

## Hierarchically Branched Nanostructures in Biomimetic Silica Films, Controlled by Counteranion-Exchange

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Inspired by biosilicification (silica biomineralization in diatoms), silica thin films have been fabricated in a nanometer scale under physiological conditions including near neutral pH, aqueous solution, room temperature, and ambient pressure.<sup>1</sup> The biosilicification in diatoms occurred by a specific interaction between silicic acid derivatives and silaffins, post-translationally modified polypeptides containing polyamines.<sup>2,3</sup> By mimicking the process, silica thin films have been formed on the flat substrates, micro/nanoparticles, and living cells.<sup>1</sup> The silica films have been formed by a typical procedure: introduction of catalytic polyamines on the certain substrates and followed by polycondensation of silica precursors along catalytic templates. Therefore, the control of catalytic templates is considered as a critical step for varying structures of silica thin films. With aims of potential applications in heterogeneous catalysis, biosensor, cell culture, and wettability control, nanostructures of the silica thin films have been controlled by various strategies.<sup>1–3</sup>

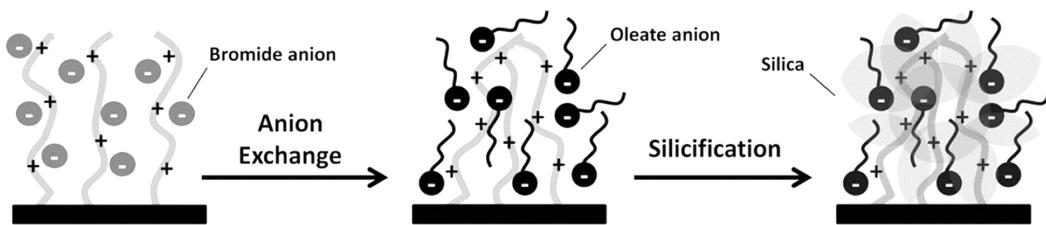
Several strategies have been developed for controlling silica thin films with polyamine film templates. 1) Silica nanostructures could be controlled by thickness of catalytic templates. When the catalytic templates were formed by layer-by-layer (LbL) assembly, roughness of silica films increased as the LbL deposition proceeded.<sup>4,5</sup> 2) Density of polymeric films formed by surface-initiated polymerization (SIP) affects silica nanostructures. The dense brush films induced dense silica nanoparticles on the surface.<sup>6</sup> 3) Silica nanostructures could be differed by counter anion of quaternary polyamine templates formed by SIP.<sup>7,8</sup> As charge density or charge valency of counteranion increased, size of nanoparticles in silica films became smaller.

Among the strategies, exchange of counteranions is the easiest because it is performed by simply immersing the polyamine templates in the aqueous solution of counteran-

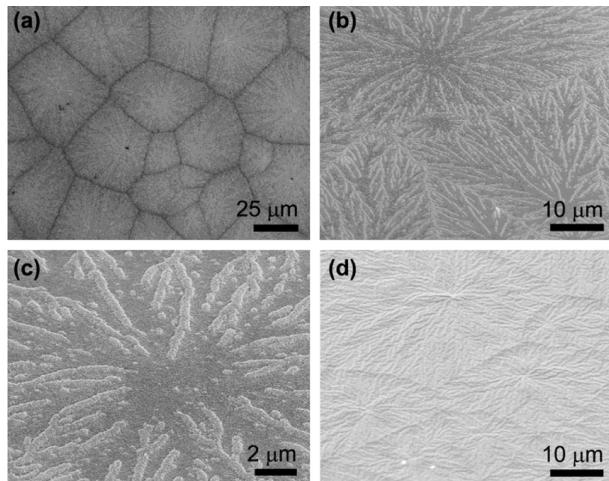
ion. The surface roughness of the quaternized poly((2-dimethylamino)ethyl methacrylate) (q-PDMAEMA) films could be varied by direct anion exchange with halide counteranions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ ) and size of nanoparticulates decreased as charge density of the counteranion increased.<sup>7</sup> For example,  $F^-$  induced compactly packed smaller silica particulates and  $I^-$  did loosely packed larger silica nanoparticles. In the other report, q-PDMAEMA films became rougher and induced nanoparticles in the films did smaller as the charge valency of counteranions increased, in which bromide counteranions had exchanged with  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ , or  $P_2O_7^{4-}$ .<sup>8</sup> Diameters of nanoparticles in silica films were controlled within 40–80 nm by series of halide counteranions and under 30 nm by polyvalent counteranions such as orthophosphate and pyrophosphate.

