Supporting Information

Robust and Efficient UV-reflecting One-Dimensional Photonic Crystals Enabled by Organic/Inorganic Nanocomposite Thin Films for Photoprotection of Transparent Polymers

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1. Supporting Experimental Details

1.1 Fabrication of PC sheet

Bare PC sheets with dimension of 100 × 100 × 3 mm^3 were injection-molded by HTF80-W2 (Haitian, China) with a processing temperature of 280 °C, a mold temperature of 80 °C, and an injection pressure of 100 MPa. And then, PC sheets were cut into small pieces of 25 × 25 mm^2 using a saw and annealed at 120 °C for 4 h in an oven.

1.2 Supporting characterization details

The chemical composition of PC sheets was measured both before and after UVC treatment using Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermoscitific, USA). Water contact angle (WCA) was evaluated using a dynamic/static optical contact angle meter (SL200B/K, Kino, USA). Digital photographs were taken by a digital camera (Canon EOS 2000D). The surface morphology of as-prepared 1DPhC film on PC was observed by polarization microscope (OlympusBX61). The morphology of nanoparticles in TiO_2 sol, SiO_2 sol and their O/I hybrid sols were observed using transmission electron microscope (TEM, FEI Tecnai G2 F20). The absorbance spectra of UV-reflecting GTS_{50} 1DPhC films coated PC before and after UVB aging test were recorded by a UV-vis-NIR spectrophotometer (PerkinElmer Lambda 1050).

1.3 Supporting theoretical analysis

Regarding thicknesses of high-index and low-index layers as fitting parameters, Monte Carlo method[1] in combination with the TMM model[2] was used to fit the experimental reflectance spectra until the correlation coefficient (r) between the simulated and measured reflectance spectra was greater than 0.85. The r was defined by the following equation (1):

$$r = 1 - \sum_{\lambda=280}^{800} (R_\lambda - R_\lambda^0)^2 \Big/ \sum_{\lambda=280}^{800} R_\lambda^{\,2} \qquad (1)$$

where R_λ and R_λ^0 were the experimental and theoretical reflectance at the wavelength of λ, respectively. The obtained theoretical layer thickness was also cross-checked with measured results from the corresponding FESEM image.

2. Supporting Figures

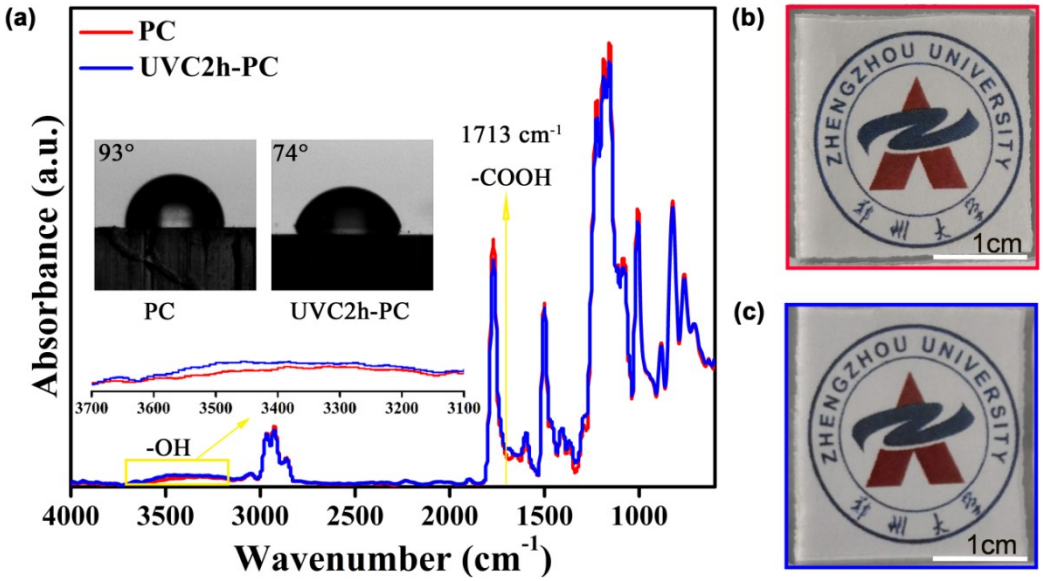

Fig. S1 (a) FTIR spectra of PC substrate before and after UVC irradiation pretreatment for 2 h (inset images are water contact angles of their corresponding surfaces); (b) and (c) are their corresponding digital photographs.

