Simple coating with polymer-functionalized silica nanoparticles of mixed sizes for controlled surface properties

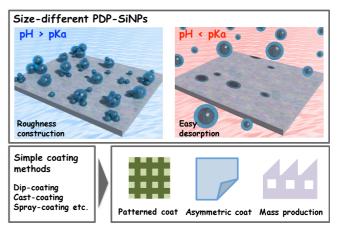
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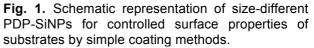
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Abstract

Water-repellent surfaces of great are importance in a wide range of fields 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. Surface properties are mainly determined by the surface energy and roughness of the materials, and the wetting phenomena can be explained by theories provided by Wenzel and Cassie/Baxter. Recently, surfaces with precisely controlled hierarchical nanostructures have been found to possess super-hydrophobicity (contact angle > 150°). However, these nanostructures 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 $\approx 120^{\circ}$. 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.^{1,2} In our previous study, SiNPs with pH-responsive poly(2-(diethylamino)ethyl methacrylate) (PDE) was prepared and used as a coating material.³

In this study, poly(2-(diisopropylamino)ethyl methacrylate) (PDP) was 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 \ge pK_a), compared to PDE, and has been used as a biomaterial. 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). 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.⁴

References

[1] Y. Kotsuchibashi *et al.*, Polym. Chem., **3** (2012) 2545-2550.
[2] Y. Kotsuchibashi *et al.*, J. Biomed. Mater. Res. A, **101A** (2013) 2090-2096.
[3] Y. Kotsuchibashi *et al.*, Polym. Chem., **4** (2013) 1038-1047.
[4] Y. Kotsuchibashi *et al.*, ACS Appl. Mater. Inter., **5** (2013) 10004-10010.