Supporting Information

Gel-based Artificial Photonic Skin to Sense a Gentle Touch by Reflection

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Materials

All chemicals were of analytical reagent grade, and used as received. Four-arm polyethylene glycol (PEG) thiol (95%, MW 5,000 Da), triethanolamine (98%), lithium bromide (LiBr) and Allura Red (85%) were gained from Aladdin Reagent Inc., China. Ammonium persulfate (APS), urea, sodium sulfide (Na$_2$S), and sodium lauryl sulfate (SDS) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Styrene (St) and acrylic acid (AA) were purchased from Xilong Scientific Co., Ltd., China. Ecoflex® 00-10 platinum cure silicone rubber kit and Sylgard® 184 silicone elastomer kit (polydimethylsiloxane, PDMS) were bought from Sigma-Aldrich, Inc. (USA) and Smooth-On, Inc. (USA), respectively. Wool fibers, polytetrafluoroethylene (PTFE) substrates (water contact angle: 115 ± 5°) and round poly(propene) (PP) tubes were provided by Tongxiang Dushi Woolen Material Co., Ltd. (China), Guangjin plastic material Co., Ltd. (China) and Mengniu Dairy Co., Ltd. (China), respectively. Ultrapure water with a resistivity of >18.2 MΩ·cm$^{-1}$ was obtained by a Milli-Q integral water purification system (Millipore Co., Ltd, USA).
Experimental

1. Preparation of the keratin-based gel

The preparation of keratin solution extracted from wool fibers followed a reductive method as described in our previous report. The keratin-based gel was prepared via the Michael addition reaction. Briefly, a tetra-thiolated PEG crosslinker (four-arm PEG thiol, 150 mg mL$^{-1}$) was ultrasonicated in triethanolamine. Then, the keratin solution (7 wt% in 1X phosphate-buffered saline) and tetra-thiolated PEG crosslinker solution were mixed with a volume ratio of 1:1, avoiding the formation of air bubbles. Finally, the mixture was drop-cast upon the substrates. After approximately half an hour, the keratin-based gel samples were ready to be used (usually immediately after preparation).

2. Preparation of keratin-based gel samples coated with 3DPC structure

Monodisperse polystyrene (PS) nanospheres (with a diameter of 280 nm) were prepared by refined soap-free emulsion polymerization as described in our previous report and were stored at 4 °C until use. Keratin-based gels were prepared via the Michael addition reaction and drop-cast upon PTFE substrates (Figure S1). Volumes of 2–3 \( \mu \)l of the PS emulsion were directly transferred by a pipette to the surface of the gel samples. After being dried under ambient conditions, the PS colloidal crystals developed a structural coloration, and the samples could be applied as pressure sensors. Alternative measurement ranges were achieved by controlling the size of the keratin-based gel, which could be adjusted by using different amounts of the newly prepared keratin-based gel, substrates, forming molds, and so on (Text S3).
3. Preparation of keratin-based gel samples coated with Allura Red dye

Keratin-based gels were prepared via the Michael addition reaction and drop-cast upon PTFE substrates. Volumes of 2–3 μl of Allura Red dye solution (0.5 mg ml⁻¹) were directly transferred by a pipette to the surface of the gel samples. The gel samples coated with Allura Red dye were achieved after being dried under ambient conditions.

4. Preparation of Ecoflex® 00-10 platinum cure silicone rubber compound samples coated with 3DPCs structure

Ecoflex® 00-10 platinum cure silicone rubber compound samples were fabricated by stirring part A and part B with a volume or weight ratio of 1:1 and later curing in about 4 hours in room temperature (as described in the Product Manual). Then the PS emulsion was dip-coat upon silicone rubber, as described in section 2.

5. Preparation of Sylgard® 184 silicone elastomer (PDMS) samples coated with 3DPCs structure

Sylgard® 184 silicone elastomer (PDMS) samples were fabricated by stirring the base part and the curing agent part with a volume or weight ratio of 10:1 and later curing in about 4 hours in oven at 60 °C (as described in the Product Manual). Then the PS emulsion was dip-coat upon silicone rubber, as described in section 2.
6. Characterization and measurements

Scanning electronic microscopy (SEM) images were obtained using a field-emission scanning electronic microscope (SU-70, Hitachi, Japan) operating at 5 kV. Microphotographs were captured by an upright microscope (Eclipse Ci-S, Nikon, Japan) operating in the reflection mode. Photographs were taken using a digital camera (EOS 700D, Canon, Japan).

