Supporting Information

Hierarchical Nanoporous Silica Films for Wear Resistant Antireflection Coatings

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1. Simulation of Reflectance for Glass Substrates with Coatings

Reflectance of glass substrates coated with low-*n* materials was simulated using multilayer interference calculation.[1] Here the refractive indices of the substrate and the coating material were supposed to be 1.5 and 1.3, respectively. For evaluation of the effect of roughness, the rough surface was approximated by multilayers of 10-nm-thick thin films with step-by-step refractive indices. In this case, the effect of the periodicity of the rough surface is not considered because the diameter of the MSN used is sufficiently smaller than the wavelength of visible light. Figure S1 shows the results of calculation for two model structures with average thickness of 100 nm. Compared to the flat low-*n* coating (Figure S1a, curve A), the glass substrate coated with low-*n* film with surface roughness of ±40 nm shows lower reflectance by 0.4–0.7%. These results indicate that surface roughness of even ±40 nm have a satisfactory effect on reducing reflection of light.

Simulation of the reflectance based on the two-layer model was also performed by roughly estimating the coating structure of MesoMSN-50 as 70 nm (n = 1.20) + 70 nm (n = 1.35) films from the cross section image (Figure S1b). Here the half of the film thickness is assumed to be top layer with high porosity because mainly two MSN layers are stacked in the film. The dependence of the reflectance on wavelength got smaller by this modeling and the reflectance curve got closer to that shown in Figure 7b.

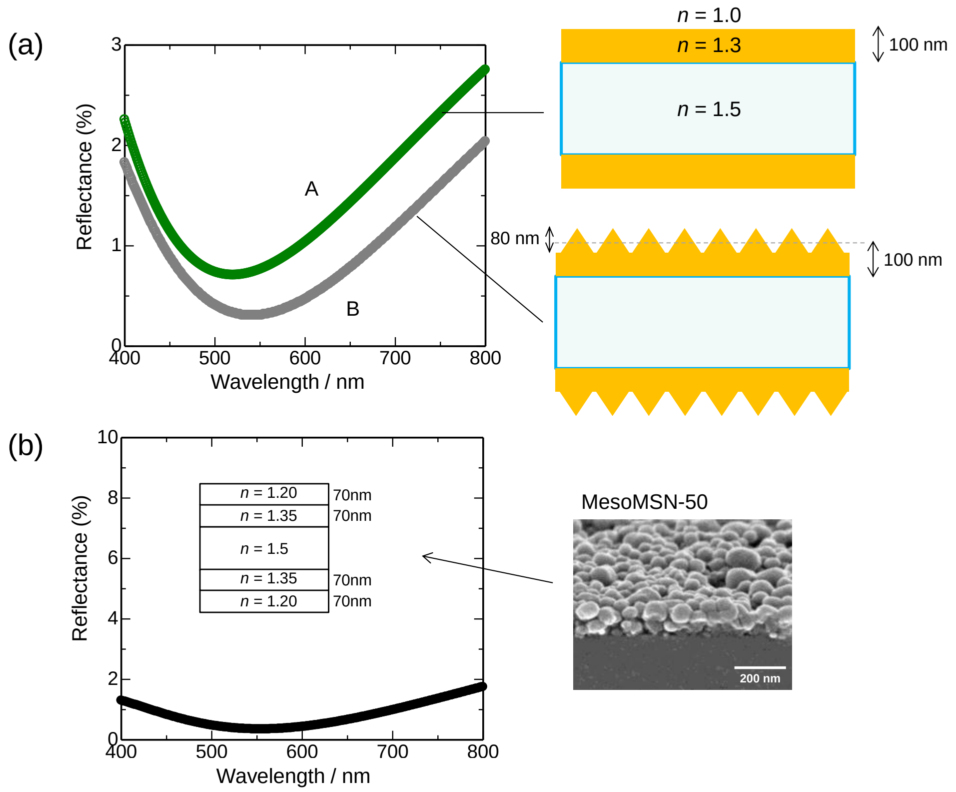


Figure S1. (a) Simulated reflectance for glass substrates coated with (A) flat low-*n* films and (B) low-n films with surface roughness of ±40 nm. (b) Simulated reflectance based on a two-layer model.

