Structural Color Painting by Rubbing Particle Powder

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Structural colors originate from purely physical structures. Scientists have been inspired to mimic the structures found in nature, the realization of these structures still presents a great challenge. We have recently introduced unidirectional rubbing of a dry particle powder on a rubbery surface as a quick, highly reproducible means to fabricate a single crystal monolayer assembly of particles over an unlimited area. This study extends the particle-rubbing process to a novel fine-art painting, structural color painting (SCP). SCP is based on structural coloring with varying iridescence according to the crystal orientation, as controlled by the rubbing direction. This painting technique can be applied on curved surfaces, which enriches the objects to be painted and helps the painter mimic the structures found in nature. It also allows for quick fabrication of complicated particle-assembly patterns, which enables replication of paintings.
Figure 1 | Single grain of 2D particle assembly by the rubbing process and its diffraction colors. (a) SEM image of a hexagonally-ordered polystyrene (PS) particle monolayer (1 μm in diameter). This particle monolayer was prepared by rubbing on a PDMS-coated glass slide (10 cm × 10 cm). (b) A magnified SEM image of the box in Figure 1a. (c, d) Photograph of the particle assembly diffraction on a black paper (c) and on a semitransparent half dome screen (d). White light was transmitted to the single grain monolayer perpendicularly through a hole; 1 cm for (c) and 4 cm for (d). The light diffracted from the (11) plane (20) plane was split into rainbow colors. Human eyes perceive different colors depending on the tilted angle (θ), azimuthal angle (φ), and the sample-to-eye distance.

Results and Discussion

Figure 1a shows a SEM image of an assembled particle monolayer obtained by repeatedly rubbing spherical 1-μm-diameter polystyrene (PS) particles on a 10 cm × 10 cm PDMS-coated glass plate. A camera image of the rubbing process is shown in the supporting information (Figure S1). Although line defects were observed, all the particles were aligned along the rubbing direction (indicated by an arrow). The particle monolayer had uniform ordering and orientation; hence, the grains were also uniform throughout the substrate surface. Except for the line defects, the particles were well-ordered hexagonally, as seen in the higher-magnification SEM image in Figure 1b.

This 2D particle assembly diffracts light at different angles depending upon the wavelength of the incident light. At a fixed incident angle (θi), the diffraction angle (θm) is determined by the wavelength (λ) and lattice distance (d) between the ordered particles, as given by: 

\[ \sin \theta_m = M \frac{\lambda}{d} \]

where M is the diffraction order, and n and m are the refractive indices of the incident and diffraction media, respectively. When the light is incident perpendicular to the flat 2D particle assembly (θi = 0), diffraction in the air (n = m = 1) yields the grating equation: 

\[ \sin \theta_m = M \frac{\lambda}{d} \]

Figure 1c shows an optical image of the diffracted light on a flat white screen when white light passing through a small, 1-cm-diameter hole was irradiated perpendicularly onto the particle assembly. Since the substrate was transparent and the interface was flat, the colors shown in Figure 1c originated from diffraction by the particle assembly, not from reflections at the interfaces. The diffraction was identical in both reflection and transmission modes (Supporting information, Figure S2). The diffracted light was split into rainbow colors according to the diffraction angle (θm), with blue at small angles, and red at large angles. Two lattices contribute to the diffraction; the diffraction from the (11) plane ranges from 32° (blue) to 48° (red), while the diffraction from the (20) plane ranges from 67° (blue) to 90° (green). Therefore, different colors appear if either the incident angle (θi) or the viewing angle (θv) is changed.

When the size of the beam irradiated onto the particle assembly is increased, the size of the diffraction ellipse also increases. Figure 1d shows the diffracted light on the semi-transparent hemispherical cover when white light was irradiated through a large 4-cm-diameter hole. The colors displayed on the hemisphere visualize the polar plot. In this case, the colors shown on the hemisphere changed continuously between the diffraction ellipses, resulting in a color change at the azimuthal angle (φ). The color change at φ indicates that human eyes perceive different colors when the particle assembly sample is rotated in its plane. This color change at φ also depends on the altitude (angle θ) on the screen. In Figure 1d, the color at the angle φ1 changes from orange to blue, but the color at φ2 changes from green to blue. Rotating the sample is equivalent to changing the orientation of the particle assembly, which means that the colors from two grains with different crystal orientations look different to the eye.

