

Electronic supplementary information (ESI)

Title: **Sustainable antireflection using recoverable nanopattern arrays**

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1. Characterization details

1.1 X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was conducted using an AXIS-His electron spectrophotometer (Kratos Ltd., UK) with a monochromatic Mg Ka X-ray source ($h\nu = 1253.6$ eV, 450 W power) and neutralized charge. The samples were prepared as a film shape attached to the Al substrate and placed on a sample holder. The samples were scanned under a high vacuum pressure (5×10^{-10} torr) at room temperature. A survey spectrum was recorded over a binding energy range from 0 to 1500 eV using a 300 eV pass energy. Analysis of the C1s regions was performed over a binding energy from 280 to 300 eV with a 150 eV pass energy. Data analysis was performed using a CasaXPS program. All collected spectra were modified to remove the charging effect of the C1s and O1s peaks of hydrocarbons at 284.5 eV and carbonyl compounds at 533.3 eV. This method was used to fit the peaks of the C1s and the O1s. Core-level spectra has been explained in detail in literature. The curve fitting of spectra peaks was conducted with a mixture of the Gaussian and Lorentzian peak shapes.

1.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the samples was measured by using a Varian 660 FTIR spectrometer. The spectral data were collected using an Attenuated Total Reflectance-Fourier Transform Infrared (ATR) mode. In the case of a transparent sample, it is difficult to measure in a general transmission mode, so the samples were ground and measured in powder form. All data were obtained at a resolution of 4 cm^{-1} in the mid infrared region from $4000\text{--}650\text{ cm}^{-1}$. The Varian Resolutions Pro software was employed to collect and analyse the data.

1.3 Dynamic mechanical thermal analysis (DMTA)

A dynamic mechanical analysis machine (TA Q800 DMA, United States) was used to analyse thermomechanical properties of SMCPAc. The specimens were prepared by cutting into hexahedron shape ($1 \times 5.3 \times 10\text{ mm}^3$). While heating the samples from -50°C to 100°C , storage and loss moduli were measured in a single frequency tensile loading mode (1 Hz). An external force of 1 N, a thermal heating rate of $5^\circ\text{C}/\text{min}$, a force track of 125 %, and a preload force of 0.001 N were employed as experimental conditions. Transition temperature was evaluated as a peak in tan delta curves.

1.4 Cyclic shape memory tests

In order to confirm the shape memory ability, a cyclic stress-strain-temperature (SST) test was carried out by using TA Q800 DMA on the 3-point bending mode. After heating to 40°C, SMCPAc was bended up to 20 mm ($\varepsilon = 3\%$) at the center. The cooling step (to 0°C) was followed while retaining the applied displacement. After the unloading step, the heating step recovered the original permanent shape.

1.5. Rheological properties

Viscosity of the SMCPAc resin was measured using a MCR 301 rheometer (Anton paar, Austria). A double gap accessory was employed under the shear rate from 0.1 to 2000 /s, and the result curves are plotted in Fig. S7.

2. Numerical simulation method for shape memory effect

A shape memory behavior of the nanopatterns was numerically simulated using a finite element method (FEM). A commercial software, ABAQUS/CAE was employed with user subroutine UMAT. A phase-dependent Hyperelastic model was used based on Neo-Hookean model. A stored strain energy function (ψ) is expressed as

$$\psi_t = (1 - \alpha)\psi_r + \int_{t_i}^{\tau} \psi_g d\tau \quad (1)$$

$$\psi_r = C_{10}(\bar{I}_{\kappa_r} - 3) + \frac{1}{D_1}(J_{\kappa_r} - 1)^2 \quad (2)$$

$$\psi_g = C_{20}(\bar{I}_{\kappa_{g(t)}} - 3) + \frac{1}{D_2}(J_{\kappa_{g(t)}} - 1)^2 \quad (3)$$

