Protection against a wide UV wavelength range by Bragg reflection from polycrystalline colloidal photonic crystals

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Polycrystalline colloidal crystals, that formed in a 50-μm-thick cell, blocked ultraviolet (UV) light of 290–400 nm, regardless of the incident angle, while maintaining transparency in the visible light region. These crystals have the potential to be employed in effective UV-protection products against the sun.

Monodisperse colloidal particles can spontaneously form three-dimensional periodic arrays in a liquid medium. This ordered state is called a colloidal crystal,^{1–4} by analogy with atomic crystals. In the same manner that atomic crystals exhibit the Bragg reflection of X-rays, colloidal crystals exhibit a reflection in the visible light region because their lattice constants are generally in the submicrometre range.^{5,6} Therefore, common colloidal crystals show a bright colour because of Bragg reflection, even though the component materials are transparent.^{7–9} The colour reflected from colloidal crystals has several distinctive features. For example, the colour can be altered easily by changing the particle size, because the Bragg reflection wavelength is determined by the Bragg's law, $\lambda = 2n_c d_{hkl} \sin \theta$, where λ is the Bragg wavelength, n_c is the refractive index of the colloidal crystals, d_{hkl} is the lattice spacing of the (*hkl*) planes, which is a function of the particle size, and θ is the Bragg angle.^{10,11} Furthermore, the colour does not degrade unless the crystalline structure is destroyed. Therefore, colloidal crystals can be used as bright-coloured pigments that do not bleach and are different from the widely used absorption-type colour pigments or dyes.^{12,13} While many practical applications based on Bragg reflection colours in the visible light region have been reported,^{14–17} studies on colloidal crystals using Bragg reflection in the ultraviolet (UV) region have not been extensively explored.

UV absorbers have been widely used to protect skin against UV light from the sun.^{18,19} However, the absorption of UV light generates reactive free radicals, which cause photodegradation and render UV protectants less

effective.^{20,21} On the contrary, colloidal crystals capable of reflecting UV light, which can be readily prepared by using smaller colloidal particles, have the potential to be employed in long-term UV protectants because they undergo less degradation under UV light. However, the width of the Bragg reflection wavelength is generally narrow, i.e., tens of nanometres at most, which cannot block the entire wavelength range of UV light reaching the earth's surface from the sun (290–400 nm). A combination of colloidal crystals with different lattice constants or colloidal crystals with graded lattice constants/refractive indices can effectively yield a wider range of Bragg reflection wavelengths via the superposition of shifted Bragg wavelengths.^{22–26} However, even if such a structure capable of reflecting UV light is prepared, it cannot block the oblique incidence of UV light because, according to the Bragg's law, the Bragg reflection wavelength shifts substantially with change in the angle of incident light. Thus, it is still a challenging task to block the entire wavelength range of UV light from various directions.

In this communication, we demonstrate that the entire wavelength range of UV light reaching the earth's surface (290–400 nm) from various directions can be almost blocked by the Bragg reflection from polycrystalline colloidal crystals, while maintaining transparency in the visible light region. These crystals have the potential to be employed in effective UV-protection products against the sun.

We used monodisperse poly(methyl methacrylate) (PMMA) particles with a diameter of 160 nm to prepare the colloidal crystals, so that the Bragg reflection wavelength derived from the hexagonal close-packed layers for normal incidence was ~400 nm, which is the largest wavelength of UV light. Although PMMA has absorption bands in the UV region (200–280 nm),^{27–29} these bands are out of the wavelength range of the UV light that reaches the earth's surface from the sun (290–400 nm). The colloidal crystals were prepared in a fluidic cell (see the ESI† for details).³⁰ Two double-stick tapes, used as spacers, were sandwiched between two quartz substrates, and one of the openings was dipped in a dispersion of PMMA particles (Fig. 1). The dispersion penetrated the

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space between the quartz substrates under the action of capillary forces. The solvent gradually evaporated from the upper opening of the cell, and the colloidal crystals grew inside and across the cell. We prepared colloidal crystals of different thicknesses in cells with different spacer thicknesses (10, 30, 50, and 70 μm). The cell containing colloidal crystals was taken out of the dispersion, and the transmission and reflection spectra were measured.

