with NON materials through the Sonogashira coupling of tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene to form PUA-NON film. The same procedures as the NON coating of PUA film were applied to the N-PUA film with aligned nanocolumns. Through varying the amount of building blocks, we prepared three N-PUA-NON films. The films with relatively thin, medium, and thick NON coatings were denoted as N-PUA-NON-1, N-PUA-NON-2, and N-PUA-NON-3, respectively.

The morphologies of PUA-NON and N-PUA-NON films were investigated by scanning electron microscopy (SEM). As shown in Figure 2a, the surface of pristine PUA film was very even. After NON coating, the surface of PUA-NON became slightly bumpy (Figure 2b). The sizes of convex NONs were 250–470 nm. The SEM image of N-PUA film showed the aligned columns having a diameter of 500 nm and an intercolumn distance of 1 μm (Figure 2c). Figures 2d, g, and j show the SEM images of N-PUA-NON-1 film, indicating that the surface of N-PUA film was incompletely coated with very small NON particles because the amount of building blocks was not sufficient. The diameter of columns in N-PUA-NON-1 film increased slightly to ~880 nm after NON coating. In the case of N-PUA-NON-2 film, the diameter of columns increased significantly to 750–930 nm (Figure 2e, h, k). Interestingly, the morphology of NON coating in N-PUA-NON-2 film was overall bumpy including the basal film. The magnified SEM image showed that the NON coating in N-PUA-NON-2 film consists of the connected NON particles with sizes of 150–250 nm (Figure 2k). The NON coating in N-PUA-NON-3 film became even through the ripening of the NON growth and the diameter of columns was ~880 nm (Figure 2f, i, l).

To further characterize the NON materials in PUA-NON and N-PUA-NON films, we etched PUA materials by treating them with NaOH in the presence of Me₄NBr. The NON materials (0.39 wt % in N-PUA-NON-1) obtained through the etching of N-PUA from N-PUA-NON-1 were ill-defined powders and too small of amounts to analyze.

The NON materials (1.02 wt %) obtained from PUA-NON film were thin films with thickness of 150–260 nm (Figure S1). In contrast, the SEM images of N-NON-2 (2.22 wt %) and N-NON-3 (3.31 wt %) films obtained through the PUA etching from N-PUA-NON-2 and N-PUA-NON-3 films, respectively, showed aligned hollow columns (Figure 3b–g). The bottom side of N-NON-2 film showed the aligned holes, corresponding to the original PUA columns (Figure 3e). Overall, the homogeneous NON coating in N-PUA-NON-2 and N-PUA-NON-3 films could be confirmed (Figure 3b, d).

The morphologies of NON materials in the N-NON-2 and N-NON-3 films were further investigated by transmission electron microscopy (TEM), revealing the hollow space in the columns. (Figures 3h–j) As shown in Figure 3i, the NON coating in N-NON-2 film was bumpy and consisted of the attached NON spheres. Thus, the thicknesses of NON coating...
in N-NON-2 film were observed in the relatively wide range of 80∼220 nm (Figure 3i). In comparison, the NON coating in N-NON-3 film was relatively even, compared with that of N-NON-2 film, and the thicknesses were observed in the range of 130∼160 nm (Figure 3j).

Figure 4a shows the N$_2$ adsorption–desorption isotherm curves of NON, N-NON-2, and N-NON-3 films. The analysis of N$_2$ isotherm curves revealed that the surface areas of NON, N-NON-2, and N-NON-3 films are similar one another with 657, 636, and 642 m$^2$/g, respectively. The pore size distribution diagrams were obtained through analysis based on the density functional theory (DFT) and showed the nanoporosity (pore sizes <2 nm) of materials (Figure 4b). In comparison, the pristine PUA and N-PUA films were nonporous (Figure S2). Thermogravimetric analysis (TGA) showed that N-PUA-NON-2 and N-NON-2 films are stable up to 190 °C (Figure S3).

