

Supporting Information

Photocatalytic color switching of transition metal hexacyanometalate nanoparticles for high-performance light-printable rewritable paper

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EXPERIMENTAL DETAILS:

Chemicals. Diethylene glycol (DEG), ethylene glycol (EG), hydroxyethyl cellulose (HEC), citric acid, poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (P123), NH₄OH, TiCl₄, FeCl₃, FeCl₂, NiCl₂, CuCl₂, CoCl₂, Co(C₂H₃O₂)₂, K₄[Fe(CN)₆], K₃[Fe(CN)₆], and K₃[Co(CN)₆] were purchased from Sigma-Aldrich and Fisher. All chemical reagents were of analytical grade and used as received without further purification.

Synthesis of TiO₂ NPs. In a typical procedure, a mixture containing TiCl₄ (1.0 mL), P123 (0.6 g), NH₄OH (1 mL) and DEG (20 mL) was heated to ~220 °C in air in a 100 mL flask with vigorous stirring, forming a transparent solution. The resulting mixture was kept at 220 °C for 3 h, and then cooled to room temperature. A mud-like precipitate was obtained upon adding acetone and centrifuging at 11000 rpm for 5 minutes. The product was washed several times with ethanol and acetone to remove residuals, and then redispersed in water at a concentration of 20 mg ml⁻¹. The XRD pattern and TEM image were shown in Figure S1.

Synthesis of NPs of PB and PBAs. In a typical synthesis of PB NPs, two aqueous solutions were first prepared separately in 20 mL of distilled water, with one containing 0.2 mmol of K₄[Fe(CN)₆] and 5 mmol of citric acid and the other containing 0.2 mmol of FeCl₃ and 5 mmol of citric acid. These two aqueous solutions were mixed at room temperature under magnetic stirring. After reaction for 30 min,

blue precipitates were obtained upon adding acetone and centrifuging at 11000 rpm for 10 minutes. The product was washed one time with ethanol and acetone to remove residuals, and then redispersed in 10 mL of distilled water. $\text{KNi}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$ and $\text{KCo}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$ NPs were synthesized by the same procedure using NiCl_2 and CoCl_2 in place of FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ in place of $\text{K}_4[\text{Fe}(\text{CN})_6]$. For preparing $\text{KCu}^{2+}[\text{Co}^{3+}(\text{CN})_6]$ NPs, two 20-mL aqueous solutions, with one containing 0.1 mmol of $\text{K}_3[\text{Co}(\text{CN})_6]$ and 5 mmol of citric acid and the other containing 0.15 mmol of CuCl_2 and 5 mmol of citric acid, were mixed to produce $\text{KCu}^{2+}[\text{Co}^{3+}(\text{CN})_6]$ NPs. $\text{KCu}^{2+}[\text{Co}^{3+}(\text{CN})_6]$ NPs were synthesized by the same procedure using $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ in place of CuCl_2 . For the preparation of $\text{KFe}^{2+}_{0.12}\text{Cu}^{2+}_{0.88}[\text{Fe}^{3+}(\text{CN})_6]$ NPs, two 20-mL aqueous solutions, with one containing 0.1 mmol of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 5 mmol of citric acid and the other containing 0.04 mmol of FeCl_2 , 0.11 mmol CuCl_2 and 5 mmol of citric acid were mixed. The $\text{KFe}^{2+}_{0.11}\text{Co}^{2+}_{0.89}[\text{Fe}^{3+}(\text{CN})_6]$ NPs were synthesized by the same procedure by replacing $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ with CuCl_2 .