In this work, nanostructures of silica films were controlled by exchanging counteranions of q-PDMAEMA films with bulky anions, oleate. Highly rough and hierarchically branched nanostructures were generated in the silica film, which had not been observed in previous reports on exchange of halide or phosphate anions. Control experiments with acetate and malate confirmed that bulkiness of anion is another factor for controlling nanostructures of silica thin films.

The q-PDMAEMA films and silica thin films were generated by following previous procedures (*Scheme 1*).<sup>6–8</sup> Briefly, DMAEMA was polymerized from the self-assembled monolayer of  $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$  on the flat gold substrate, by atom transfer radical polymerization (ATRP), and then quaternized by a substitution reaction with bromomethane. The bromide anions were exchanged by immersing the films in 100 mM aqueous solution of sodium acetate, sodium malate, or sodium oleate. Anion exchange was confirmed with disappearance of peaks assigned as Br 3d in spectra of X-ray photoelectron spectroscopy (XPS) (data not shown).<sup>7,8</sup> After that, silica was formed in a biomimetic



**Scheme 1.** Procedure for oleate anion exchange and biomimetic silicification at surfaces.



**Figure 1.** (a) Optical micrograph and (b, c) SEM micrographs of silica thin films formed on oleate-exchanged q-PDMAEMA films. (d) SEM micrograph of oleate-exchanged q-PDMAEMA film.

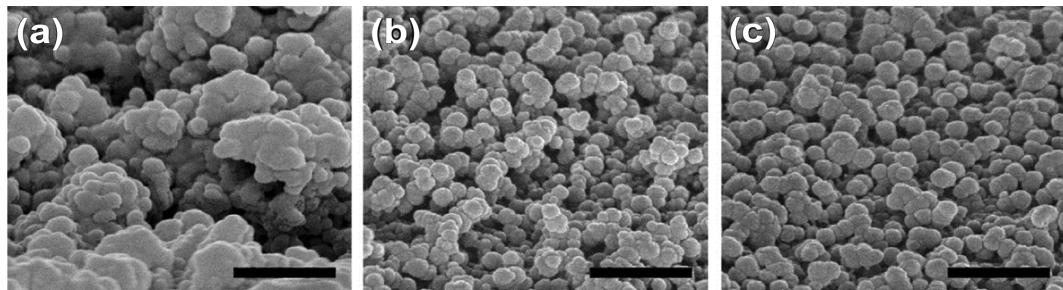
manner, which was confirmed by IR spectra with peaks at about 1230, 960 and 800 cm<sup>-1</sup> assigned as Si-O-Si asymmetric stretching, Si-O- stretching, and Si-O-Si symmetric stretching, respectively (data not shown).<sup>4-8</sup>

The silica film was observed with optical microscopy (*Figure 1a*). The surface is divided by domains, in which the hierarchically branched structures radially arranged toward the center. Overall size of domains was within 25–50 μm. Detailed structures were investigated with scanning electron microscopy (SEM) (*Figure 1b, c*). The branches hierarchically overgrew from the boarder of domains to the