where α is the glassy phase parts ('1- α ' is the rubbery phase part), ψ_t is the total stored strain energy function, ψ_r is the stored strain energy function at rubbery region, ψ_g is the stored strain energy function at glassy region, $\bar{I}_{\kappa_r}$ and $\bar{I}_{\kappa_{g(t)}}$ are the first invariants of the isochoric part of the right Cauchy-Green deformation tensor at each phase region, and J_{κ_r} and $J_{\kappa_{g(t)}}$ are the jacobian matrices. $C_{10}(=\mu_r/2)$ and $C_{20}(=\mu_g/2)$ are the material input parameters related to shear modulus (μ) at rubbery and glassy phase, respectively. $D_1(=2/K_r)$ and $D_2(=2/K_g)$ are the material parameters related to bulk modulus (K). The glass content (α) dependent on temperature is calculated by linearizing temperature variation as the following equation,

$$\alpha = \frac{T_{gla} - T}{T_{gla} - T_{rub}} \quad (4)$$

, where T is the current temperature, T_{gla} is the temperature in a fully rubbery state (60°C), and T_{rub} is the temperature in a fully glassy state (-30°C). The material parameters were obtained by measuring elastic modulus of SMCPAc at 60°C (fully rubbery phase, $\alpha=0$) and -30°C (fully glassy phase, $\alpha=1$). Poisson's ratio was assumed to 0.35. By using these material parameters, the shear and bulk moduli were calculated and listed in Table S2. These parameters were used for coding UMAT subroutine when running ABAQUS/CAE program.

The nanopattern geometry resembling the real topology (*i.e.*, a 200 nm height, a 200 nm spacing, and a 200 nm diameter) was constructed in 3-D (Fig. S8a). The 4 steps used in the simulation consisted of loading, cooling, unloading, and heating step. In the loading step, temperature was set to 40°C ($\alpha=0.125$), and the Encastre boundary condition was imposed on the ground plate. In the deforming step, the nanopatterns were compressed to 70 nm as the same in the SEM image, by using an analytical rigid plate. The followed cooling step increased the glass content up to 0.625. At the unloading step, the plate was removed from the nanopatterns, and the applied heating recovered the deformed geometry. The colour contour of the von Mises stress was shown in Fig. 3d.

3. EMT analysis for theoretical transmittance

An effective medium theory (EMT) method was employed to provide a mechanism for sustainable antireflection by theoretically comparing transmittance according to the shape of the nanopatterns. The unit cells were obtained from compression simulation (Figs. S8a-b) and used for the analysis. After splitting the nanopatterned layer into 20 layers, a volume fraction of air and the substrate was calculated at each layer. The effective refractive index (n_e) of each layer is defined as,

$$n_e = ((V_f(n_c))^{2/3} + (1 - V_f))^{3/2} \quad (5)$$

, where V_f is the volume fraction of nanopatterns at each layer, and n_c is the refractive index of SMCPAc. The refractive indices of SMCPAc were semi-empirically determined from the measured transmittance data by calculating Fresnel equation (Table S3). The experimental refractive indices of SMCPAc were expected to be about 1.4 at 550 nm since the refractive index of PEGDMA is 1.466, 1.411 for MMA, and 1.422 for BMA. The inversely calculated refractive indices were overestimated due to the immiscibility between the material phases. Moreover, the surface roughness contributes to this disagreement. Theoretical transmittance for normal incident light was obtained by using multilayer Fresnel equation with MATLAB.