2. Structural Properties of MSNs

Figure S2 shows structural properties of TMS-protected MSN without calcination. The average particle size was determined to be ca. 100 nm by dynamic light scattering method (Figure S2a). The pore size was calculated to be 3.5 nm from the nitrogen adsorption–desorption isotherm (Figure S2b). Direct observation of nanostructures was performed by TEM observation (Figure S2c).

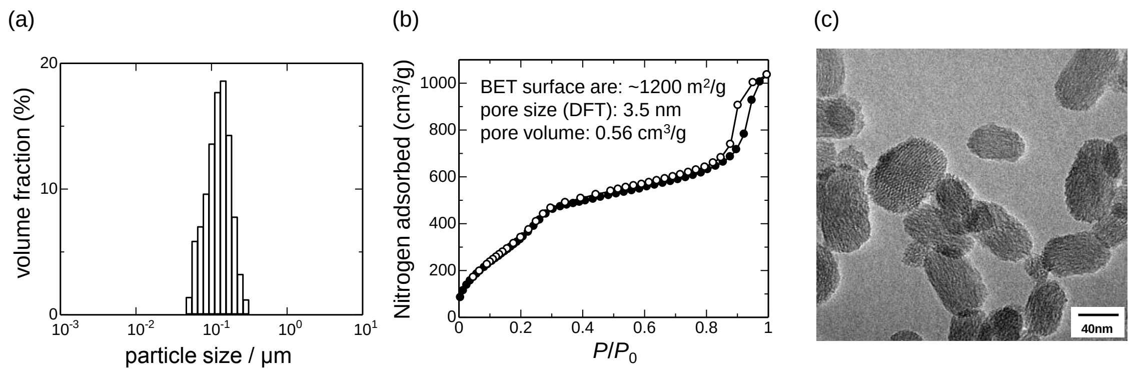


Figure S2. (a) Particle size distribution, (b) nitrogen adsorption–desorption isotherm, and (c) TEM image of the TMS-protected MSN without calcination.

3. TEM Images of Mesoporous Materials

Figure S3 shows TEM images of Meso-F and MSN after calcination. For the calcined Meso-F, the pore diameter was calculated to be ca. 4.0 nm from nitrogen adsorption–desorption isotherm. For the MSN, the calcination resulted in contraction of the silica framework and nanopore diameter as discussed in the main text.

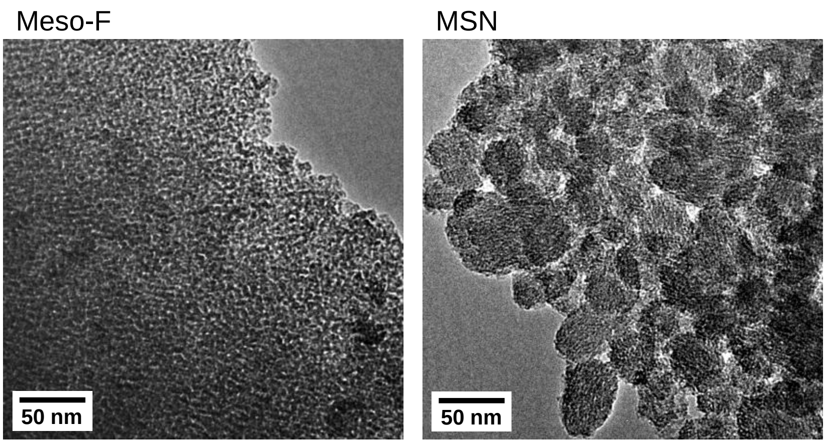


Figure S3. TEM images of Meso-F and MSN after calcination.