Characterization. Powder X-ray diffraction patterns were recorded on a PANalytical Empyrean with $\text{Cu K}\alpha$ radiation. The morphology of the nanostructures was investigated using a Philips Tecnai T12 transmission electron microscope at an accelerating voltage of 120 kV. The samples for TEM observation were prepared by drop casting a diluted solution on a carbon film supported on a copper grid. Microscopic images of photo-printed microscale patterns on the rewritable paper were obtained under an Omano OM339P optical microscope operating in a transmission mode. The absorption UV-Vis spectral measurements of the nanoparticle powders were measured on a UV-Vis spectrometer (Schimadzu UV2550). Cyclic voltammetry (CV) measurement was conducted in 0.1 M KCl solution in a typical three-electrode system, using PB modified FTO, Pt plate and commercial saturated calomel electrode (SCE) as working, counter and reference electrodes, respectively. All data were recorded using the VersaSTAT4 software package. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on a Perkin-Elmer Optima 7300 DV ICP-OES apparatus with an SCD detector and an echelle optical system. The atomic ratio of Fe:Cu and Fe:Co in $\text{KFe}^{2+}_{0.12}\text{Cu}^{2+}_{0.88}[\text{Fe}^{3+}(\text{CN})_6]$ and $\text{KFe}^{2+}_{0.11}\text{Co}^{2+}_{0.89}[\text{Fe}^{3+}(\text{CN})_6]$ was measured by ICP-OES. Samples were dissolved and incubated in HCl and H_2O (4:1 v/v) for 24 h before the measurement. The atomic ratio of Fe:Cu and Fe:Co were 1.137 and 1.125, respectively.

For X-ray absorption spectroscopy (XAS) measurement, powder samples were

transferred onto the Indium foil and then were pressed into thin films. Thereafter these samples were exposed to the UV lamp. All samples were prepared under atmosphere and then transferred to the beamlines for the Fe L-edge and K-edge XAS measurements. To avoid surface contamination and possible beam damage, bulk sensitive Total Fluorescence Yield (TFY) signal was collected, and no self-absorption effect was observed. All the experiments are performed at the Advanced Light Source, Lawrence Berkeley National Laboratory. Fe L-edge XAS data were measured on two soft X-ray beamlines: BL 8.0.1.3, which is an undulator beamline with energy ranges of 80-1200 eV and BL 6.3.1.2, which is a bending magnet beamline with energy range of 250-2000 eV. The Fe L-edge XAS data were recorded with a channeltron. The energy scale for all the spectra was calibrated to the first peak of a Hematite sample, which located at 709.5 eV. Moreover, Fe K-edge XAS data were collected at the hard X-ray beamline: BL 10.3.2, which is a bending magnet beamline with energy range of 2.2-17 keV. The Fe K-edge XAS data were collected with a silicon drift detector. The possible energy shift for the spectra was calibrated to the Fe foil using transmission model by assuming the edge position of 7110.75 eV. The energy resolutions of Fe L-edge and Fe K-edge XAS were set to be 0.1 eV and 1.0 eV, respectively.

Color switching reaction. In a typical fabrication of solid films for color switching system, TiO₂/H₂O dispersion (800 μl), PB/H₂O dispersion (200 μl), HEC/H₂O stock solution (33.3 mg ml⁻¹, 200 μl), and EG (800 μl) were mixed together and sonicated to form a homogenous solution. The solution was drop cast directly on a glass substrate, and then dried in an oven at 80 °C for 12 h to form a solid film. The solid film was further annealed at 120 °C for 30 minutes. Photoirradiation was performed using a typical laboratory 365-nm UV lamp (8 W, Spectroline EN-180). The UV-Vis absorption spectra of the solid film were measured by UV-Vis spectrophotometer (HR2000CG-UV-NIR, Ocean Optics).

Preparation of rewritable paper. Typically, TiO₂/H₂O dispersion (4 ml), PB/H₂O dispersion (2 ml), HEC/H₂O stock solution (5 ml), and EG (4 ml) were mixed and sonicated to form a homogenous solution. The solution was drop cast directly on a glass substrate (50 x 65 mm² and 90 x 110 mm²) and then dried in an oven at 80 °C for 12 h to form a PB/TiO₂/HEC solid thin film. Other rewritable paper using PBA NPs as the imaging media were fabricated by the same procedure. When conventional paper was used as a substrate, the mixed aqueous solution was drop cast on paper and

then dried at 40 °C for 72 h. The dried rewritable paper was pressed between two glasses to form a flat rewritable paper.

Photo-printing process. The letters and patterns were photo-printed by UV irradiating the rewritable paper through photomasks. The photomask was pre-produced by ink-jet printing on a plastic transparency using commercial printer.