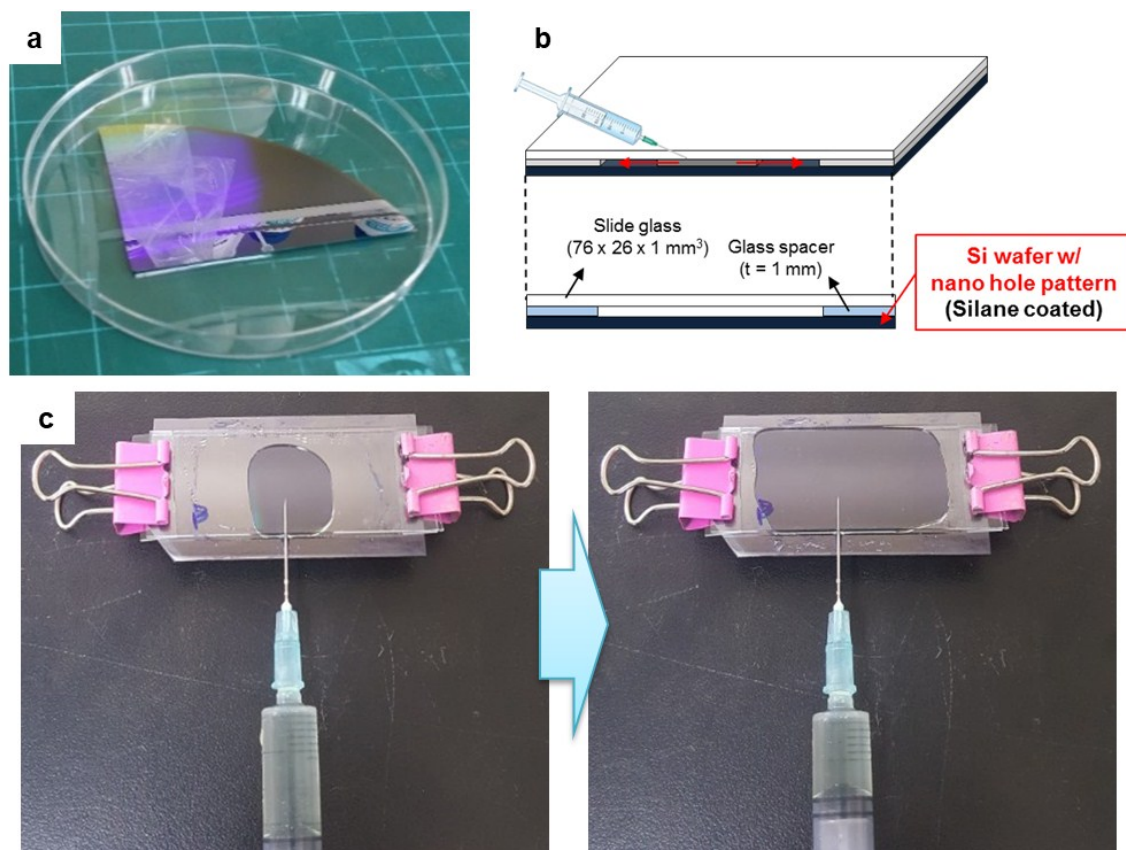


Fig. S1. Experimental set up for the nanopatterning process. (a) Optical photograph of the fabricated Si wafer. (b) Schematic illustration of the used mold. (c) Optical photograph of injection of the SMCPAc resin into the mold.

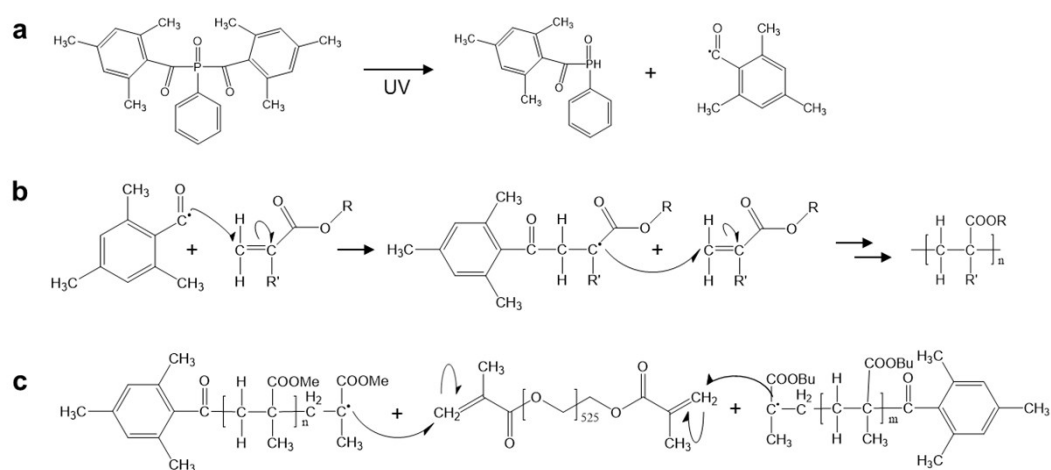


Fig. S2. Synthetic scheme of SMCPAc: (a) initiation of reaction by irradiating UV light, (b) generation of the pre-polymer chains, and (c) chemical crosslinking of the pre-polymer chains with PEGDMA.