Human eyes perceive mixed colors at a small distance (d) from the sample to the hemispherical cover increases. Due to good conformity between the particle monolayers and the wafer yields different color sets for the same painting, similarly to "structural color paintings." Figures 2c and 2d demonstrate one such painting, "A tree on a lawn on a windy day." It was created on a 4-inch PDMS-coated Si wafer by rubbing a 1-μm-diameter PS particles with a rubber-coated pen. Since the color of the particle assembly depends on the incident angle of the light, slightly tilting the wafer yields different color sets for the same painting, similarly to lacquer work inlaid with mother-of-pearl. Structural coloring based on the 2D photonic crystal painting can also be applied on curved surfaces that have rubbery characteristics. Due to good conformity between the particle monolayers and the curved surfaces, the samples displayed distinct colors depending on the viewing angle. By combining the color tuning and arbitrary painting capabilities, the use of photonic crystal painting was...
Mechanical rubbing requires a certain level of adhesion energy. The color of the monolayer changes according to the rubbing direction and the viewing angle. The numbers indicate the rubbing sequence. The second rubbing impeded in the area receiving the first rubbing, creating a grain boundary. A structural color painting, “A tree on a lawn on a windy day,” which was drawn by rubbing the PS beads with a rubber pen. Depending on the viewing angle, the picture appears differently in terms of both color and texture, similar to lacquer work inlaid with mother-of-pearl. Rubbing particles on a substrate with topological variations can diversify the resulting colors and designs. For example, the particle monolayer formed on the concave surface of a hemisphere displays different colors depending on the curvature of the concavity. We applied the particle rubbing process on an array of 4-cm-wide and 3.5-cm-deep hemispherical concavities fabricated on a PDMS substrate. A powder of 1.5-μm-diameter spherical silica beads was rubbed with a motorized rotating rubber ball (Supporting Information, Figure S5). The (11) plane was directed concentrically around the walls of the concavities (Supporting Information, Figure S4). Hence, the colors also varied concentrically, gradually changing from the center to the edges. When the rubbing was done in random directions, the color was not concentric (Supporting Information, Figure S5). Due to the curvature of the concavity and the particles, when white light is perpendicularly incident on the substrate from the bottom, wavelengths of 375, 450, and 488 nm are diffracted at 45, 60, and 70° curvatures, respectively (Figure 3c). The concavity looked mostly blue when viewed from a greater distance (d = 40 cm) (Figure 3d). When the viewing distance was small (d = 10 cm), different colors were perceived blue at the center, green in the middle, and yellow at the edge (Figure 3e). An array of the concavities displayed blue at d = 40 cm (Figure 3f). When the array sample was tilted, the concavities looked colorful (Figure 3g). The concentric colors were not observed at the tilted angles, and the structure of the colors continued changing as the tilting angle increased (Figure 3h).

The monolayer assembly of micro-scale particles resulting from mechanical rubbing requires a certain level of adhesion energy (≥ 0.01 gf·mm⁻¹) of the substrate. Rolling the particles enables the hexagonal packing, but if the adhesion is too low, the particle aggregates tend to slide across the substrates and therefore, are not separated into individual particles. Taking into account the minimum adhesion energy of the substrates, patterning of a colloidal monolayer could be readily achieved by modifying the surface adhesion of the substrates. Figure 4a shows the experimental procedure for the patterning of the assembled monolayer. The PDMS substrate was exposed to ultra-violet-ozone (UV-O) through a metal mask before the particle powder was rubbed on the surface. The adhesion energy (E) of the UVO-treated surface was reduced to nearly zero (E = 0.001 gf·mm⁻¹). As a result, the particles slipped in the non-sticky regions during rubbing and were assembled only in the neighboring sticky regions (E = 0.05 gf·mm⁻¹)². Unidirectional rubbing on the UVO-treated pattern led to uniform crystal orientation throughout the particle assembly. Figure 4b shows an example of the patterned assembly of particles (PS, 1 μm in diameter). Figure 4c is a magnified image of a 50-μm-wide line pattern. The crystal structures in the other areas had the same single domain and an identical crystal orientation (Supporting Information, Figure S7). Thus, using a mask allows for repeated production of the same assembly features. Figures 4d–f depicts four structural color letters manufactured using the same mask. The left halves of the letters were rubbed upwards and downwards, whereas the right halves were rubbed from left to right. The colors of the four letters were clearly distinguished in the middle and continued changing as the tilting angle was increased.

In summary, the process of rubbing particle powder on a rubber substrate leads to monolayer assembly of the particles and allows the crystal orientation to be changed simply by changing the rubbing direction. Crystal domains with different crystal orientations display distinct structural colors when the incident light is large, as is the case in daily life. The colors could be recolored repeatedly by changing the...
crystal orientation. We extended this color-tuning capability to a novel type of fine art painting, structural color painting. This unique painting technique can be applied on both curved and flat surfaces, which allows for drawing on most everyday goods, such as the mug in this study. Rubbing particles on concave or convex surfaces enables us to mimic natural objects showing structural colors. By patterning the adhesion energy of a substrate, complicated patterns of colloidal monolayers could be fabricated.

