Supporting Information

Single-process fabrication of antireflective acrylic hard coating via surface segregation of porous silica nanoparticles

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Supporting Experiment

Supporting Figures

Experimental

Synthesis of microporous silica nano particle used in Fig. 6 and Fig. S-6.

Methanol (852.8 g), distilled water (245.2 g), and 28% NH3 (109.6 g) were mixed in a 2 L four-neck flask at 20 °C. Methanol (180.4 g), DDA (37.1 g), and TMOS (137.2 g) were mixed in PE container, and were then injected into the first flask with a tube pump for 120 min under vigorous stirring. The molar ratio of the reaction solution was TMOS/DDA/NH3/H2O = 0.5/0.1/1/10. The reaction solution was stirred for another 1 h after completion of the injection. The resulting precipitates were collected by centrifugation and dried at 120 °C in air for 2 h, and calcined in air at 600 °C for 6 h to remove DDA. (Yield: 48.9 g)

The diameter and the specific surface area of the resultant silica particles are 100 nm and 130 m^2/g, respectively. The pore volume was 0.04 cm3/g, which the pore volume estimated ca. 10 %.

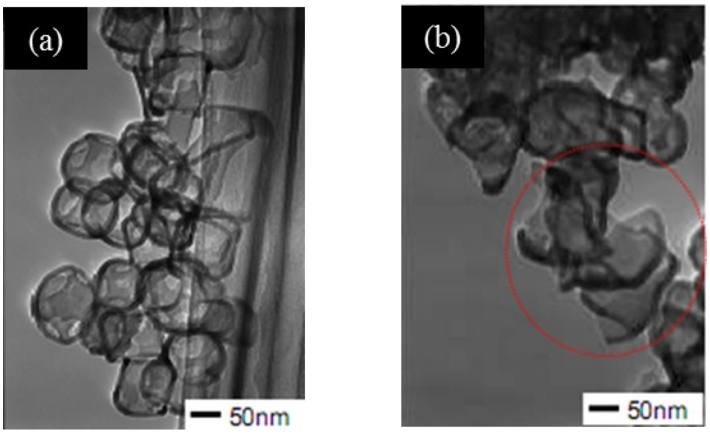


Fig. S-1 The TEM images of hollow silica particles (a) before and (b) after jet mill process.

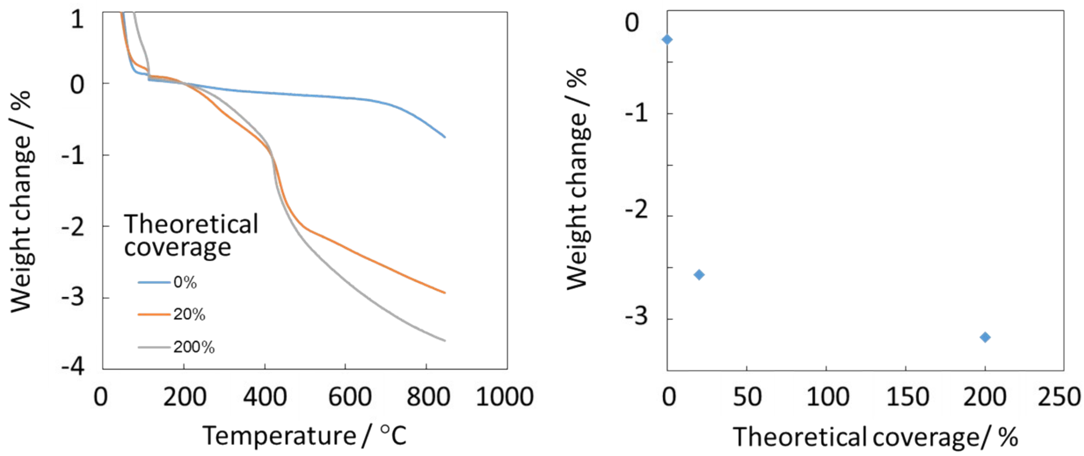


Fig. S-2. Thermal gravimetric analysis (TGA) of HDMS modified porous silica particles. (a) TGA curves of theoretical coverage of 0%, 20%, and 200%, here the weight loss is normalized at 200°C. (b) Weight loss of 200°C to 800°C.

The weight loss is not linear to the theoretical coverage, but the porous silica of larger the theoretical coverage exhibit more weight loss. The weight loss is mainly due to the burning out of HDMS. A small loss observed for 0% coverage is considered to be due to the water condensation of residual silanols.