The powder X-ray diffraction (PXRD) patterns of PUA, N-PUA, PUA-NON, and N-PUA-NON films showed the strong diffraction peaks at 2θ of 26°, corresponding to the packing structure of PUA materials (Figure 4c). In comparison, the NON, N-NON-2, and N-NON-3 films were noncrystalline (Figure 4c), which is the conventional properties of NON materials prepared by the Sonogashira coupling in the literature.²⁸ The chemical structure of NON materials in PUA-NON and N-PUA-NON film was characterized by infrared absorption (IR) and nuclear magnetic resonance (NMR) spectroscopy. The IR spectra of PUA, N-PUA, PUA-NON, and N-PUA-NON films showed exclusively the CO vibration peaks of PUA materials at 1729 cm$^{-1}$ because of the relatively minor contents of NON materials (Figure 4d). In comparison, the IR spectra of NON, N-NON-2, and N-NON-3 films showed major vibration peaks at 1501 and 821 cm$^{-1}$, corresponding to the C=O and C−H vibrations of aromatic groups, respectively (Figure 4d). Solid state $^{13}$C NMR spectra of NON, N-NON-2, and N-NON-3 films showed $^{13}$C peaks at 64, 91, and 116−151 ppm, corresponding to benzyl carbon, internal alkynes, and aromatic groups in the materials (Figure 4e). The IR spectra
and $^{13}$C NMR spectra of NON, N-NON-2, and N-NON-3 were identical to those of the NON materials prepared by the Sonogashira coupling of the same building blocks, indicating that the NON materials were successfully incorporated into the surface of PUA and N-PUA films.

According to water contact angle measurements, the pristine PUA film showed water-compatibility with a water contact angle (WCA) of 78° due to the existence of polar groups (Figure 5a). The PUA-NON film became slightly hydrophobic with a WCA of 115° due to the organic nature of NON materials (Figure 5b). Although the N-PUA film showed hydrophilic nature with advancing and receding WCAs of 87° and 75°, respectively, the hydrophobicity gradually increased from N-PUA-NON-1 film to N-PUA-NON-2 and N-PUA-NON-3 films with advancing WCAs of 112, 150, and 135°, respectively (Figure 5c–f, a photograph in Figure 1, and Figure S4). The receding WCAs of N-PUA-NON-1, N-PUA-NON-2, and N-PUA-NON-3 films were measured to be 103, 146, and 129° with hysteresis values of 9, 4, and 6°, respectively. Interestingly, the N-PUA-NON-2 film showed a bigger WCA than the N-PUA-NON-3 film (Figure 5e, f). This observation is attributable to the difference in the morphology of the NON coating on the materials. Although the NON coating of N-PUA-NON-3 film is relatively even with thicknesses in the range of 130–160 nm, that of N-PUA-NON-2 film is bumpy with thicknesses in the range of 80–220 nm. The similar role of secondary bumps on the aligned columns in a lotus leaf was reported in the literature.

Next, the adsorption properties of PUA, N-PUA, PUA-NON, and N-PUA-NON films were studied toward PM (Figures 5g–n). Through literature survey, we figured out that convincing PM can be generated by burning cigarettes and was used in the studies of PM capture materials. Thus, in our study, the adsorption studies of the films toward PM were conducted using a commercial cigarette as a PM source ($PM_{tot}$ 0.63 ± 0.05 mg/30 mL; $PM_{10}$ 657 ± 4 μg/m$^3$; $PM_{2.5}$ 423 ± 11 μg/m$^3$). $PM_{tot}$, $PM_{10}$ and $PM_{2.5}$ correspond to total PM, PM with smaller sizes than 10 μm, and PM with smaller sizes than 2.5 μm. The surfaces of PUA, N-PUA, PUA-NON, and N-PUA-NON films were exposed to the PM in air. The adsorbed amounts of PM were analyzed through the direct weighing and the measurement of concentration changes. Figure 5 summarizes the results. The pristine PUA film showed very poor adsorption toward PMs with a removal efficiency (RE) of 6 ± 4%. RE corresponds to $[(C_i - C_f)/C_i]100$, where $C_i$ is initial concentration and $C_f$ is final concentration. With a coating of NON materials, the removal efficiency of PUA-NON film toward PMs was slightly increased to 9 ± 1%. Although the N-PUA films also showed poor adsorption behavior toward PMs with a RE of 8 ± 3%, the N-PUA-NON-1, N-PUA-NON-2, and N-PUA-NON-3 films showed enhanced adsorption performance toward PMs with REs of 27 ± 11, 67 ± 7, and 40 ± 10%, respectively. We speculate that the porosity and high surface areas of NON coating enhance the primary adsorption of small PMs and the adsorbed PM can induce the secondary aggregation of larger PMs. Various interactions of PM with nanoporous materials have been reported in the literature. The removal efficiency trend of PUA, N-PUA, PUA-NON, and N-PUA-NON films toward $PM_{10}$ and $PM_{2.5}$ are the same as that of the total PM. However, as the sizes of PM decreased, the removal efficiencies of N-PUA-NON-2 film were decreased to 39 ± 4 and 28 ± 4% for $PM_{10}$ and $PM_{2.5}$ which is attributable to the better suspension ability of $PM_{2.5}$ and $PM_{10}$ than that of the bigger PM.