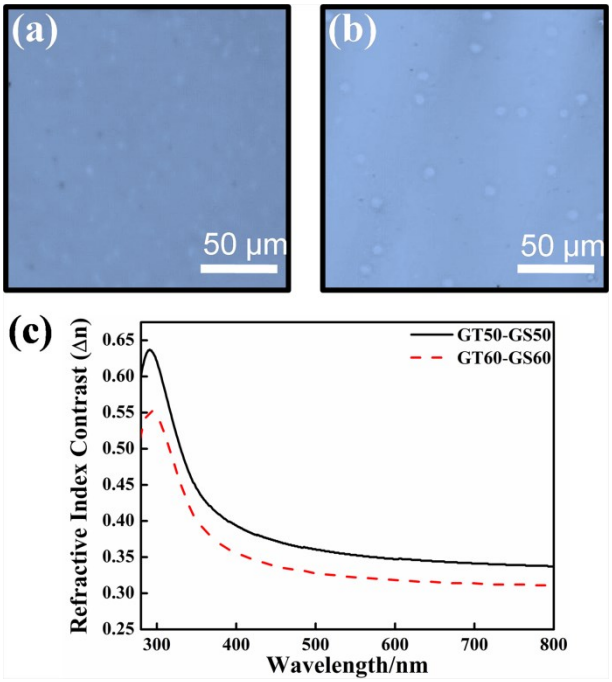

Fig. S2 Optical microscope images of (a) GTS_{50} and (b) GTS_{60} 1DPhC films coated PC; (c) Refractive index contrasts (△n) between GT_{50} and GS_{50} and between GT_{60} and GS_{60}, respectively, in the wavelength range of 280-800 nm.

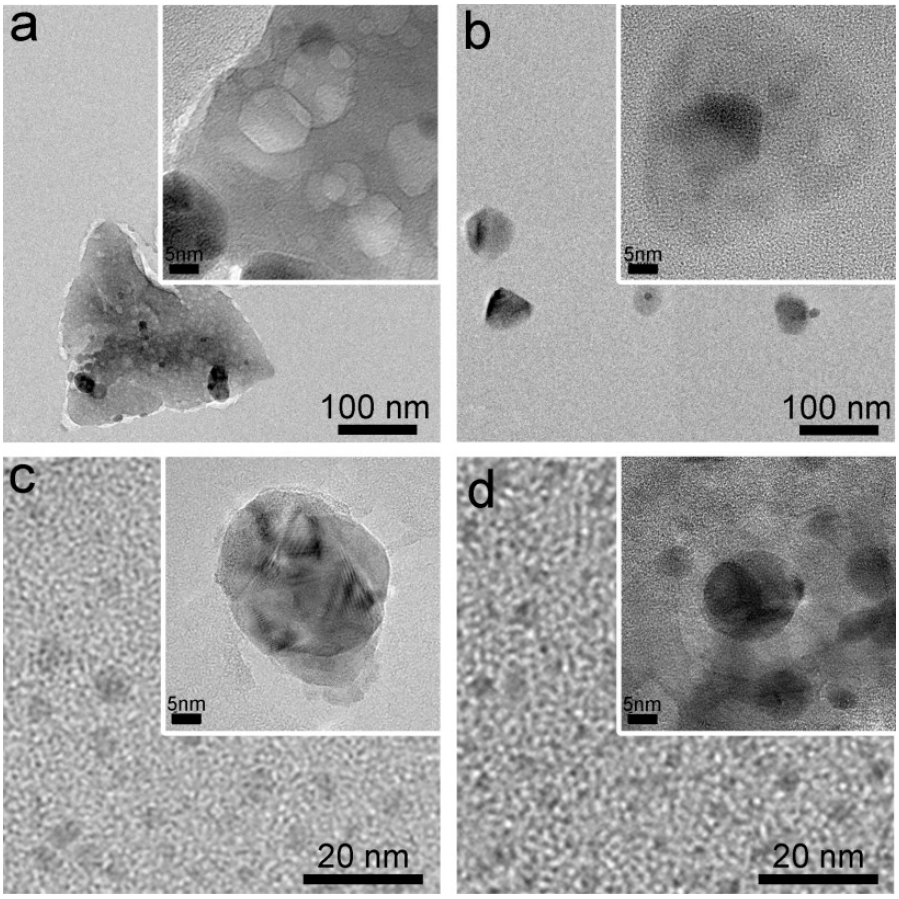

Fig. S3 TEM images of (a) SiO_2 sol, (b) GS_{50} sol, (c) TiO_2 sol and (d) GT_{50} sol. The inset images are their corresponding enlarged views.

