ASSOCIATED CONTENT

Supporting Information

Non-iridescent biomimetic photonic microdomes by inkjet printing

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Experimental section

Materials

Dopamine hydrochloride (DA), tris(hydroxymethyl)aminomethane (Tris), and methanol, ethylene glycol (purity 99%), formamide, and surfactant BRIJ 30 were obtained from Sigma-Aldrich. Deionized water was used in all the experiments. All chemicals and solvents were of reagent grade and used as received.

Synthesis of melanin nanospheres

DA (1-2.0 mg/mL), Tris (5.4 g), and water/methanol (4/1) solution (100 mL) were placed in a glass beaker without lid, and the mixture was stirred at 30 °C for 30 h. The melanin dark brown nanoparticles were separated and purified repeatedly by three times centrifugation (1200 rpm for 15 min) and then redispersed in deionized water.

Preparation of substrate and melanin ink for printing

Inkjet printing was performed on silicon wafers, glass slides, freestanding poly-dimethylsiloxane (PDMS) films and on PDMS films coated on glass substrates. Large area printing was also performed on silicon wafers coated with a thin layer of PDMS mixed with carbon nanotubes (~4 wt. %) to create black substrates. All substrates were treated with octadecyltrichlorosilane (OTS) to increase hydrophobicity. The melanin inks were prepared by first dispersing the MNPs in deionized water (with concentration of ~ 5 wt %). Suitable MNP inks for inkjet printing was then prepared by mixing MNP solution with binary mixture of formamide and ethylene glycol to adjust viscosity whereas surfactant was used to reduce surface tension of the ink. Non-optimized inks were prepared using single solvent of formamide. The ratio of solvents and surfactant were varied to achieve printable inks. The inks were treated ultrasonically and filtered through a 0.5 μm nylon mesh filter. The optimal surfactant concentration was 30 µL of 1 vol.% of Brij 30 surfactant per 1.5 mL ink, resulting in surface tension around 28 mNm^{-1} and desired viscosity 7 cP was achieved by mixing two parts of binary solvent and one volume part of MNP ink.

Inkjet printing of melanin photonic crystal microdome

For inkjet printing of melanin inks, Fujifilm Dimatix Materials printer DMP (2831) was used with cartridges having a drop volume of 10 pL. Printing on substrates was performed with drop spacing value ranging from 20 µm to 150 µm and substrate temperature at 30°C unless otherwise specified.

Preparation of thin film photonic crystals by convective assembly

Glass slides and silicon wafer were cut into desired pieces and were used for thin film photonic crystal samples. Prior to use, the substrates were thoroughly cleaned by washing with DI water and IPA solution. To increase the hydrophilicity, substrates were treated with piranha solution containing 30% hydrogen peroxide and 70% sulfuric acid for 30 min. Subsequently, they were rinsed several times in IPA, sonicated in DI water and dried in a stream of nitrogen. Thin film photonic crystal films were prepared using an aqueous suspension of MNPs at 1 wt. %. A clean glass slide is then placed into 20 mL of MNPs suspension in a clean scintillation vial. The entire setup was covered by a large beaker to keep out external airflow and contamination. Saturated salt of NaCl were also used to maintain constant humidity of around 60%. The slow evaporation of solvent leads to the formation of multilayer colored thin film photonic crystals.

Characterization

SEM images were obtained using a field-emission scanning electron microscope (JSM-6700F, JEOL, Japan), after deposition of a thin gold layer on the samples. Surface morphology and cross sections of photonic microdome were performed on a Zeiss 1540 RsB focused ion beam. Optical microscopy images and reflectance spectra from single pixels were obtained using a custom-made micro-spectroscopic setup. The pixels were illuminated using a 50W halogen lamp attached to a microscope (Nikon Eclipse L200N, Japan) and the reflected light was collected from the camera port with an optical fiber connected to a spectrometer (Ocean Optics HR 4000, USA). An objective lens with 50x magnification, corresponding NA = 0.80, was used to record spectra. To conduct angle-resolved reflection and scattering spectroscopy, the samples were mounted at the rotation center of a goniometer. Collimated white light was incident on the sample. Reflected or scattered light was collected by an optical light guide connected to a spectrometer (Andor Shamrock 303i, with a Newton CCD detector). The angular resolution was about 10°. Both the sample and the detector arm on which the fiber were mounted could be rotated.