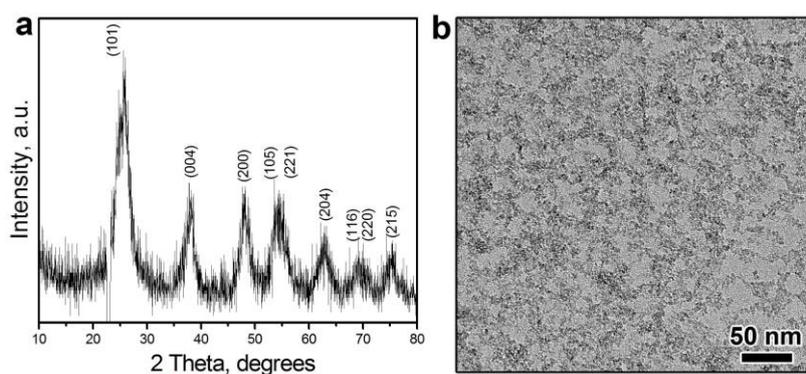


Figure S1. Typical (a) XRD pattern and (b) TEM image of the TiO₂ nanoparticles.

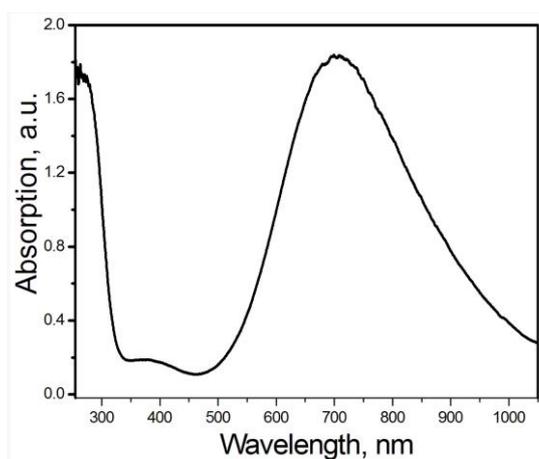


Figure S2. UV-Vis absorption spectrum of Prussian blue nanoparticles.

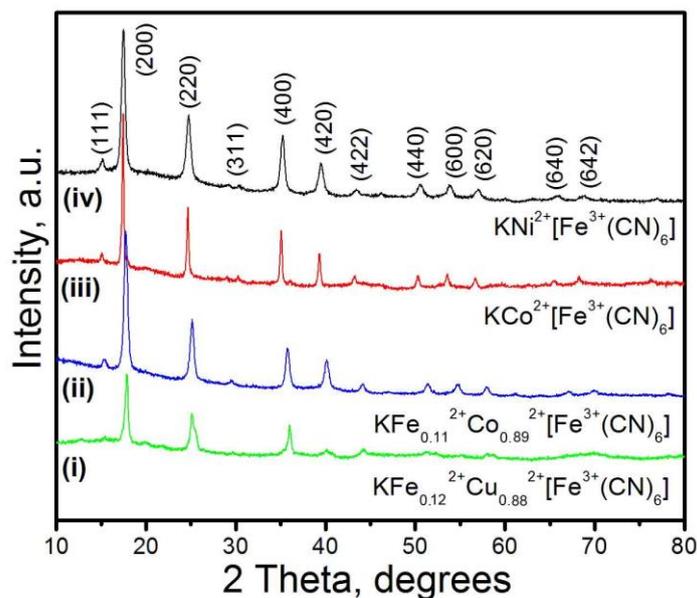


Figure S3. XRD patterns of the transition metal hexacyanometalate nanoparticles. (i) $\text{KFe}^{2+}_{0.12}\text{Cu}^{2+}_{0.88}[\text{Fe}^{3+}(\text{CN})_6]$, (ii) $\text{KFe}^{2+}_{0.11}\text{Co}^{2+}_{0.89}[\text{Fe}^{3+}(\text{CN})_6]$, (iii) $\text{KCo}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$, and (iv) $\text{KNi}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$.