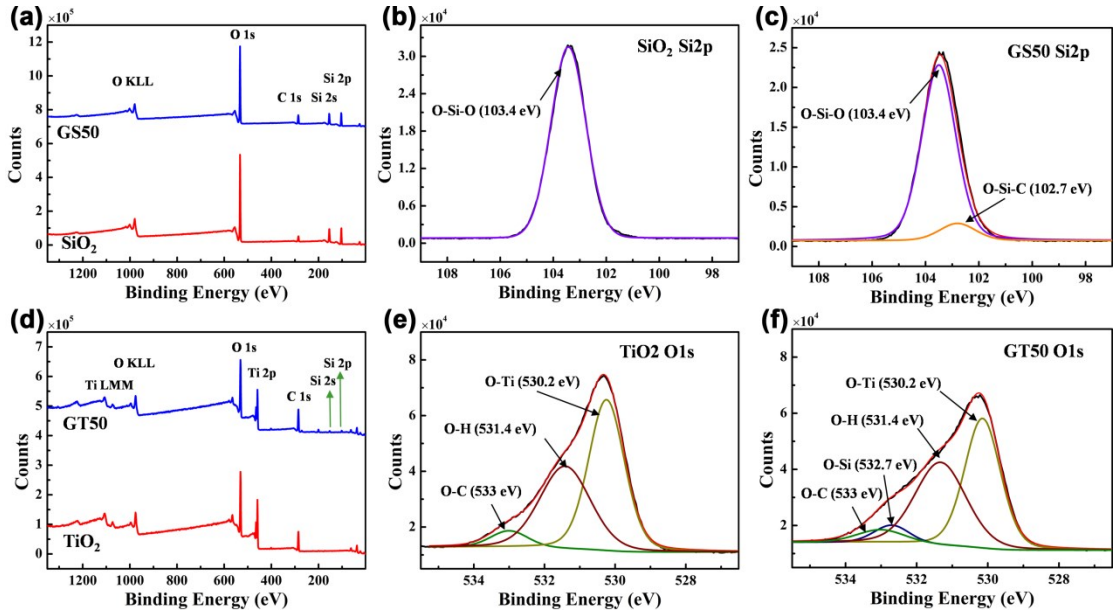

Fig. S4 XPS spectra of SiO_2 and GS_{50} (a) survey scan, and high resolution Si2p scan of (b) SiO_2 and (c) GS_{50}; XPS spectra of TiO_2 and GT_{50} (d) survey scan, and high resolution O1s scan of (e) TiO_2 and (f) GT_{50}.

XPS measurements were performed to gain further insight into the chemical structure of GS_{50} and GT_{50} nanocomposites by comparing them with SiO_2 and TiO_2. As shown in Fig.S4a, C, Si, and O elements were detected from GS_{50} and SiO_2, and the C1s peak intensity of GS_{50} was much greater than that of SiO_2 suggesting the successful modification of GPTMS. Moreover, the high resolution Si2p peak was Gauss fitted to indicate the composition of chemical bonds. It was found from Fig. S4 b and c that SiO_2 contains O−Si−O (103.4 eV) bond[3] only, while GS_{50} is composed of O−Si−C(102.7eV) and O−Si−O (103.4 eV) bonds. These results provide evidence for the covalent linkage between SiO_2 nanoparticles and GPTMS molecules[4]. Figure S4d shows the survey scan of TiO_2 and GT_{50}. It is clear that not only the C1s peak intensity was increased with the GPTMS modification, but also two characteristic peaks belonged to Si2s and Si2p were appeared on GT_{50}. These features demonstrated that organosilane has been incorporated into TiO_2 as well. High resolution O1s peaks are also fitted as shown in Fig. S4e and f. TiO_2 showed three typical bonds that are

assigned to O−Ti (530.2 eV), O−C (531.4 eV) and O−H (533 eV), respectively[5], suggesting successful synthesis of TiO_2. However, a peak assigned to O−Si (532.7 eV) appeared on the O1s curve of GT_{50} indicating the formation of Ti−O−Si and Si−O−Si bonds[6], which confirmed that GPTMS molecules have been covalently bonded to TiO_2 nanoparticles and undergone self-condensation reaction.