A polypropylene (PP) hollow cylindrical tube (cut to 5 mm in height) and a digital balance (TL 50 g/0.001 g, Diheng Technology Co., Ltd., China) were designed to press and hold the samples during measurements, respectively (Text S3). One precision translation stage was attached to the PP tube to control pressure levels, and the digital balance was used to read the corresponding pressure values, with the sample secured between them. The size of the PP tube was acquired by a Vernier caliper with an outer diameter of 4.634 ± 0.071 mm and an inner diameter of 3.876 ± 0.117 mm. Pressure values were calculated by dividing the force by the cross-sectional area of the PP tube.

The spectra were acquired by a fiber-optic spectrometer (USB2000+, Ocean Optics, USA) through an upright microscope (Eclipse Ci-S, Nikon, Japan) set in reflection mode. For more scientific illustration, the unity-based normalization (a typical normalization) was used to bring all values into the range of [0,1]. So the response ability is characterized as “normalized intensity”. All spectra data were firstly performed an optimum smoothing of every three adjacent numbers. The maximum intensity of reflection spectra ($I_{max}$) was selected in the wavelength range of 450–800 nm. Then, all spectra data in the series were performed the unity-based normalization to bring all values into the range of [0,1]. All average values were obtained from more
than 10 measurements. The pressure responses in Figure 3 were measured more than
300 times.

The mechanical properties of the keratin-base gel/PDMS/silicone rubber were
measured by a microtester (5948, Instron, UK). For each measurement, 8 cycles were
set with a strain from 10% to 80% and a tensile speed of 0.05 mm s\(^{-1}\). The keratin-
based gel and Ecoflex® 00-10 Platinum Cure silicone rubber were cut into circular
cylinders 5 mm in diameter and 3 mm in height, while the Sylgard® 184 silicone
elastomer (PDMS) was cut into circular cylinders 4 mm in diameter and 3 mm in
height.

7. Simulation of colloidal arrangement

The simulation of reflection spectra was directly calculated from the incident angle
with respect to the [1 1 1] direction using the finite-difference time-domain (FDTD)
method and a commercial software named FDTD Solutions (Lumerical Inc., Canada).
The system was set as finite in the z- direction with a total of 12 layers of balls (each
with a diameter of 0.28 \(\mu\)m) stacked in the ABCABC format; this system was a
periodic superprimary cell with 30*28 balls per layer in the xy- plane. When the
randomness was equal to 0, the system was close-packed. The refractive indexes of
the balls and air voids were 1.59 and 1.00, respectively. The colloidal arrangement
with different randomness was simulated by two operations in the xy- plane: the
original lattice was added with a disorderly perturbation at a random angle and with a
random amplitude, and the lattice was correspondingly stretched according to the
randomness of the set, avoiding overlapping of the balls as much as possible. The
randomness is one of vital structural parameters, and the definition is given in Text
S2. The perturbation and periodic stretching were adjusted with the radius as reference.
Text S1

Reflection peak positions:

Photonic crystals (PC) are of a periodic optical nano/micro structure. The 3DPC material in this manuscript is composed of close-packed polystyrene (PS) colloids, containing PS (with a refractive index of 1.59) and air (with a refractive index of 1.00). Some photons (behaving as waves) with special wavelengths ($\approx \lambda_0$) cannot propagate through the structure, which contributes to remarkable reflection. The reflection spectra recorded by spectrometer are peaked at $\lambda_0$. The value of $\lambda_0$ can be tuned by many parameters, such as refractive index of materials and structural periodicity.

For opal photonic crystals, structural periodicity can be tuned by adjusting the diameter of colloids (with different lattice constant), which means that the utilization of colloids in different diameters contributes to various reflection peak positions. In this work, PS colloids with a diameter of 280 nm were applied to fabricate 3DPC structure (Experimental), and the measured reflection spectra were peaked at 665 nm. According to our experimental results, reflection spectra of closed-packed PS colloids with the diameter of 250 nm and 300 nm were peaked at 590 nm and 690 nm, respectively.
Text S2

Definition of randomness:

\[ a' = \left(1 + \text{randomness} \cdot \text{radius} / a \right) \cdot a \]

\[ x' = x + \text{randomness} \cdot \text{radius} \cdot \cos \theta \]

\[ y' = y + \text{randomness} \cdot \text{radius} \cdot \sin \theta \]

where \( a \) and \( a' \) is the original and changed lattice constant; \( x \) and \( y \) are the original horizontal value and the original vertical value of the particle in a xy-coordinate plane; \( x' \) and \( y' \) are the changed horizontal value and the changed vertical value of the particle in a xy-coordinate plane; radius is the distance between the particle and “0” in xy-coordinate plane.

