

Supplementary Information for

Bioinspired Dynamic Camouflage from Colloidal Nanocrystals Embedded Electrochromics

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1. Experimental Details

- 1.1 Materials and reagent.** Ethanol (99.5%), chloroform and niobium ethoxide (99.95%), hydrogen chloride (HCl, 33-38%) were purchased from Fisher Scientific. The propylene carbonate (PC), lithium bis(trifluoromethane) sulfonimide (LiTFSI), poly(ethylene glycol) diacrylate ($M_n = 575$) (PEGDA), poly(ethylene glycol) methacrylate ($M_n = 360$) (PEGMA), platinum wire (99%, 0.5 mm), tetraethylorthosilicate (TEOS, 98%), aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%), ethylene glycol (EG, 99%), and 2,2-hydroxy-2-methyl propiophenone (HMP, photoinitiator, 97%) were purchased from Sigma-Aldrich. All chemicals were used as received unless otherwise specified.
- 1.2 Preparation of solid electrochromic device.** Electrochromic polymers (ECP-black, magenta, dark green, blue) were synthesized according to the previously reported methods. They were firstly dissolved in the chloroform with concentration of 40 mg/mL and stirred overnight to form homogeneous ECP/chloroform solutions for later use. ITO/glasses ($8\text{--}12 \Omega/\text{sq}$) as substrates were cleaned by sonicating in chloroform and ethanol for 10 minutes sequentially and put in an oven at 90°C for a few minutes to dry out. Then the ECP/chloroform solutions were coated on ITO glasses using spin-coating method at spin speed of 1500 rpm and dried at the 90°C oven to form ECP thin film. On the other hand, Nb_2O_5 ion storage layer was prepared by sol-gel reaction of niobium ethoxide precursor on clean ITO/glass at room temperature and a following annealing process at 150°C for 10 minutes. The niobium ethoxide precursor was prepared based on reported method.¹ The thin films were then ultraviolet ozone treated for 20 minutes to remove organic residues for use. Gel electrolyte was prepared by mixing PEGDA with 0.2 M LiTFSI in PC with the volume ratio of 1:1 and stirred overnight in a nitrogen-filled glovebox. Before use, 10 vol% HMP was added in the gel electrolyte. In the device assembly, 0.2 mL of the gel electrolyte was dropped on ECP-coated ITO/glass and the Nb_2O_5 -coated ITO/glass was placed on top to form sandwich structure. After the electrolyte spread out evenly between these two ITO substrates by capillary force, the electrolyte was crosslinked by the application of UV light for 10 minutes. Finally, the device was transferred out of glovebox and taped with copper strip on both side of ITO/glass for later test. Flexible device could be fabricated following the same protocol on ITO/PET substrates.
- 1.3 Preparation of gel colloidal crystal.** The monodispersed SiO_2 particles were first synthesized using Stöber method. They were (0.04 cm^3) well dispersed in the mixture of EG (45 μL), PEGMA (15 μL , with 10 vol% HMP) and ethanol (1.0 mL) at room temperature by sonication and put in an oven at 90°C for 2 hours to form colloidal crystal suspension with volume of 100 μL . 30 μL of it was sandwiched between two parallel ITO glass plates with an interval of 1 mm and placed without disturbance for 10 minutes, during which some of the SiO_2 nanoparticles participated out to form crystalline domains while rest of the particles were still evenly dissolved in the solvent as the amorphous domains. This phase separation structure was fixed by UV-crosslinking. A desired colloidal crystal pattern could be easily prepared by using hollow photomask during the UV-crosslinking. The colloidal crystal liquid under the hollow part of mask would be crosslinked whereas the rest un-crosslinked liquid was washed away using EG.