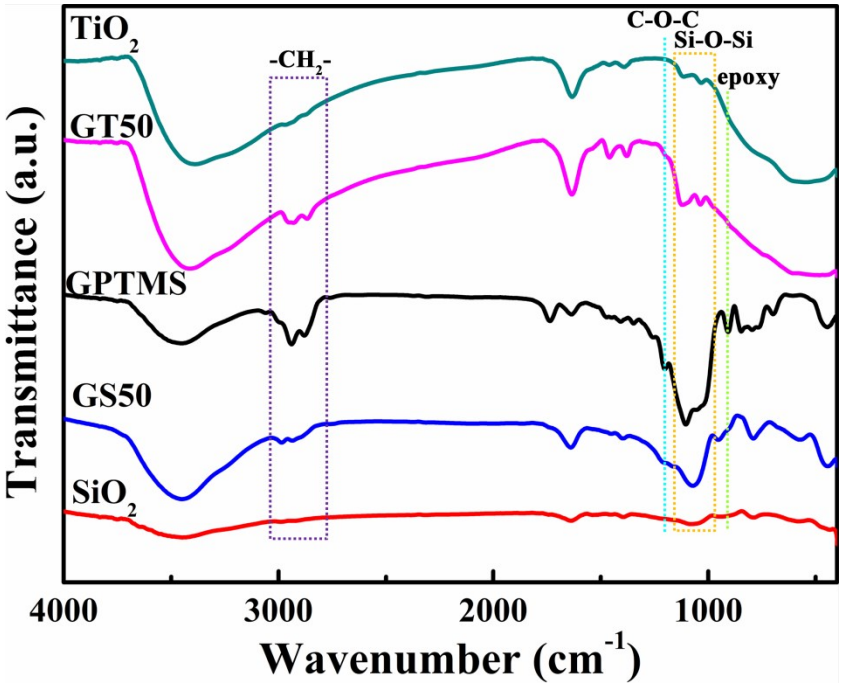

Fig. S5 FTIR spectra of TiO_2, GT_{50}, GPTMS, GS_{50} and SiO_2

To further confirm the formation of organosilicate network, FTIR measurements of TiO_2, SiO_2, GPTMS, and GT_{50} and GS_{50} hybrid nanocomposites were performed. As shown in Fig. S5, the absorption peaks at 622 cm^{-1} in TiO_2 spectrum and 1080 cm^{-1} in SiO_2 spectrum were corresponding to the stretching vibration of Ti−O−Ti and Si−O−Si bonds, respectively, which were generated by the condensation reaction of hydrolyzed TBT and TEOS[6, 7]. After being modified with GPTMS, it is obvious that both GT_{50} and GS_{50} spectra showed the characteristic peaks at 2938 cm^{-1} and 2879 cm^{-1} corresponding to the asymmetrical and symmetrical stretching vibration of propyl groups, the peak at 1201 cm^{-1}ascribed to the ether C−O−C stretching, and the peak at 910 cm^{-1} assigned to stretching vibration of epoxy ring, which is in consistent with GPTMS spectrum[8-10]. More importantly, the enhanced absorption band at 1100 cm^{-1} for GT_{50} and GS_{50} nanocomposites, which represents the asymmetrical stretching vibration of linear Si−O−Si, indicated that the hydrolyzed GPTMS has undergone condensation among themselves to achieve an organosilicate network[11]. The FTIR

results are in consistent with the XPS analysis. Thus, it is conducive to improve the robustness of the hybrid film against cracking formation.