Fig. 1 (a) Schematic diagram for the preparation of colloidal crystals in a fluidic cell. (b) Photograph of the generated colloidal crystals.

Fig. 2a shows the transmission spectra at normal incidence for the colloidal crystals formed in the cells with different thicknesses. The 10- μm -thick colloidal crystals exhibited a dip with a half-width of ~ 20 nm at ~ 400 nm, which was caused by the Bragg reflection from hexagonal close-packed layers parallel to the cell surface (ESI,[†] Fig. S1). Surprisingly, on increasing the cell thickness, transmittance in the UV region shorter than the dip wavelength decreased substantially compared to that in the visible light region. The 30- μm -thick crystals exhibited less than 15% transmittance in the UV region and, eventually, the 50- μm -thick crystals almost completely blocked the UV light in the 290–400 nm range, while maintaining a transmittance of 57–85% in the 470–700 nm visible light region. The 50- μm -thick colloidal crystals blocked the entire wavelength range of the UV light reaching the earth's surface at both normal as well as oblique incidences. Fig. 2b shows the transmission spectra of 10- and 50- μm -thick crystals when the angle of incident light is changed from the direction normal to the cell surface to 40° . The spectrum of the 10- μm -thick crystals changed significantly as a function of the incident light angle, following the Bragg's law. In contrast, the spectrum of the 50- μm -thick crystals changed only slightly when the incident angle was changed.

To examine the effect of light absorption and scattering by PMMA particles, the transmission spectrum of 50- μm -thick colloidal crystals with equal particle concentration (~ 74 vol%) but smaller particle diameter (80 nm) at normal incidence was measured, and is illustrated by a dotted line in Fig. 2c. The spectrum exhibited transmittance above approximately 300 nm. This suggests that the UV protection property of the colloidal crystals with the particle diameter of 160 nm is not mainly caused by the light absorption of PMMA. In addition,

Fig. 2 (a) Transmission spectra of the colloidal crystals formed in the cells with different thicknesses at normal incidence. (b) Transmission spectra of 10- and 50- μm -thick colloidal crystals when the incident light angle is changed from the direction normal to the cell surface to 40° in steps of 5° . (c) Transmission spectra of the aqueous dispersion of the PMMA particles with a particle diameter of 160 nm and different particle volume concentrations in the 50- μm -thick cell. The red and dotted lines represent the transmission spectra of 50- μm -thick colloidal crystals with the particle diameters of 160 and 80 nm, respectively.

the transmission spectra of the aqueous dispersions of the PMMA particles with the particle diameter of 160 nm and different particle volume concentrations in the 50- μm -thick cell are shown in Fig. 2c. At the concentration of 0.1 vol%, the

spectrum showed a dip at 265 nm due to the absorption band attributed to the carbonyl group in PMMA^{27–29} (ESI,† Fig. S2) and a high transmittance at a wavelength longer than the dip. When the particle concentration was increased, the dip became deeper and broader because of the increase in the amount of light absorption and scattering by the PMMA particles. However, the change in the transmittance as a function of wavelength was gradual, and the transmittance in both the UV and visible light regions reduced greatly. Therefore, the low and high transmittances in the UV and visible light regions, respectively, for the 50- μm -thick crystals, i.e., the steep gradient of transmittance at ~ 400 nm, which is shown as the red line in Fig. 2c, cannot be achieved by the absorption and scattering of incident light.