1.4 Preparation of Colloidal Crystals-Embedded Electrochromics. First, electrochromic polymer (ECP), Nb₂O₅ thin films were coated on ITO/glass and gel colloidal crystal was prepared following the protocol described above. They were all transferred to N₂ filled glovebox for assembly. In glovebox, the colloidal crystal gel thin film was carefully transferred onto the ECP-coated ITO/glass, and 300 μ L of electrolyte was dropped on top of it. Then the Nb₂O₅-coated ITO/glass was placed on top forming a sandwiched structure device. After the electrolyte had spread out and fully covered the colloidal crystal gel, the electrolyte was crosslinked under UV light. The obtained colloidal crystal embedded electrolyte has a thickness of around 1.1 mm. Devices with other shapes were fabricated following the same protocol except the ITO/PET substrate need to be cut into relevant shapes or patterned by selective HCl etching beforehand.

1.5 Characterization. The SEM images were obtained by a FEI Nova NanoSEM. Most of the reflection spectra were recorded by ocean optics Flame spectrometer coupled to a reflection probe, where both the incident and reflective angles were fixed at 0°. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in the dark-field mode. Angle-dependent spectra were collected using an optical spectrophotometer (PerkinElmer Lambda 1050 UV/Vis Spectrophotometer) with integrated sphere detector and total absolute measurement system (TAMS) with variable incident angles. In the measurement, incident light and the detector are synchronously tuned. All the electrochemical measurements were performed using a Biologic SP-150 potentiostat. Ellipsometry experiments were conducted on a spectroscopic ellipsometer (J.A. Woollam RC2) with variable angles (55°, 65°, and 75°) and spectrum range from 210 nm to 2500 nm.

2. Supplementary Figures

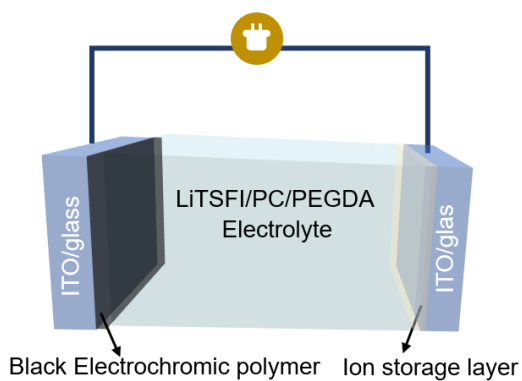


Figure. S1. A schematic of a solid electrochromic device, where ECP-black and Nb_2O_5 serve as working and counter electrodes (ion storage layer), respectively. LiTFSI-based gel electrolyte is sandwiched between the two electrodes.

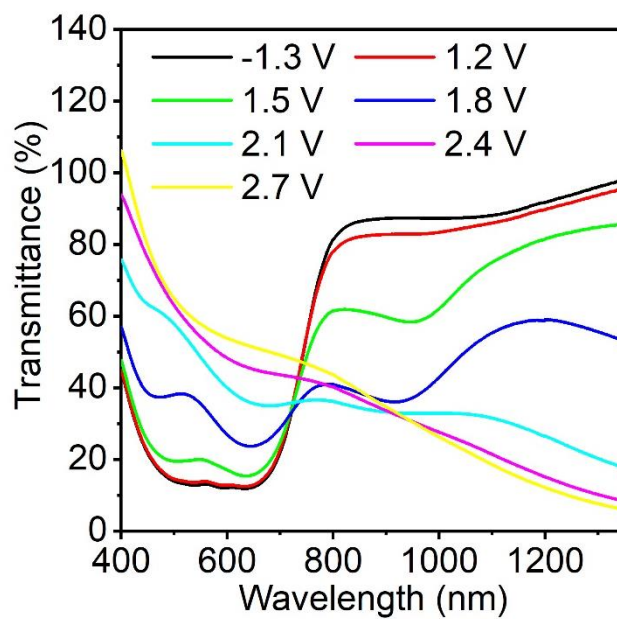


Figure. S2. Spectroelectrochemistry of the ECP-black/ Nb_2O_5 two electrode cell.