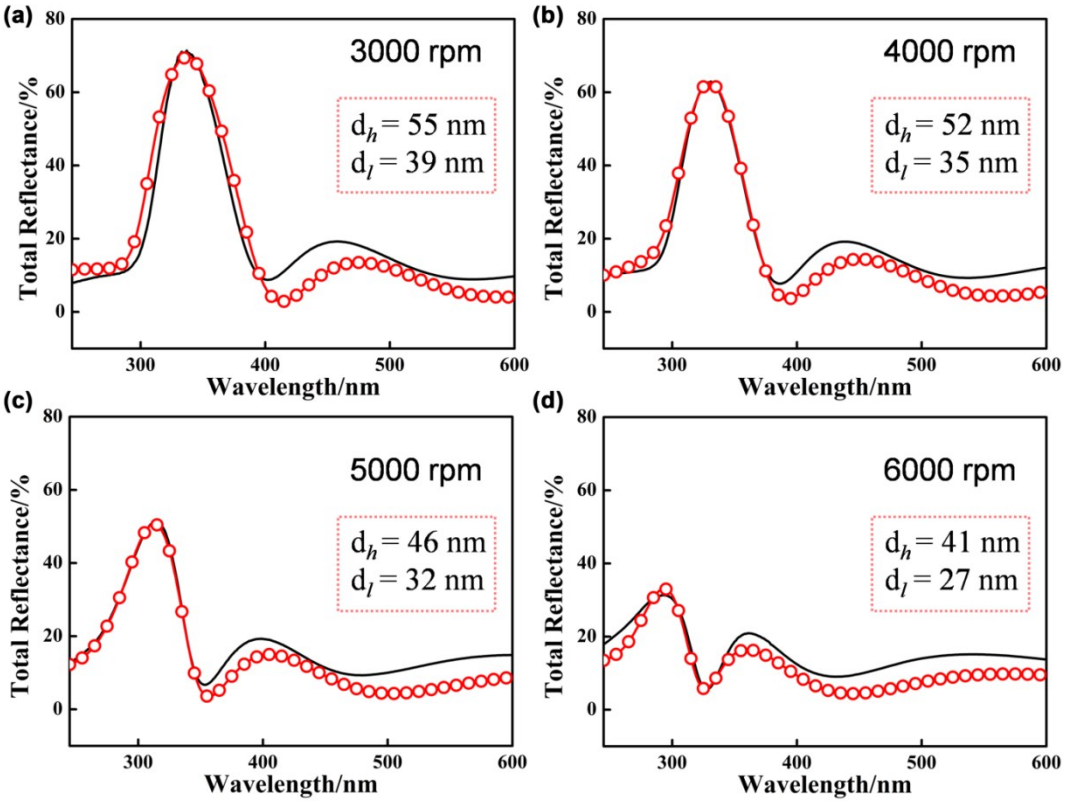

Fig. S6 Measurement and simulation of reflectance spectra of GTS_{50} 1DPhC films coated PC prepared at different rotation speed ranging from 3000 rpm to 6000 rpm. The fitted thicknesses for their corresponding high refractive index layer and low refractive index layer were given in the inset red rectangle respectively.

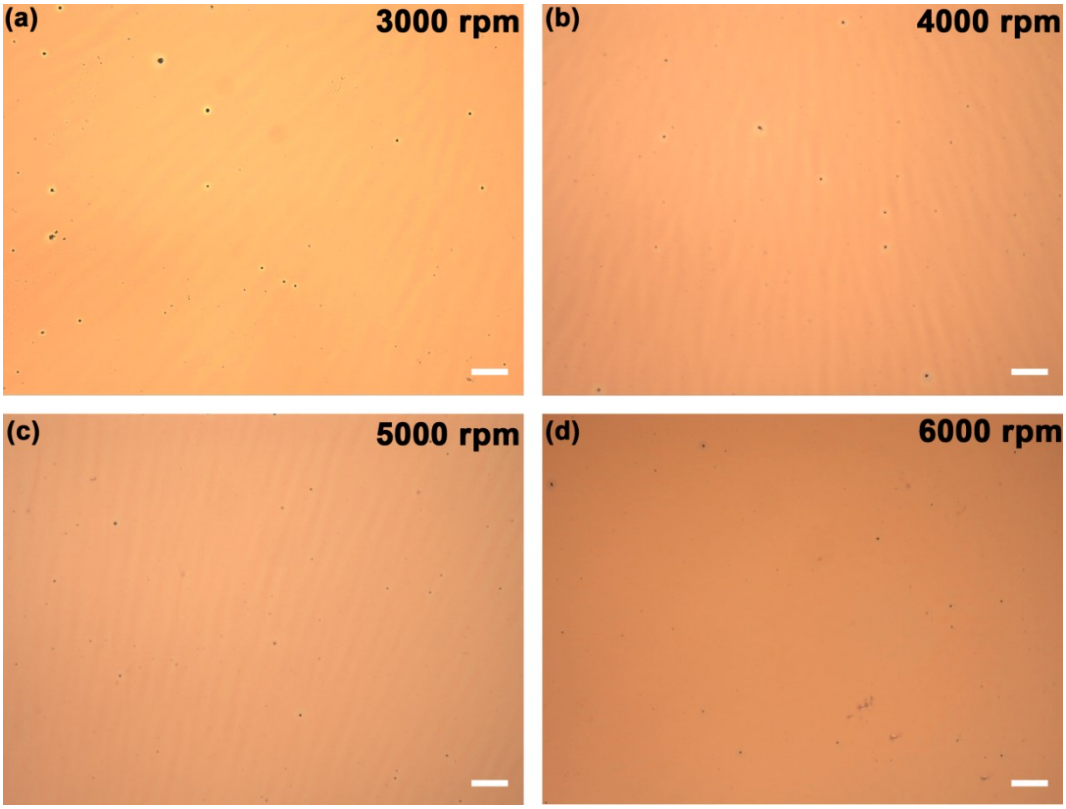

Fig. S7 Optical images of GTS_{50} 1DPhC films coated PC prepared at different rotation speed of (a) 3000 rpm, (b) 4000 rpm, (c) 5000 rpm and (d) 6000 rpm (scale bar = 100 μm).

