Supporting Information

Path-Guided Hierarchical Surface Relief Gratings on Azo-Films Induced by Polarized Light Illumination through Surface-Wrinkling Phase Mask

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**Figure S1.** Chemical structure and UV–vis absorption spectrum of PDO₃.

**Figure S2.** Typical optical microscopy images (a) of the surface-wrinkling PDMS templates with different wrinkle wavelengths and the dependence of the wrinkle wavelength on the exposure time to oxygen plasma (b), the pre-strain of the PDMS substrate (c), and the weight ratio (n:1) of the base/curing agent used for preparation of the PDMS(n:1) substrate (d), respectively.
Figure S3. Optical microscope image of the PDO$_3$ film after exposure to non-polarized light through the surface-wrinkling phase mask.

Figure S4. Optical images of the surface-wrinkling phase mask with $\lambda_{\text{phase mask}} = 2$ $\mu$m (a) and the induced microstructures on the PDO$_3$ film after exposure to the linearly polarized light through the phase mask at $\theta = 0^\circ$ (b) and $90^\circ$ (c), respectively.
**Figure S5.** Optical microscopy images of the surface-wrinkling PDMS phase mask of different \( \lambda_{\text{phase mask}} \) (a\(_1\)–c\(_1\)) and the corresponding hierarchical SRGs (a\(_2\)-c\(_2\)). \( \lambda_{\text{phase mask}} = 1.99 \ \mu m \) (a\(_1\),a\(_2\)), 7.15 \ \mu m \) (b\(_1\),b\(_2\)), and 19.82 \ \mu m \) (c\(_1\),c\(_2\)), respectively.
**Figure S6.** Morphology evolution of the PDO$_3$ film during exposure to the polarized light through the surface-wrinkling phase mask for 10 s (a), 24 s (b), 30 s (c), and 40 s (d), respectively. Frames e and f show the diffraction image of the light-exposed PDO$_3$ film for the exposure duration of 24 s and 40 s, corresponding to Frames b and d, respectively.
**Figure S7.** SEM image of the cross-section azo-film after exposure to the polarized light through the surface-wrinkling phase mask.
**Figure S8.** Optical microscope images of the surface-wrinkling PDMS phase mask (a) and the phase mask-directed SRGs (b-e) with different thickness $h_{\text{spacer}}$ of the glass spacers inserted between the surface-wrinkling phase mask and the PDO$_3$ film. $h_{\text{spacer}} = 0$ (b), 0.1 mm (c), 1 mm (d), and 2 mm (e), respectively. Frame f shows the dependence of the wavelength (i.e., $\lambda_{\text{SRG-1}}$ and $\lambda_{\text{SRG-2}}$) of the phase mask-directed double-scale SRGs on $h_{\text{spacer}}$. Inset of frame b shows the induced patterns on the PDO$_3$ film when the surface-wrinkling phase mask is conformally contacted, followed by heating imprinting.
**Figure S9.** Optical microscope images (a-e) of the surface-wrinkling phase mask-directed double-scale SRGs on different thickness $h_{\text{PDO3}}$ of PDO3 films. $h_{\text{PDO3}} = 0.495 \ \mu\text{m}$ (a), $0.91 \ \mu\text{m}$ (b), $1.35 \ \mu\text{m}$ (c), $2.32 \ \mu\text{m}$ (d), and $4.02 \ \mu\text{m}$ (e), respectively. Frame f shows the dependence of the wavelength ($\lambda_{\text{SRG-1}}$ and $\lambda_{\text{SRG-2}}$) of the resulting double-scale SRGs on $h_{\text{PDO3}}$. 
Figure S10. Optical microscope images of the induced SRGs on different $h_{\text{PDO3}}$ of PDO$_3$ films without the phase mask employed. $h_{\text{PDO3}} = 0.91$ μm (a), 1.35 μm (b), 2.32 μm (c), 3.21 μm (d), and 4.02 μm (e) respectively. (f) Dependence of the wavelength of the induced SRGs on $h_{\text{PDO3}}$. 
**Figure S11.** Optical microscopy images of the PDMS phase masks replicated from a CD template (a) and a Si mask (c), as well as the corresponding PDMS phase mask-directed SRGs (b,d), respectively.

**Figure S12.** Optical microscope images of the surface-wrinkling phase mask-directed triple-scale SRGs on different $h_{\text{PDO3}}$ of PDO$_3$ films at $\theta = 0^\circ$. $h_{\text{PDO3}} = 1.5$ μm (a), 2.1 μm (b), and 3.4 μm (c), respectively.
**Figure S13.** Optical images of the induced SRGs from different moving velocity $v$ of the moving illumination. $v = 0$ mm/s (a), 0.01 mm/s (b), 0.03 mm/s (c), 0.05 mm/s (d), 0.1 mm/s (e), and 0.2 mm/s (f), respectively. Frame g shows the dependence of the induced $\lambda_{SRG-1}$ and $\lambda_{SRG-2}$ on $v$.

**Figure S14** Reversible morphological evolution of the PDO$_3$ film during exposure to non-polarized light and polarized light, respectively.