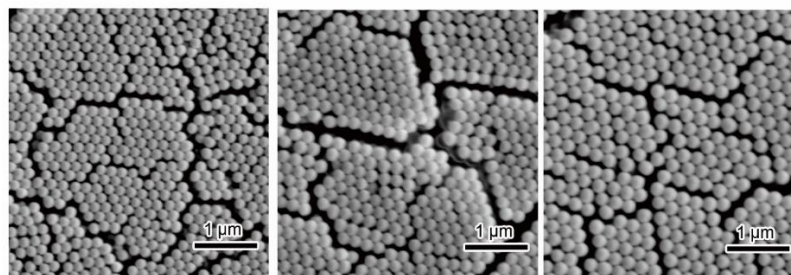


Figure. S3. Scanning electron microscopy images of monodisperse silica nanoparticles with different sizes. From left to right, the sizes are: 170 nm, 200 nm, 220 nm.

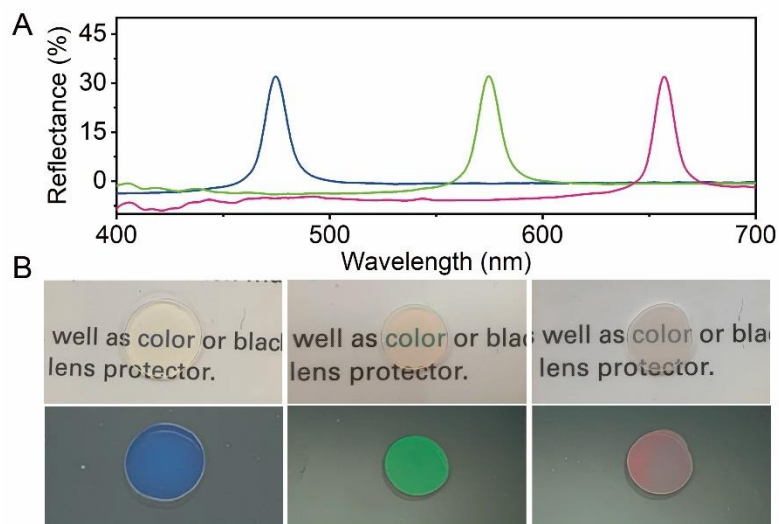


Figure. S4. (A) reflectance spectra of colloidal nanocrystal thin films composed of silica nanoparticles with diameter of 170 nm, 200 nm and 220 nm from left to right. (B) The digital pictures of the three nanocrystal thin films in front of white (upper) and black (lower) background.

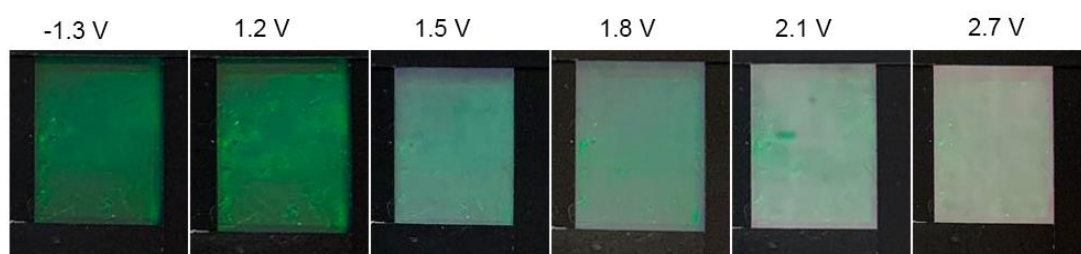


Figure. S5. Pictures of the electrochromic device under different applied voltages.