4. SEM Images of MesoMSN Coatings

Figure S4 shows SEM images of MesoMSN coatings at low magnification. MesoMSN-35 formed a relatively flat surface due to embedment of MSNs within the matrix. MesoMSN-50 had a rough surface over the whole film surface. Although MesoMSN-65 containing a large amount of MSN also exhibited the formation of rough surface, there were a lot of cracks and voids in the coating.

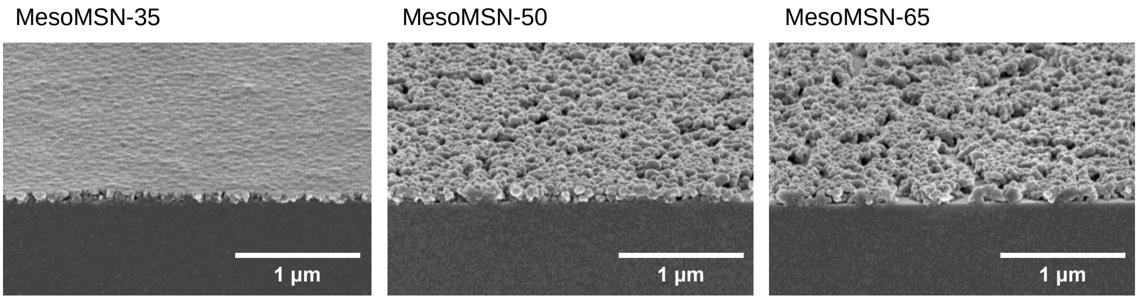
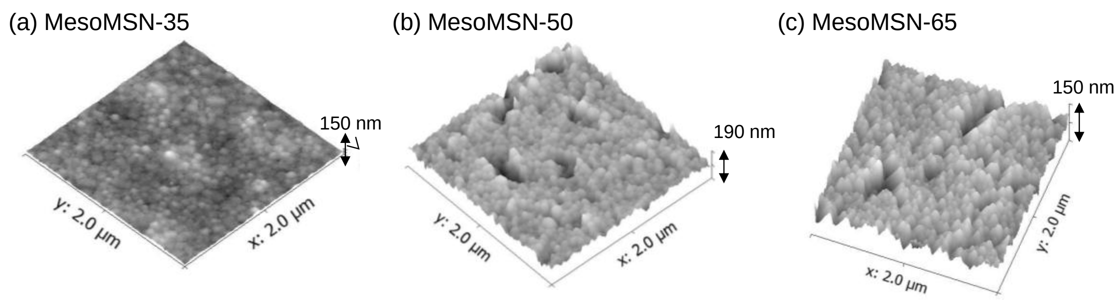


Figure S4. SEM images of MesoMSN coatings at low magnification.

5. Evaluation of Surface Roughness

Figure S5 shows AFM topographic images of MesoMSN coatings. The roughness of the coatings was compared using arithmetic average of absolute values (R_a). The value of R_a was 2.2 and 16.0 nm for MesoMSN-35 and MesoMSN-50, respectively. For MesoMSN-65 having large cracks, the R_a was calculated for the crack-free region to be 13.0 nm. Although these values are probably underestimated because the AFM probes cannot enter interparticle voids deeply and the AFM images were constructed by the integration of the surface contours, the relatively large R_a of MesoMSN-50 indicates the spontaneous formation of nano-rough surface by the protrusion of MSNs.



	(a)	(b)	(c)
R_a (nm) $\left(= \frac{1}{\ell}\int_0^{\ell} \lvert f(x) \rvert \, dx\right)$	2.2	16.0	13.0

Figure S5. AFM images of (a) MesoMSN-35, (b), MesoMSN-50, and (c) MesoMSN-65 and calculation of R_a.

Reference:

[1] Structural Color Association Home Page. http://www.syoshi-lab.sakura.ne.jp/excelde/excelde.html (accessed July 27, 2015).