The steep gradient of transmittance at ~ 400 nm and the low angle dependence for the 50- μm -thick colloidal crystals can be a consequence of the increase in the number of polycrystalline domains in the colloidal crystals with an increase in the cell thickness. When the space between the substrates of the cell is narrow, the hexagonal close-packed layers of the colloidal particles are aligned well and are parallel to the cell surface, owing to the support from the flat surface of the substrates. On the contrary, upon increasing the cell thickness, the surface of the substrates cannot support the layers in the middle of the cell, resulting in the generation of polycrystalline domains there. Considering the Bragg reflection conditions, the longest Bragg wavelength occurs when the incident light is normal to the hexagonal close-packed layers, i.e., $\theta = 90^\circ$, which corresponds to the dip in the wavelength shown in Fig. 2a. When the sample contains polycrystalline domains with random orientations, various Bragg reflections with different incident light angles, i.e., $0^\circ \leq \theta \leq 90^\circ$ can occur at a wavelength shorter than the dip. Therefore, upon increasing the cell thickness, the transmittance in the wavelength region shorter than the dip wavelength significantly reduces when there is an increase in the number of polycrystalline domains. In contrast, since Bragg reflection is absent at wavelengths longer than the dip wavelength, the transmittance in the visible region is not affected. Eventually, sufficient randomly oriented polycrystalline domains are formed to block the entire wavelength range of the UV light regardless of the incident light angle, while maintaining transparency in the visible light region.

To confirm the presence of polycrystalline domains, the angle-dependent reflection spectra of the 50- μm -thick colloidal crystals were measured (Fig. 3a). The light in the wavelength range of 350 to 1050 nm was illuminated normal to the cell surface, and the reflection spectrum was measured at different angles of the detector δ . As shown in Fig. 3b, the spectrum at $\delta = 0^\circ$ showed a reflection peak at ~ 400 nm due to Bragg reflection by the hexagonal close-packed layers which are parallel to the cell surface. When the angle of the detector was increased, a shift in the reflection peak to a shorter wavelength was observed. Fig. 3c shows the plot of the peak wavelength vs. the angle of the detector, δ , determined from Fig. 3b. These plots are in good agreement with the Bragg's law, $\lambda = 2n_c d_{hkl} \sin \theta$, for $\theta = 90^\circ - \delta/2$. This indicates that the

Fig. 3 (a) Schematic diagram for the angle-dependent reflection spectral measurement. The light is illuminated normal to the cell surface, and the reflection spectrum is measured at different angles of the detector δ . (b) Reflection spectrum of the 50- μm -thick colloidal crystals at different angles of the detector δ . (c) Plot of the peak wavelength vs. angle of the detector δ determined from b. The solid line is the calculation curve obtained using the Bragg's law, $\lambda = 2n_c d_{hkl} \sin \theta$, for $\theta = 90^\circ - \delta/2$. The value of $n_c d_{hkl}$ was determined from the reflection spectral measurement at $\delta = 0^\circ$.

declined hexagonal close-packed crystalline planes or the polycrystalline domains with random orientations reflecting different wavelengths of UV light are present in the cell. These results suggest that the UV protection property of the 50- μm -thick colloidal crystals is mainly due to the Bragg reflection with minor contribution from the light absorption and scattering by the PMMA particles.

In summary, we have demonstrated UV protection by Bragg reflection from polycrystalline colloidal photonic crystals. Colloidal crystals, in which the Bragg reflection wavelength for hexagonal close-packed layers for normal incidence was the largest UV wavelength (~ 400 nm), were prepared in cells with different thicknesses. We found that upon increasing the cell thickness, the transmittance in the wavelength region shorter than the Bragg wavelength significantly reduced. Eventually, the 50- μm -thick crystals blocked almost the entire wavelength range of the UV light reaching the earth's surface from the sun (290–400 nm), regardless of the incident light angle, while maintaining transparency in the visible light region. These crystals have the potential to be used in developing effective UV-protection products against the sun.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- 1 P. Pieranski, *Contemp. Phys.*, 1983, **24**, 25.