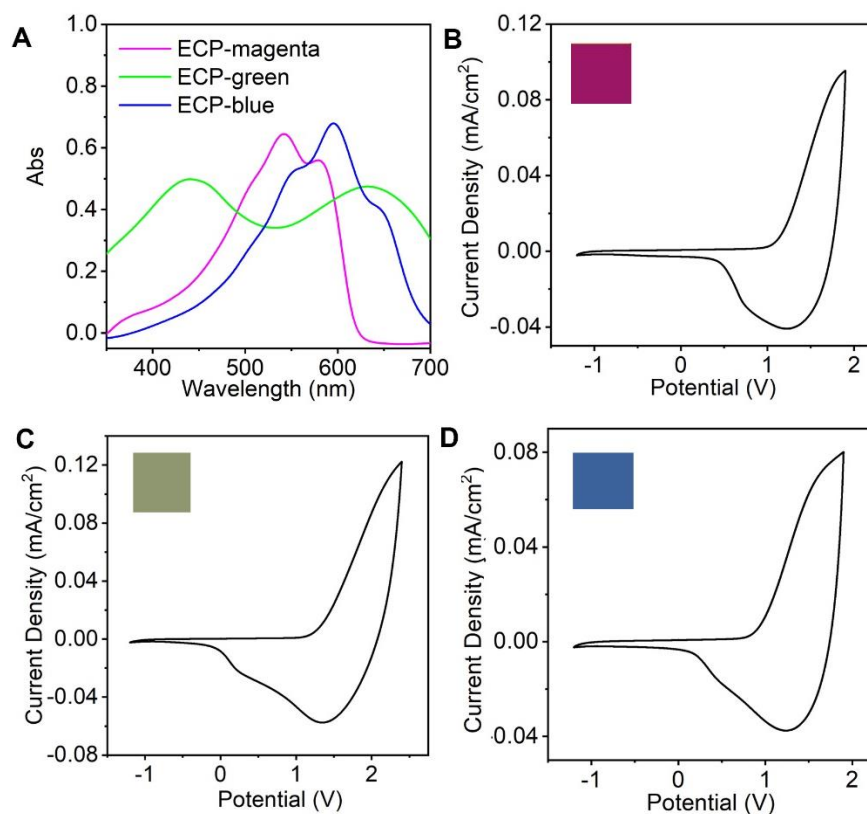


Figure. S6. (A) Absorbance spectra of ECP-magenta, ECP-green, and ECP-blue. Cyclic voltammograms of (B) ECP-magenta/Nb₂O₅, (C) ECP-green/Nb₂O₅ and (D) ECP-blue/Nb₂O₅ two-electrode solid electrochromic device. Insets show the colors of the relevant devices.

3. Supplementary Table

Table S1. XYZ values calculated for three devices in Figure 4

Spectrum	X	Y	Z
T % (ECP-magenta + CC-green)	16.57	8.70	13.38
R % ((ECP-magenta + CC-green)	3.17	4.79	0.76
Addition 1	19.76	13.49	14.14
T % (ECP-dark green + CC-green)	24.96	28.97	19.60
R % (ECP-dark green + CC-green)	1.86	2.53	0.39
Addition 2	26.82	31.4	19.99
T % (ECP-Blue + CC-green)	12.05	11.88	32.67
R % (ECP-Blue + CC-green)	4.19	5.05	0.75
Addition 3	16.24	16.93	33.42

^aT % and R % represent transmittance and reflectance spectrum respectively. For explanations of other abbreviations, see main text.

4. Supplementary Notes

Human eyes have three cone cells that can sense light with different ranges of wavelength, which underlies color perception. Three parameters that quantify the level of the stimulus of the three cone cells can be used to define human color sensation. In 1931, International Commission on Illumination (CIE) developed XYZ color space, in which XYZ tristimulus values are used to specify all the colors visible to human, and it serves as the standard reference to other color spaces.

For a specific object, its color appearance is determined by how it interacts with light at different wavelengths. Thus, given the reflectance or transmittance spectrum of this object, its color can be conveniently described by XYZ tristimulus values, which can be calculated from the spectrum.