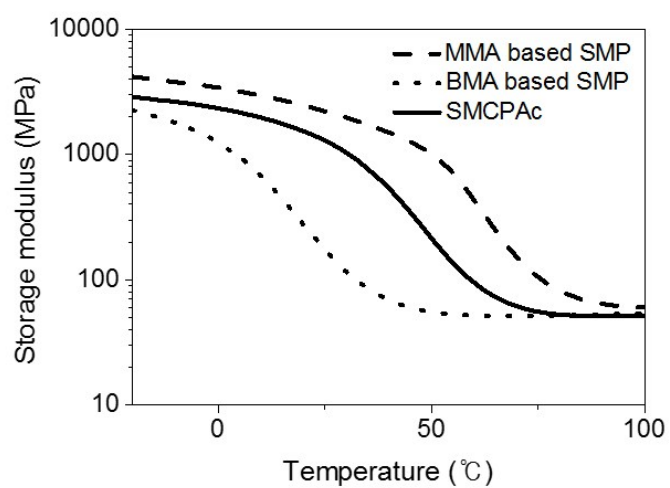


Fig. S3. DMTA curves of MMA-based SMP, BMA-based SMP, and SMCPAc.

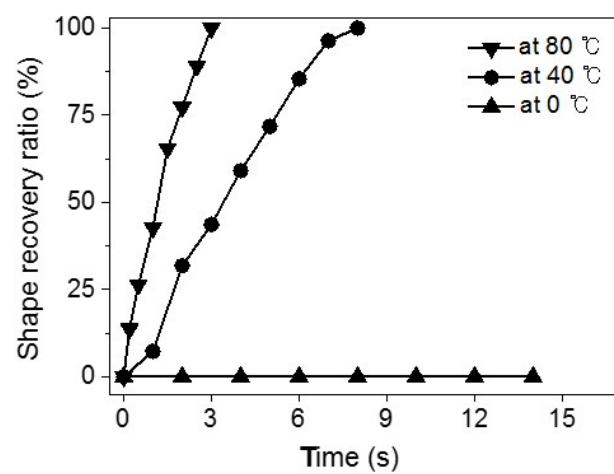


Fig. S4. Transient shape recovery tests for SMCPAc at 80°C, 40°C, and 0°C.