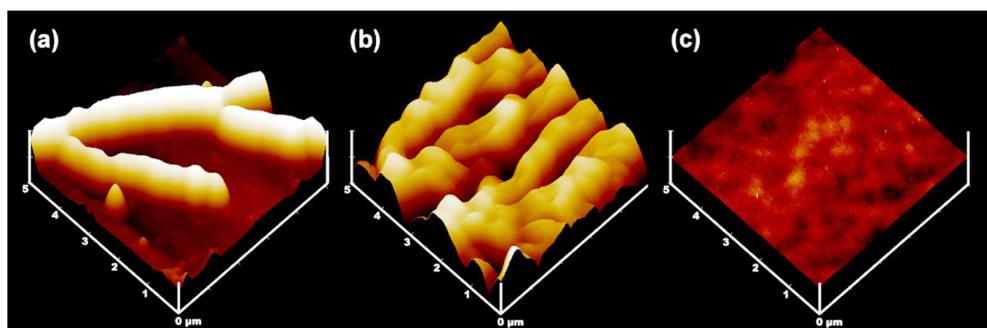
center of each domain. As control experiments, acetate and malate-exchanged silica films were also prepared respectively and investigated by SEM but no distinct structure was observed. To find out the origin of structures, oleate-exchanged q-PDMAEMA film was observed with SEM (*Figure 1d*). Domains and radially branched structures were also found in the film although the features in the film were less pronounced than those of silica films. It implies that the silica nanostructures are originated from catalytic templates modified by anion exchange.

In magnified SEM micrographs, the silica films were composed of densely packed nanoparticulates (*Figure 2*). In comparison with acetate and malate, the sizes of nanoparticulates were similar but surface from malate is a little rougher than one from acetate because of a high charge valency. The overall morphologies are similar with previous reports.<sup>7,8</sup> However, oleate induced a highly rough silica surface and nanoparticulates were coalescent, which were completely different from the previous reports.<sup>7,8</sup>

Morphologies of counteranion-exchanged q-PDMAEMA films were observed with atomic force microscopy (AFM) (*Figure 3*). The surfaces get rougher and more crinkled as bulkiness of counteranion increased. For instance, oleate induced rougher polymeric films than acetate or malate. 5×5 μm<sup>2</sup> area was scanned and the root-mean-square (rms) values were calculated as criteria for roughness, which were 0.93, 5.32, and 8.76 nm for acetate, malate, and oleate, respectively. The rms values clearly confirmed the tendency of roughness. It is noticeable that oleate changed the films



**Figure 2.** SEM micrographs of silica thin films formed on anion exchanged q-PDMAEMA films: (a) oleate, (b) malate, (c) acetate. The scale bar is 500 nm.



**Figure 3.** AFM micrographs of anion exchanged q-PDMAEMA films: (a) oleate, (b) malate, (c) acetate. The width is 5  $\mu\text{m}$  and the height is 20 nm.

dramatically rougher in comparison with previous reports on halide or phosphate anions.<sup>7,8</sup>

It is known that the nanostructures of silica thin films are directly influenced by those of catalytic templates.<sup>4-8</sup> The size and density of silica nanoparticles are mainly determined by association of polymers caused by electrostatic interaction between cationic chains and exchanged anions.<sup>1,6-8</sup> In cases of acetate and malate, charge density or valency of them is as much as halide or phosphate, resulting in general degree of association within cationic chains. However, oleate induces different level of association between cationic chains because it has long hydrophobic alkyl chains. Because of a bulky and hydrophobic chain in oleate, the polymeric chains should be assembled in ordered structures, resulting in hierarchical branches and divided domains. It is supposed that the structures are determined by steric and hydrophobic effects, which are important factors for self-assembly of building blocks.

In summary, hierarchically branched and highly rough nanostructures in silica thin films were generated by using

bulky alkyl chain counteranions. It was found that bulkiness and hydrophobicity as well as charge density and charge valency are important factors for controlling nanostructures of catalytic templates and silica thin films. The simple strategy would be useful to control structures of silica thin films and expand the range of applications of them.

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