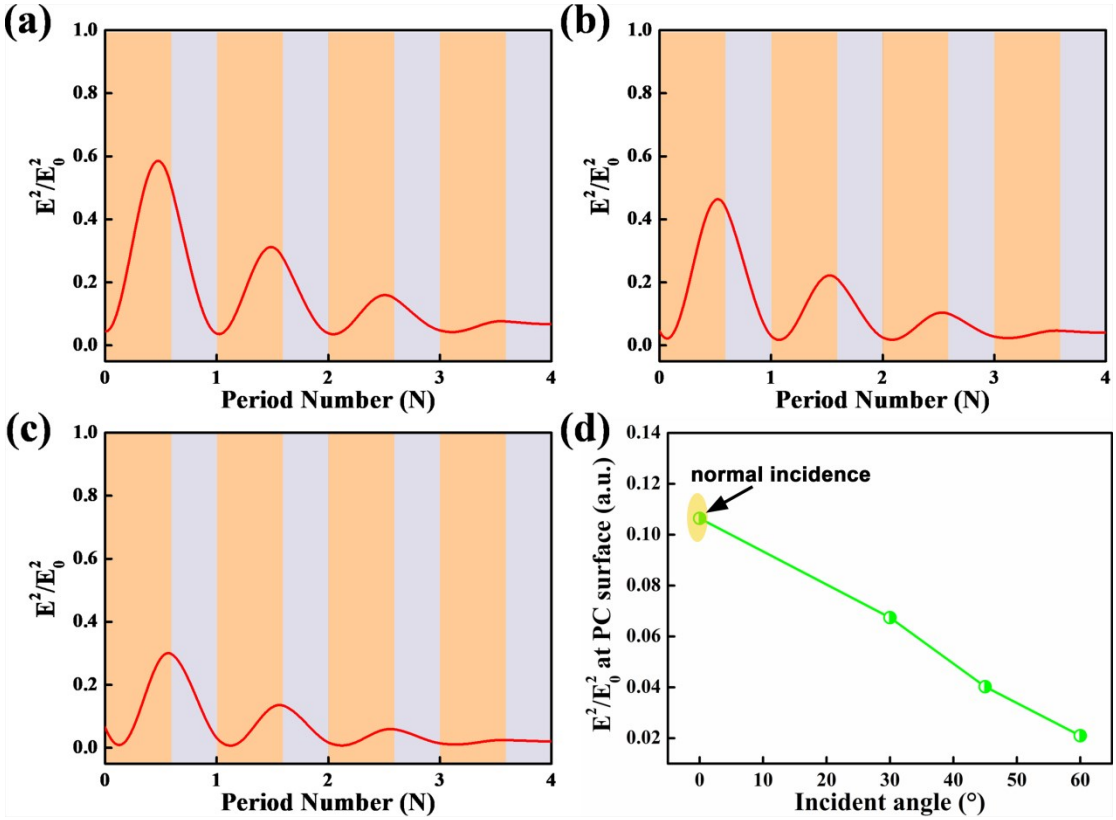

Fig. S8 Spatial distribution of electric field, E^2/E_0^2, along the cross section of the GTS_{50} 1DPhC film prepared at 5000 rpm, for the light of wavelength at 313 nm with different incident angles: (a) 30°, (b) 45° and (c) 60°, (d) the E^2/E_0^2 values at PC surface under different light incident angles.