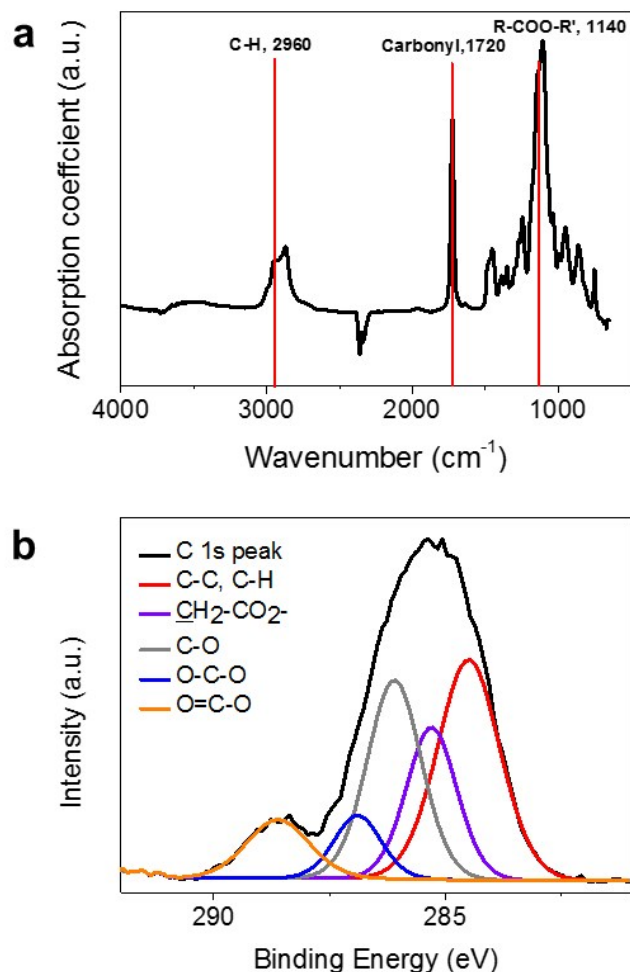


Fig. S5. Spectroscopic spectra of SMCPAc. (a) FT-IR spectra of SMCPAc. All the peaks of SMCPAc were assigned as follows: The CH₃ vibrations, CH₂ vibrations, carbonyl vibrations, C-O vibrations of MMA/BMA, and C-O vibrations of cross linker indicate the peaks of 2955, 2870, 1720, 1140, and 1105 cm⁻¹. (b) XPS curves OF SMCPAc. The positions and area percent of each peak were listed in Table S1. The first peak at 284.50 (Area percent=35.36%) is related to the binding energy of carbon for C-C and C-H, and the second peak at 285.30 (19.75%) for CH₂-CO₂⁻, the third peak at 286.10 (27.71 %) for C-O, the forth peak at 286.90 (7.67%) for O-C-O, and the last peak at 288.61 (9.51%) for O=C-O. All the peak positions and the area percent of peaks agreed with the reference data.

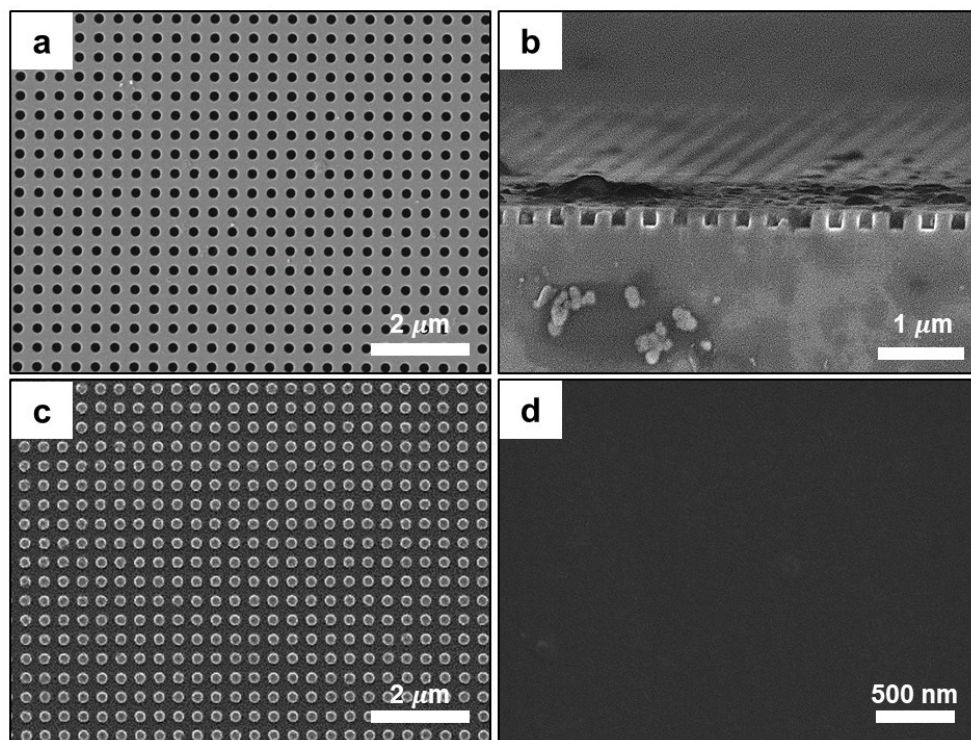


Fig. S6. SEM images of the Si master and the nanopatterned surfaces: (a-b) top and tilted view of the master, (c) top view of the nanopattern arrays, and (d) the surface of the bare sample.