Supporting figures

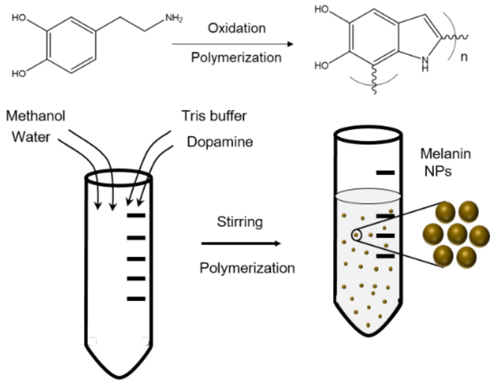

Figure S1. Reaction scheme for the formation of melanin nanoparticles (MNPs) via oxidative polymerization of Dopamine HCL monomer at 30°C.

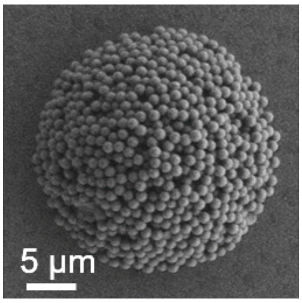

Figure S2. SEM image of satellite droplet formed by inkjet printing using a non-optimized ink, showing non-closed packing of MNPs.

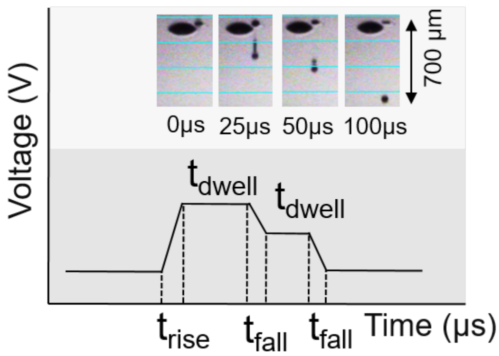

Figure S3. Jetting waveform used to control the piezoelectric transducer of the inkjet printheads for the deposition of the melanin nanoparticles suspension. Inset shows a series of snapshots of the injected MNP ink showing single drop formation captured at different times after injection.

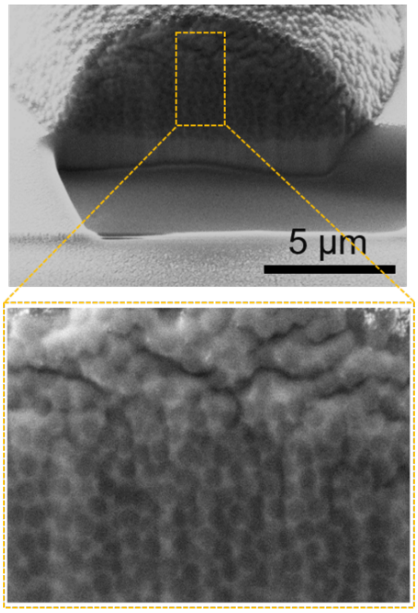

Figure S4. SEM image of a photonic MNP microdome that was cut using a focused ion beam (FIB), aiming to reveal the interior of the microdome. The bottom panel shows a magnified image of the center area of the dome. The scale bar corresponds to 5 µm.

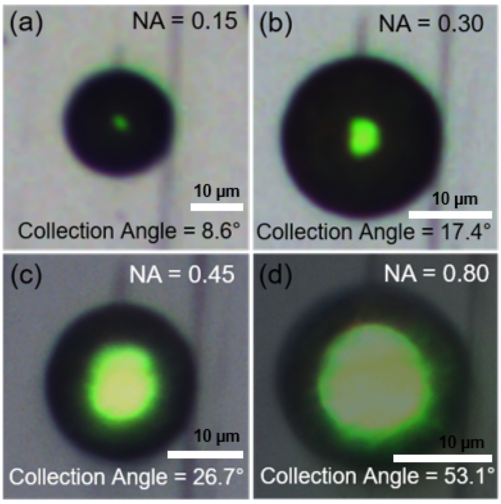

Figure S5. The numerical aperture of the microscope objective defines the colored area of the photonic microdome. (a-d) shows photographs of a photonic MNP microdome captured with different magnification objective lenses corresponding to 5x, 10x, 20x, and 50x respectively. Higher magnification lenses, corresponding to larger numerical aperture, leads to an increased diameter of the observed colored area.