Note that the randomness is one of vital structural parameters, i.e., not the only cause of the reflection shifting. The randomness is used to evaluate the deformation behaviors of the flexible PC in simulation, but it doesn’t mean the randomness is the only reason for the reflection shifting. In our work, the change of lattice constant/spacing is also an important cause of reflection shifting.
Text S3

Measurement strategy and dimensions of gel:

(1) Measurement strategy

In this work, reflection spectra were recorded through a designed measurement setup (Figure S6 and Experimental). Briefly, a hollow cylindrical tube was designed to apply pressure. The hollow shape was designed for reflection measurements. The area of contact between the hollow cylindrical tube and the sample was calculated with the cross-sectional area of the hollow cylindrical tube. The pressure strategy in this work is different from the popular pressure strategies used in the field of sensing research in electric pressure sensors.

(2) Dimensions of gel

The keratin-based gel materials were acquired through drop-casting method (Experimental). Three dimension parameters, named as diameter, thickness and contact angle (between gels and substrates), are used to characterize the shape of gel materials (Figure S7). Note that the volume of drop-cast solution and substrate types can tune the dimension parameters.

(3) The gel dimensions can influence the photonic outputs of 3DPC-coated samples.

The gel dimensions are tunable, but the shape of the hollow cylindrical tube remains constant in this work. Note that the contact surface of the force is not the entire surface of the gel, but the cross-section of the hollow cylindrical tube. Considering the coloration stability of 3DPC materials, the focus region in reflection measurements is the section of the gel surface coated with 3DPC, i.e., not the contact surface of the force. The focus region of the sample undergoes deformation when the gel is pressed.
with the hollow cylindrical tube. The focus region of samples with different gel
dimensions (diameter, thickness, and contact angle) undergoes various deformations
as the force is applied. Therefore, the dimensions of the sensitive element (the gel
materials) can influence the photonic outputs of the 3DPC-coated samples.
Figure S1. Characterizations of the keratin-based gel. (a) Reaction scheme for preparing the keratin-based gel via the Michael addition reaction. Stable thioether linkages, which arise from thiols, can quickly and efficiently react with $\alpha$, $\beta$-unsaturated carbonyls with a Michael-type conjugate addition. (b) Photographs and (c) schematic of the morphological changes of the keratin-based gel after approximately 0.5 hours of polymerization. (d) Top- and (e) tilt-view photographs of keratin-based gels fabricated on PTFE substrates. The scale bars are 1 cm. (f-g) SEM images of freeze-dried keratin-based gel samples. The scale bars are 100 $\mu$m.
Figure S2. Mechanical property of (a) Ecoflex® 00-10 platinum cure silicone rubber and (b) Sylgard® 184 silicone elastomer (polydimethylsiloxane, PDMS).
Figure S3. Characterizations of PS colloidal crystals. (a) SEM image and (b) microphotograph of PS colloidal crystals. The scale bars are (a) 500 nm and (b) 500 µm.
**Figure S4.** Pressure response of a gel-PC sample. The reflection intensity change when the keratin-based gel sample is pressed or released regularly. The detailed spectra changes refer to Figure 1e and f.
Figure S5. Pressure sensing of a dye-coated gel sample. (a) Reflection spectra of keratin-based gel samples coated with photonic crystals and the Allura Red dye, respectively. (b) Pressure-response comparison of keratin-based gel samples (with a diameter of 1 cm) coated with photonic crystals and the Allura Red dye, respectively.
Figure S6. Schematic of measurement setup.
Figure S7. Dimensions of gel. (a) Top- and (b) tilt-view schematics of gel samples fabricated on a substrate. Three dimension parameters, named as diameter, thickness, and contact angle (between gel and substrates), are labeled with $d$, $h$ and $\theta$, respectively.
References