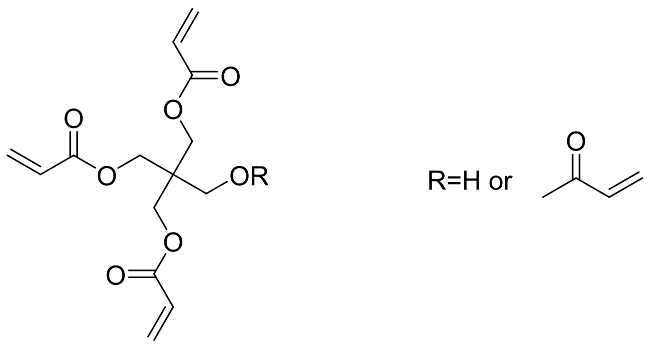


Fig. S-3 Molecular structures of ARONIX M-306.

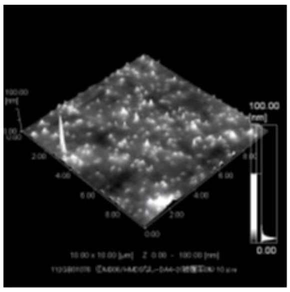
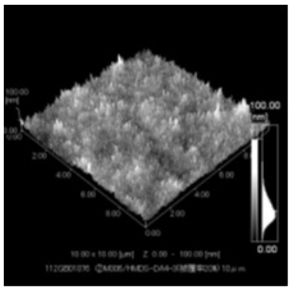
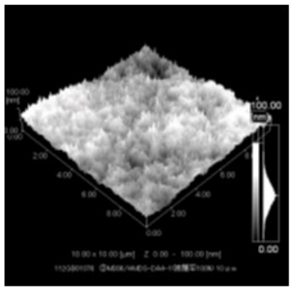
Theoretical coverage (%)	0	20	100
AFM Images			
Ra (nm)	2.6	8.9	12.0
HAZE	1.34	1.39	1.79

Fig. S-4 The AFM images, surface roughness and HAZE of surface of coating film containing porous silica particle modified with HMDS (a) 0, (b) 20 and (c) 100 area%.

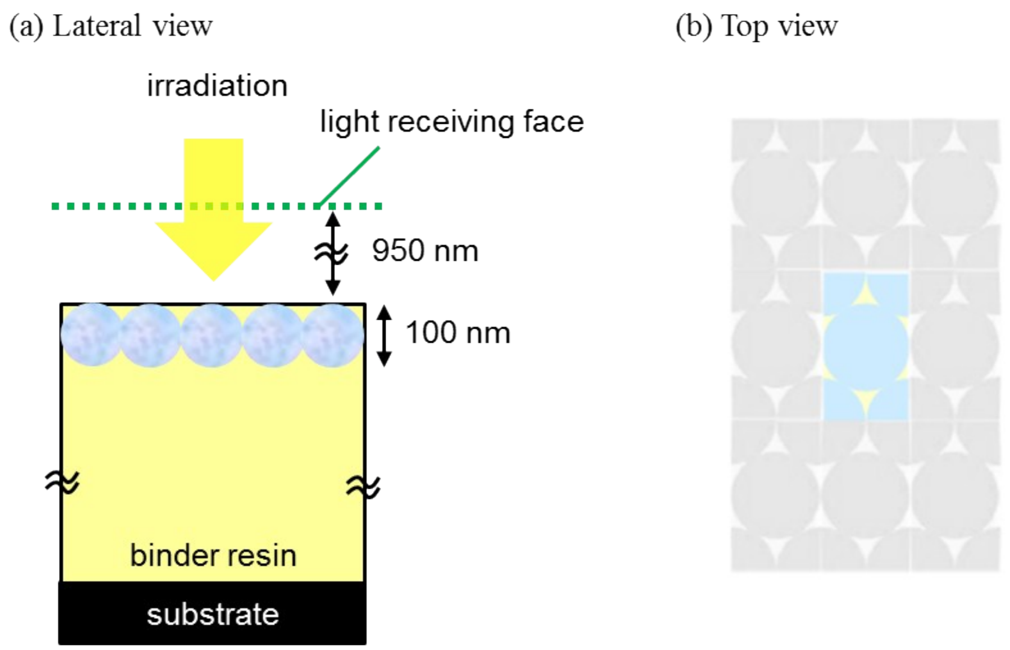


Fig. S-5 The model diagrams of optical simulation of reflectance spectra of the present AR films constituting of segregated silica layer calculated by Finite-Difference Time-Domain (FDTD) method (K.S. Yee: "Numerical Solution of Initial Boundary Value Problems Involving Maxwell's Equations in Isotropic Media", IEEE Trans. AP-14, pp.302-307 (1966)); (a) a lateral view and (b) a top view.