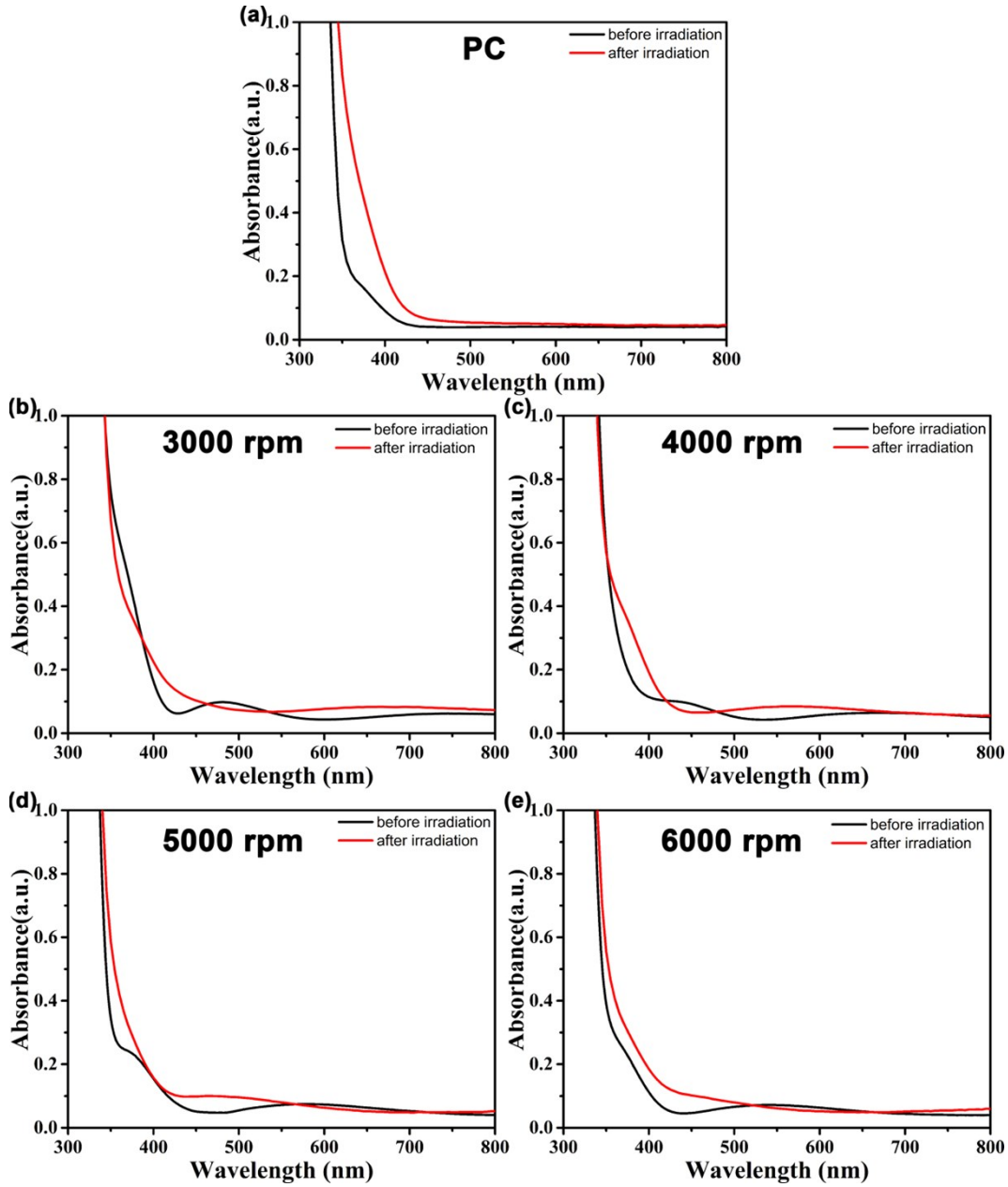

Fig. S9 Absorbance spectra of bare PC (a) and GTS_{50} 1DPhC films coated PC prepared at different rotation speed of (b) 3000 rpm, (c) 4000 rpm, (d) 5000 rpm and (e) 6000 rpm, which were measured both before and after UVB irradiation.