4.1 Converting a Spectrum to a Color

Converting a spectrum to XYZ tristimulus values can be realized using the following equations:

$$X = \frac{K}{N} \int_{\lambda} S(\lambda) I(\lambda) \bar{x}(\lambda) d\lambda$$

$$Y = \frac{K}{N} \int_{\lambda} S(\lambda) I(\lambda) \bar{y}(\lambda) d\lambda$$

$$Z = \frac{K}{N} \int_{\lambda} S(\lambda) I(\lambda) \bar{z}(\lambda) d\lambda$$

Where

$$N = \int_{\lambda} I(\lambda) \bar{y}(\lambda) d\lambda$$

K is a scaling factor (1 or 100); S(λ) is the reflectance or transmittance spectrum of a measurement; I(λ) is standardized illuminant radiance spectrum; $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ are CIE color matching functions.

Here, the limits of the integral are $\lambda \in [380, 780]$. D50 spectral power distribution I(λ) and CIE 1931 2-deg color matching functions are adopted for calculation, which are shown below.² In our implementation, Agilent Color Application software was used to calculate the tristimulus values.

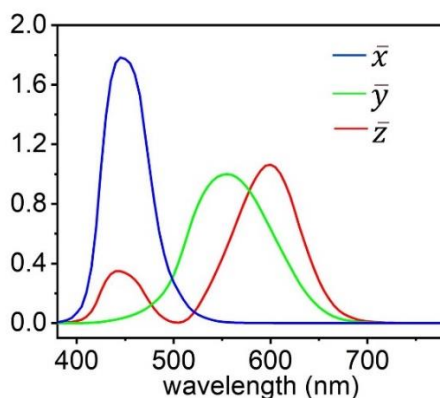


Figure. S7. CIE 1931 2-deg color matching functions

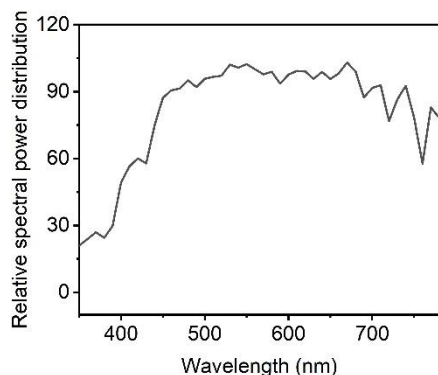


Figure. S8. D50 spectral power distribution

4.2 Color Mixing

Color mixing is conducted based on Grassmann's law.³ The XYZ tristimulus values calculated from transmittance and reflectance spectra respectively serve as the strengths of primaries to match the light beams coming from the back and front of the device. The perceived color is the combination of the two beams, which can be approximately quantified by summing the individual components:

$$X = X_1 + X_2$$

$$Y = Y_1 + Y_2$$

$$Z = Z_1 + Z_2$$

Where X_1 , Y_1 , Z_1 are computed from reflective spectrum, X_2 , Y_2 , Z_2 are computed from transmittance spectrum. The relevant numerical values are shown in table S1.

4.3 Finite element analysis (FEA) simulation

FEA was implemented using COMSOL Multiphysics TM (COMSOL Multiphysics 5.4 Wave Optics Module, Sweden). The system is approximated as a two-dimensional geometry, where the silica nanoparticles (average diameter of 200 nm) are dispersed in the PEGDA matrix and an electrochromic polymer layer is on the bottom. Some silica nanoparticles are periodically packed to simulate the crystalline region, while others are sparsely distributed to represent the amorphous region. In the simulation, the refractive index (n) and extinction coefficient (k) of electrochromic black polymer were obtained by the ellipsometry experiment and that of PEGDA and silica particles were retrieved from materials library. The depolarized light at different wavelengths was applied normally to the system from top to bottom, three representative results with incidence wavelengths of 450, 535 and 650 nm are shown in figure below. At an incidence wavelength of 535 nm, an obvious decrease of the electromagnetic field intensity was observed within the crystalline region compared with the uniform distribution of the electromagnetic field intensity in the surrounding amorphous region. The pronounced decrease of the electromagnetic field intensity in the orderly packed nanoparticles could be due to the photonic bandgap of the colloidal crystal nearby this wavelength, which forms due to periodic change in dielectric properties at nanoscale; while the electrochromic polymer exhibits homogeneous electromagnetic field distribution out of the uniform light absorbance. In the other two wavelengths (650 nm and 450 nm), the electromagnetic field distribution is consistently high in the colloidal crystal layer as it has minimal reflection outside of the photonic bandgap, while the electromagnetic field intensity in the electrochromic polymer layer changes because the polymer has distinct absorbances at various wavelengths. This inhomogeneous electromagnetic field distribution indicates different colors will be observed at different micro-regions in the device, which are essentially enabled by the crystalline-amorphous phase separation of the colloidal nanocrystal. The simulated electromagnetic field distributions are in agreement with transmittance and reflectance spectra of colloidal crystals and electrochromic polymers. More specifically, the color of the light reflection is mainly contributed by the crystalline region of colloidal crystals, as the light reflected by amorphous region and electrochromic polymer are weak compared with that