- 2 A. Toyotama, T. Okuzono and J. Yamanaka, *Sci. Rep.*, 2016, **6**, 23292.
- 3 H. Sugiyama, T. Sawada, H. Yano and T. Kanai, *J. Mater. Chem. C*, 2013, **1**, 6103.
- 4 T. Kanai, N. Boon, P. J. Lu, E. Sloutskin, A. B. Schofield, F. Smullenburg, R. van Roij, M. Dijkstra and D. A. Weitz, *Phys. Rev. E*, 2015, **91**, 030301.
- 5 T. Kanai, T. Sawada and K. Kitamura, *Langmuir*, 2003, **19**, 1984.
- 6 T. Kanai, T. Sawada, I. Maki and K. Kitamura, *Jpn. J. Appl. Phys.*, 2003, **42**, L655.
- 7 H. Fudouzi and Y. Xia, *Adv. Mater.*, 2003, **15**, 892.
- 8 S.-H. Kim, J.-M. Lim, W. C. Jeong, D.-G. Choi and S.-M. Yang, *Adv. Mater.*, 2008, **20**, 3211.
- 9 D. Yang, S. Ye and J. Ge, *Chem. Commun.*, 2015, **51**, 16972.
- 10 Z. -Z. Gu, A. Fujishima and O. Sato, *Chem. Mater.*, 2002, **14**, 760.
- 11 T. Kanai, T. Sawada, and J. Yamanaka, *J. Ceram. Soc. Jpn.*, 2010, **118**, 370.
- 12 J. H. Moon, G.-R. Yi, S.-M. Yang, D. J. Pine and S. B. Park, *Adv. Mater.*, 2004, **16**, 605.
- 13 D. Ge, L. Yang, G. Wu and S. Yang, *Chem. Commun.*, 2014, **50**, 2469.
- 14 J. M. Weissman, H. B. Sunkara, A. S. Tse and S. A. Asher, *Science*, 1996, **274**, 959.
- 15 T. Kanai, S. Yamamoto and T. Sawada, *Macromolecules*, 2011, **44**, 5865.
- 16 S. Furumi, T. Kanai and T. Sawada, *Adv. Mater.*, 2011, **23**, 3815.
- 17 Q. Fu, A. Chen, L. Shi and J. Ge, *Chem. Commun.*, 2015, **51**, 7382.
- 18 K. Morabito, N. C. Shapley, K. G. Steeley and A. Tripathi, *Int. J. Cosmet. Sci.*, 2011, **33**, 385.
- 19 R. M. Bissonnette, *Skin Ther. Lett.*, 2008, **13**, 5.
- 20 A. Kikuchi and M. Yagi, *Chem. Phys. Lett.*, 2011, **513**, 63.
- 21 S. Scalia and M. Mezzena, *Photochem. Photobiol.*, 2010, **86**, 273.
- 22 P. Jiang, G. N. Ostojic, R. Narat, D. M. Mittleman and V. L. Colvin, *Adv. Mater.*, 2001, **13**, 389.
- 23 J. R. C. Smirnov, M. E. Calvo and H. Míguez, *Adv. Funct. Mater.*, 2013, **23**, 2805.
- 24 J. Li, L. Xue, Z. Wang and Y. Han, *Colloid Polym. Sci.*, 2007, **285**, 1037.
- 25 J. H. Park, W. S. Choi, H. Y. Koo, J. C. Hong and D. Y. Kim, *Langmuir*, 2006, **22**, 94.
- 26 T. Kanai, T. Sawada, A. Toyotama, J. Yamanaka and K. Kitamura, *Langmuir*, 2007, **23**, 3503.
- 27 P. Maji, R. B. Choudhary and M. Majhi, *J. Non-Cryst. Solids*, 2017, **456**, 40.
- 28 M. Ghamari and G. Farzi, *J. Mater. Sci.: Mater. Electron.*, 2017, **28**, 16570.
- 29 V. Doddapaneni, Y. C. Zhao, F. Ye, R. Gati, H. Edin and M. S. Toprak, *Powder Metall. Met. Ceram.*, 2015, **54**, 397.
- 30 M. Ishii, H. Nakamura, H. Nakano, A. Tsukigase and M. Harada, *Langmuir*, 2005, **21**, 5367.