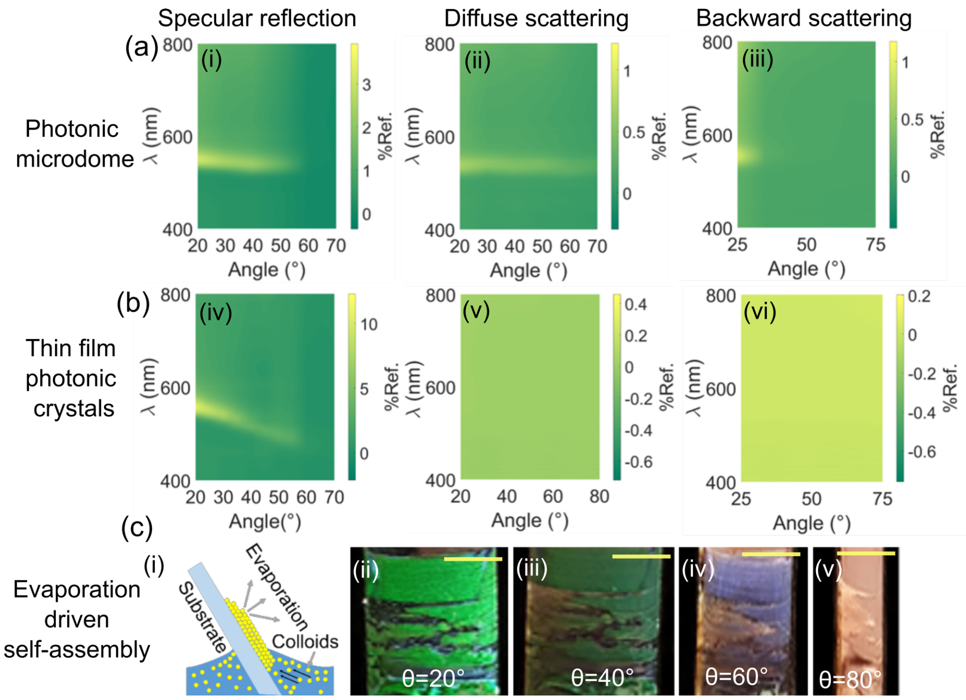

Figure S6. (a,b), False color maps showing the intensity of specularly, diffusively scattered, and backward scattered light, as a function of angle and wavelength, from the photonic dome and thin film photonic crystal samples. The experimental setup is illustrated in Figure 4. Peak and shoulder positions were determined with the help of second derivatives. (c) (i) Schematic illustration of evaporative assembly to fabricate thin film colloidal photonic crystal. C (ii-v) Optical images of a thin film photonic crystal sample viewed at different viewing angles, showing perceived iridescence. The scale bar in the image corresponds to 1cm.

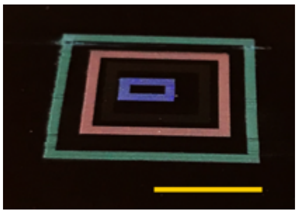

Figure S7. Digital photograph of multicolor concentric squares inkjet printed using three different sizes of MNPs (on silicon wafer treated with OTS). The scale bar corresponds to 1 cm.

§1. Bragg-Snell law

$$m\lambda_{max} = 2d_{hkl}\sqrt{n_{eff}^2 - sin^2\,\theta}$$

where m is the diffraction order, λ_{max} is the diffracted wavelength, n_{eff} is the effective refractive index, and θ is the incidence angle with respect to the normal. d_{hkl} is the interplanar nanoparticle separation between the (hkl) crystallographic planes which is given by:

$$D\sqrt{2}(h^2 + k^2 + l^2)^{-1/2}$$

with D being the diameter of the colloidal particles. For FCC photonic crystals, (hkl) corresponds to (111) planes.

§2. Estimation of effective refractive index for two material system:

$$n_{eff}^2 = n_{mel}^2 \cdot f_{mel} + n_{air}^2 \cdot (1 - f_{mel})$$

where n_{mel} (≈ 1.8) is the refractive index of the MNPs, n_{air} is the refractive index of the air between MNPs. Assuming that the structure takes a close-packed face-centered-cubic arrangement where 0.74 and 0.26 are the volume fractions for the MNPs and air respectively, the calculated effective refractive index is 1.63.