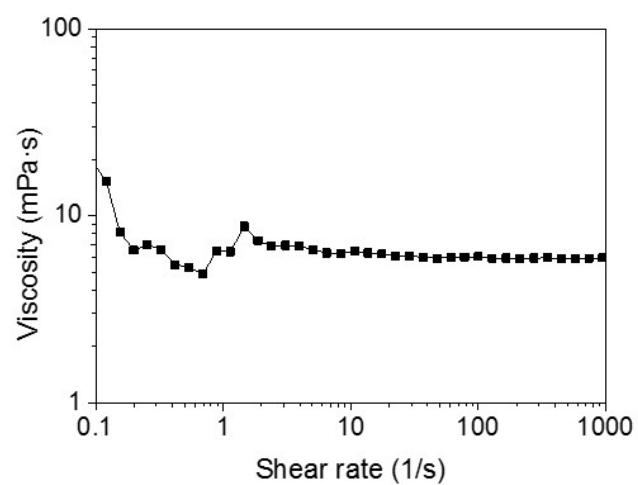


Fig. S7. Viscosity of the SMCPAc resin.

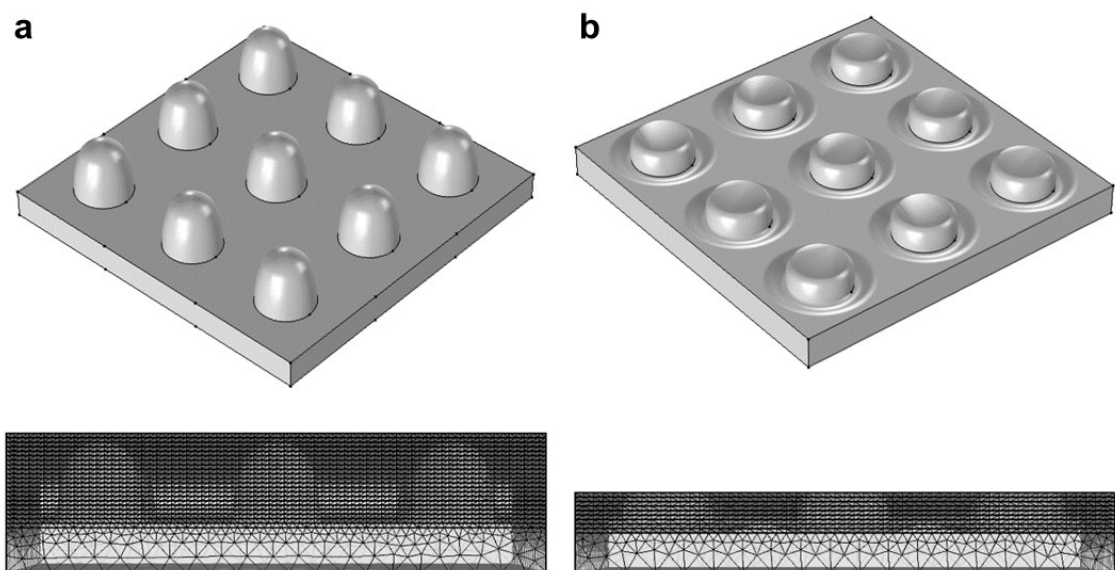


Fig. S8. Unit cells constructed for the EMT analysis: the surface of (a) the original and (b) the deformed samples.

Table S1. XPS peak information of SMCPAc.

SMCPAc		
#	Name	Position (At%)
1	C-C, C-H	284.50 (35.36)
2	$\underline{\text{C}}\text{H}_2\text{-CO}_2\text{-}$	285.30 (19.75)
3	C-O	286.10 (27.71)
4	O-C-O	286.90 (7.67)
5	O=C-O	288.61 (9.51)

Table S2. The material parameters employed for the Hyperelastic model.

SMCPAc	
$T_{r^{a)}} [^{\circ}\text{C}]$	60
$T_{g^{b)}} [^{\circ}\text{C}]$	-20
$C_{10} [\text{MPa}]$	6
$C_{20} [\text{MPa}]$	370
$D_1 [1/\text{MPa}]$	0.06
$D_2 [1/\text{MPa}]$	0.001
$\nu^{c)} [-]$	0.35

a) T_r : Temperature for fully rubbery phase;

b) T_g : Temperature for fully glassy phase;

c) ν : Poisson's ratio.

Table S3. The calculated refractive indices of SMCPAc.

Wavelength (nm)	Refractive index
900	2.193189
850	2.219151
800	2.181369
750	2.260984
700	2.243690
650	2.251259
600	2.302070
550	2.383295
500	2.347006
450	2.392323
400	2.601424
350	2.959534