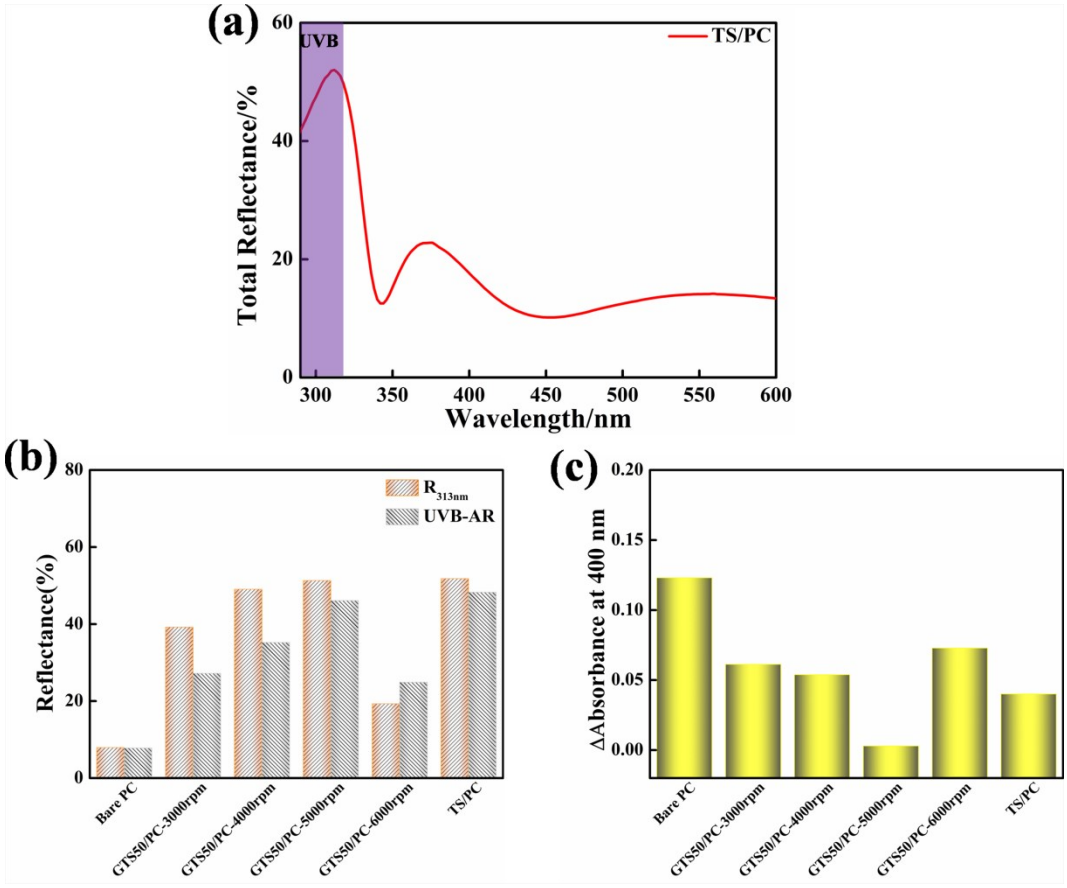

Fig. S10 (a) Total reflectance spectrum for the TS/PC sample; (b) the reflectance at wavelength of 313 nm (R_{313nm}) and UVB-AR of bare PC, TS/PC and GTS_{50}/PC samples; (c) the absorbance change at 400 nm after UVB aging for bare PC, TS/PC and GTS_{50}/PC samples.

For comparison, the optical property and photoprotection performance of conventional TS/PC was also analyzed. It was clear that the reflectance at wavelength of 313 nm and the average reflectance in the UVB region of the TS/PC sample were nearly the same as that of the GTS_{50}/PC sample prepared at 5000 rpm. As expected, the absorbance change at 400 nm, which indicated the degradation of PC substrate, of TS/PC as well as GTS_{50}/PC prepared at 5000 rpm were lower than that of other samples. Nonetheless, the absorbance change at 400 nm of GTS_{50}/PC sample prepared was much lower than that of TS/PC sample after UV aging test, suggesting that the GTS_{50} 1DPhC film had superior photoprotection effect. This may be because

the surface cracks on TS 1DPhC film expedited the contact of oxygen and UV light with the substrate, which led to a more serious photo-oxide degradation of PC than the crack-less GTS_{50} 1DPhC film coated PC.

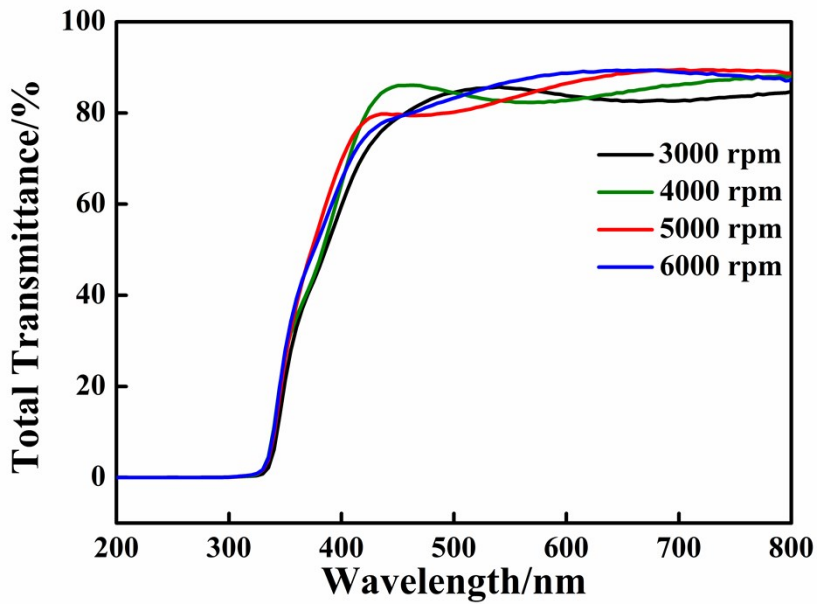

Fig. S11 The transmittance spectra of GTS_{50}/PC samples after UVB irradiation test

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