In general, the color reflectance of a monolayer particle array is lower than the multilayer particle arrays, especially in the white background. The color reflectance depends on the target applications and on the intensity of the light. Simple monolayer gratings such as compact disks (CDs) have good color visibility and are often used in in-door or out-door decoration. The color visibility can be greatly enhanced by increasing the refractive index of the periodic features. In the particle rubbing, using high-index ceramic particles such as TiO₂ or the organic/inorganic composites will improve the color visibility. There are several commercial products, so-called effect pigments, which display sophisticated color interplay depending on the angle of observation. Such effects are achieved on curved objects²⁹. The use of spherical particles containing colorants can be another approach to diversify the monolayer structural coloring in real paintings. We expect this new painting and patterning technique can be used for lithography, diffraction masks, cosmetics, and decorations on a variety of surfaces, from small, everyday necessities to large surfaces like cars and walls.

Methods

PDMS (Sylgard 184) was purchased from Dow Corning. The pre-polymer and cross-linker were mixed at a weight ratio of 10:1. For the rubber substrate, the mixed PDMS liquid was poured onto a polystyrene petri dish with uniform thickness (5 mm), and the cast liquid was cured at 80°C for 12 h. The wafer and glass substrates coated with PDMS were prepared by spin-coating the mixed PDMS liquid at 3000 rpm for 30 s and then cured. To pattern the adhesion energy of the rubber surface, the PDMS surfaces were exposed to ultraviolet-ozone (UVO) for 60 min. To coat PDMS on curved objects, the mixed PDMS liquid was painted with a brush and then cured. PDMS substrates with concavities were prepared by arranging nine steel balls (1 cm in diameter, 3 × 3) on a glass substrate and pouring the mixed PDMS solution, followed by thermal curing.

Any rubber that is not too sticky (E > 10 gf mm) and not too hard (E ≤ 0.001 gf mm) can be used ref. 28. Practically, the adhesion energy of ‘too sticky’ is that of the adhesive tape, and adhesion energy of ‘too hard’ is that of a bare plastic surface. The adhesion energy of most elastic materials is in between the two regions. Therefore, the species of rubbers applicable in this process is wide enough, including PDMS rubber with a diverse crosslinker mixing ratios, block copolymer rubber film, and polyurethane rubber, etc.

To obtain the single-crystal monolayer, a dry PS powder (with particles 1 μm in diameter) was sandwiched between PDMS-coated glass substrates. The top substrate

Figure 3 | The structural color paintings on curved surfaces. (a, b) photographic images of structural color painting on a mug. On a PDMS-coated mug, a PS particle powder (1 μm in diameter) was rubbed. The colors changed according to the viewing angle. (c) A schematic for observing diffraction from a concave hemisphere with assembled particle monolayer on its surface. (d, e) Color difference depending on the viewing distance (d). The color looks differently; concentric rainbow at short distance at d = 10 cm (d), but a blue monocolor at d = 40 cm (e). (f) Photographic image of the diffraction colors from concave hemisphere array, shown from the front at d = 40 cm (f) and from tilted angle (θ = 30°).

Figure 4 | Patterning of the assembled particle monolayer. (a) Schematic of particle monolayer micro-patterning. A PDMS surface was exposed to ultraviolet ozone (UVO) through a metal mask. The exposed regions became non-sticky. The particles tended to slide from the non-sticky regions and assembled only on the sticky regions. (b, c) Micro-pattern of the particle monolayer with the same crystal orientation (b) and a magnified optical image of the box (c). (d, e, f) Replication of the structural color painting letters. The left halves were rubbed upwards and downwards. The right halves were rubbed from left to right. The colors look differently according to the viewing angles.
was pressed by a palm and moved unidirectionally left and right five times. For drawing large features, a long PDMS piece (1 cm × 10 cm) was cut from the PDMS thick plate (1 cm in thickness) prepared in a square petri dish (10 cm × 10 cm). For fine-art painting, the tip of a ball-point pen was coated with PDMS and used as a rubber brush. Then pen was dipped in the PDMS prepolymer solution, taken out, and heated at 70 °C for 2 h in a heating chamber. The pictures were drawn by rubbing the particle powder on a PDMS-coated wafer. The pressure and shear force required to rub the particle powder does not need fine control. If the external force overcomes the adhesion between the particles and the substrate, rubbing the particles is accomplished. Readers can imagine the drawing images with a pastel, as shown in Figure S1.

For the concavity experiment, 10-mm iron bearings were arrayed with a 3 × 3 structure. Additional PDMS was poured onto the thickness of PDMS reached the bearing radius. After curing, bearings were removed. A 10-mm iron bearing was held in front of an electric drill tip, and coated with PDMS. Silica powder (1.5 μm in diameter) was put in the hemispheres, and the bearing in the electric drill tip was electrically spun at 100 rpm for 10 sec. Patterned particle monolayers were fabricated by rubbing the particle powder on PDMS-coated wafers with adhesion energy patterns. The powder was covered by a large PDMS substrate and rubbed in the same way to prepare the single-crystal monolayer.

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Author contributions

U.J. designed the experiments and guided the project. C.J.P. performed the experiments. K.S.K. contributed to particle preparation. All authors discussed the results and commented on the manuscript at all stages.

Additional information

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