Interestingly, the N-PUA-NON-2 film showed better removal performance toward PM than N-PUA-NON-3 film. The low magnification SEM images of PUA, N-PUA, PUA-NON, and N-PUA-NONS obtained after the adsorption of PMs showed that the adsorbed PM increased in the order of PUA < N-PUA < PUA-NON < N-PUA-NON-1 < N-PUA-NON-3 < N-PUA-NON-2 (Figure 5i–n and Figure S5). We speculate that the bumpy morphology of NON coating in N-PUA-NON-2 can induce the efficient contact of NON materials with PM. The N-PUA-NON-2 film could be recycled through water washing and showed the retention of REs of 67,

**Figure 5.** Water contact angles of (a) PUA, (b) PUA-NON, (c) N-PUA, (d) N-PUA-NON-1, (e) N-PUA-NON-2, and (f) N-PUA-NON-3 films. (g) PM removal efficiencies and PUA, PUA-NON, N-PUA, and N-PUA-NONS (average values of three sets; film area, 1.54 cm$^2$; $PM_{tot}$ 0.63 ± 0.05 mg/30 mL; $PM_{10}$ 657 ± 21 μg/m$^3$; $PM_{2.5}$, 423 ± 11 μg/m$^3$). (h) Recyclability of N-PUA-NON-2 for the removal of PM. SEM images of the PM-adsorbed (i) PUA, (j) PUA-NON, (k) N-PUA, (l) N-PUA-NON-1, (m) N-PUA-NON-2, and (n) N-PUA-NON-3 films (also see Figure S5).
66, 64, 63, and 65% toward PM$_{2.5}$ at first, second, third, fourth, and fifth cycles, respectively, indicating the potential of outdoor applications as stationary self-cleaning adsorbents under natural surroundings (Figure 5h). According to SEM analysis, the original surface morphology of N-PUA-NON-2 film was retained after the five successive adsorption tests (Figure 5e).

In conclusion, this work shows that NON chemistry can be applied to the chemical engineering of stationary adsorbents, artificial adsorptive leaves, and toward pollutants in air. The NON coating of the nanostructured PUA film resulted in the conversion of hydrophilic surface to superhydrophobic one. In addition, the NON-coated N-PUA film showed the enhanced adsorption performance toward PM and recyclability through water washing of the adsorbed PM. The adsorption performance of N-PUA-NON film toward PM was dependent on the morphology of NON coating. We believe that the chemical properties of NON coating can be further tuned through scanning the building blocks.

**ASSOCIATED CONTENT**

2 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b18300.

Experimental procedures of synthesis and adsorption studies; SEM images of NON materials obtained from PUA-NON through the etching of PUA; N$_2$ sorption isotherm curves and IR spectra of PUA and N-PUA films; TGA curves of PUA, N-PUA, PUA-NON, and N-PUA-NONs; additional SEM images of adsorbed PMs on PUA, N-PUA, PUA-NON, and N-PUA-NON films; and SEM images of N-PUA-NON-2 film retrieved through water washing after adsorption tests (PDF)

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Notes
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**ACKNOWLEDGMENTS**

This work was supported by Basic Science Research Program (2016R1E1A1A01941074) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning and the grants CAP-15-02-KBSI (R&D Convergence Program) of National Research Council of Science & Technology (NST) of Korea.

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