It was assumed that a diameter of the porous silica particle is 100 nm, refractive index of silica as 1.32 (pore volume of silica particle = 30 %), 1.27 (pore volume of silica particle = 40 %) or 1.22 (pore volume of silica particle = 50 %) and refractive index of binder resin as 1.50. The film thickness of binder resin was assumed enough large compared with the surface silica layer. The irradiation light is surface light source of vertical incidence. The distance between the light incidence face and surface of film is set to 950 nm. It is assumed the horizontal direction was replicated endlessly and silica particle is in the closed packing.

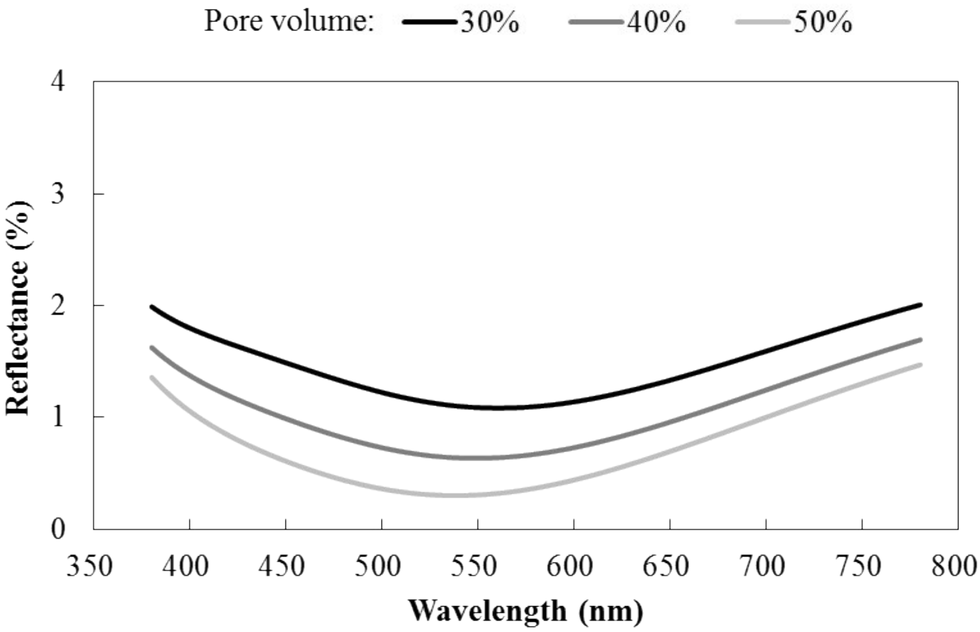


Fig. S-6 The optical simulation of reflectance spectra using the model of Fig. S-5 calculated by software "Poynting for Optic".

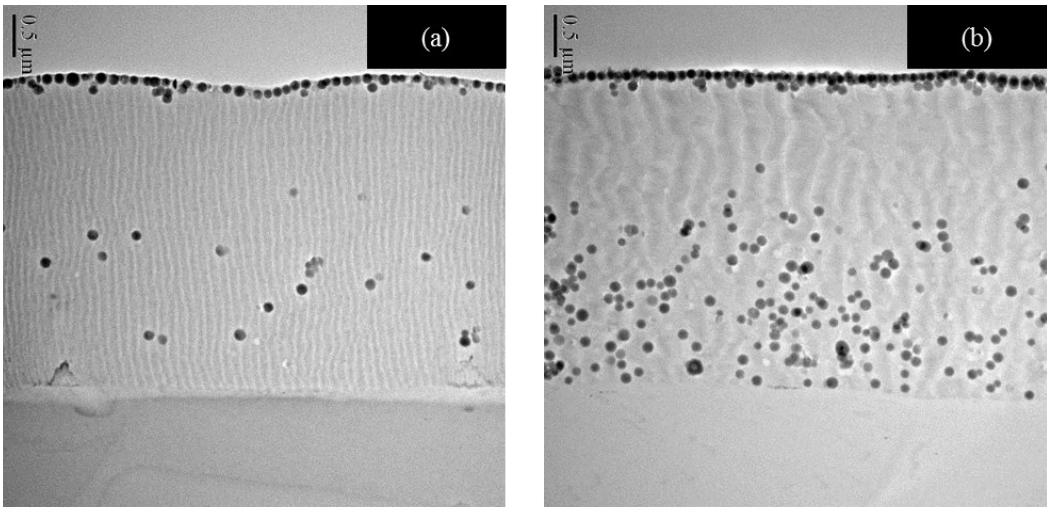


Fig. S-7 The TEM images of cross section of coating film containing (a) 5 and (b) 15 wt% of porous silica particle synthesized in supporting experiment, which the pore volume was 0.04 cm^3/g and pore volume was estimated ca. 10 %. In case of 15 wt% silica particles containing system, however, the silica particles formed only monolayer at air surface and other particles were remained and dispersed uniformly in coating film.