by colloidal crystal. However, the color of the transmission light is determined by both amorphous and crystalline regions of colloidal crystals. In amorphous region, since the colloidal crystal/PEGDA is optically transparent, which is validated by UV-Vis and optical microscopic measurements, the color of the transmission light is determined by the coloring state of the electrochromic polymer. While in crystalline regions, the color of transmission light is determined by the combination of transmittance spectra of colloidal crystals and electrochromic polymers. Though the volumetric ratio of crystalline region and amorphous region is hard to be precisely measured in the composite device, the amorphous region is supposed to be predominant in the gel electrolyte, as we only see small negative peaks near 535 nm wavelength in transmittance spectra of the device in Figure. 4A. Such that it is reasonable to approximate that the color of the transmitted light is mainly contributed by the electrochromic polymer. This analysis rationalizes the similarity between T and R color blocks with images of electrochromic polymers and colloidal crystals in Figure. 4B-G.

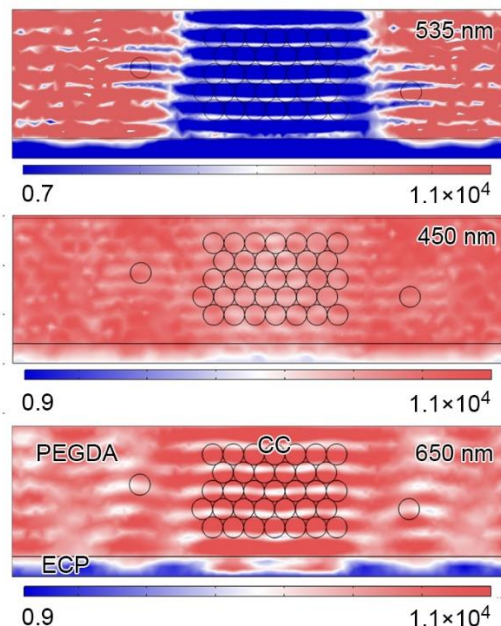


Figure. S9. Finite element analysis (FEA) simulation results illustrating the electromagnetic field distribution in the adjacent layers of electrochromic polymer and colloidal crystal /PEGDA.

5. Supplementary References

- (1) Özer, N.; Chen, D.-G.; Lampert, C. M. Preparation and Properties of Spin-Coated Nb₂O₅ Films by the Sol-Gel Process for Electrochromic Applications. *Thin Solid Films* **1996**, 277 (1–2), 162–168. [https://doi.org/10.1016/0040-6090\(95\)08011-2](https://doi.org/10.1016/0040-6090(95)08011-2).
- (2) Fairman, H. S.; Brill, M. H.; Hemmendinger, H. How the CIE 1931 Color-matching Functions Were Derived from Wright-Guild Data. *COLOR research and application* **1997**, 22 (1), 13.
- (3) Shamey, R.; Kuehni, R. G. *Pioneers of Color Science*; Springer International Publishing: Cham, 2020. <https://doi.org/10.1007/978-3-319-30811-1>.