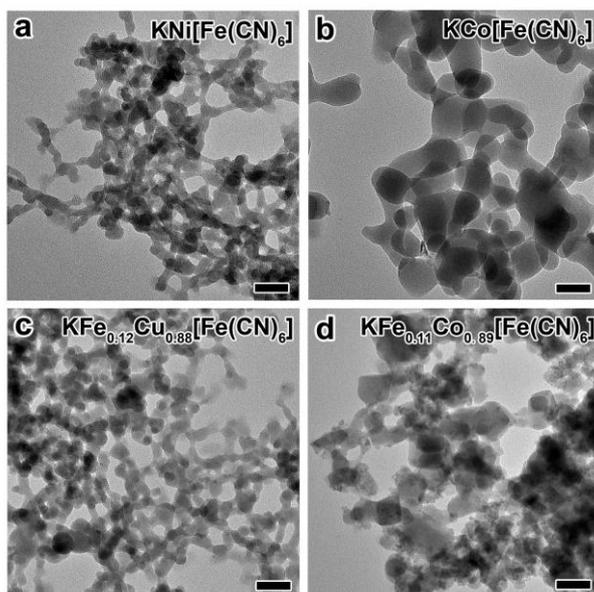


Figure S4. TEM images of the transition metal hexacyanometalate nanoparticles. Scale bar: 50 nm. (a) $\text{KNi}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$, (b) $\text{KCo}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$, (c) $\text{KFe}^{2+}_{0.12}\text{Cu}^{2+}_{0.88}[\text{Fe}^{3+}(\text{CN})_6]$, and (d) $\text{KFe}^{2+}_{0.11}\text{Co}^{2+}_{0.89}[\text{Fe}^{3+}(\text{CN})_6]$.

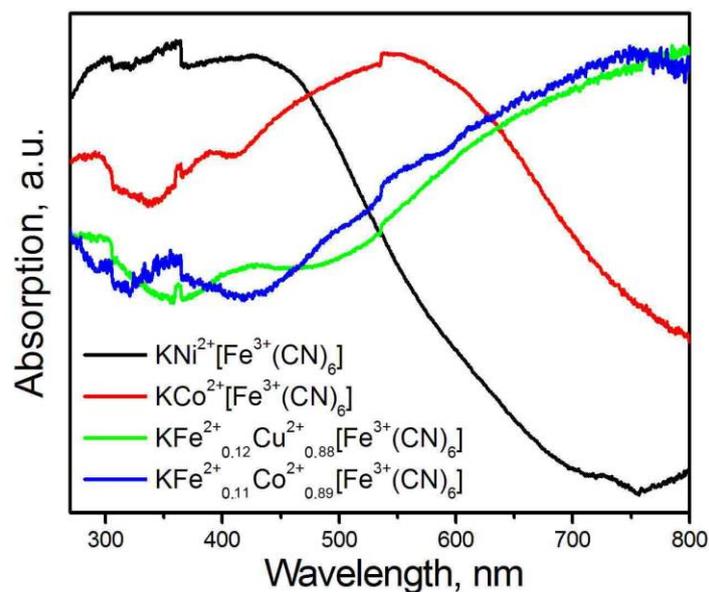


Figure S5. UV-Vis absorption spectra of Prussian blue analogues nanoparticles.

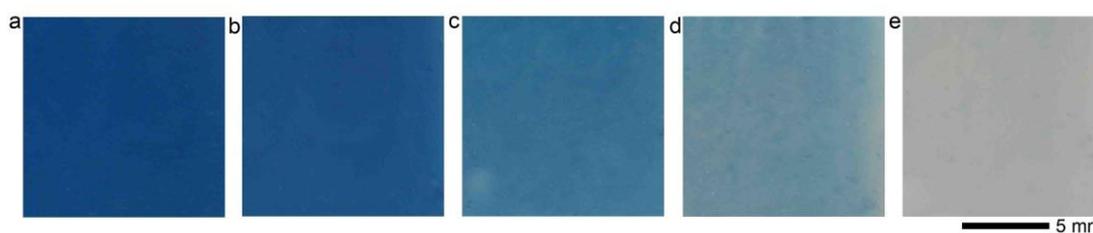


Figure S6. Digital photographs of the TiO₂/PB/HEC film with UV light irradiation for different times. (a) 0 sec, (b) 5 sec, (c) 10 sec, (d) 20 sec, (e) 30 sec.

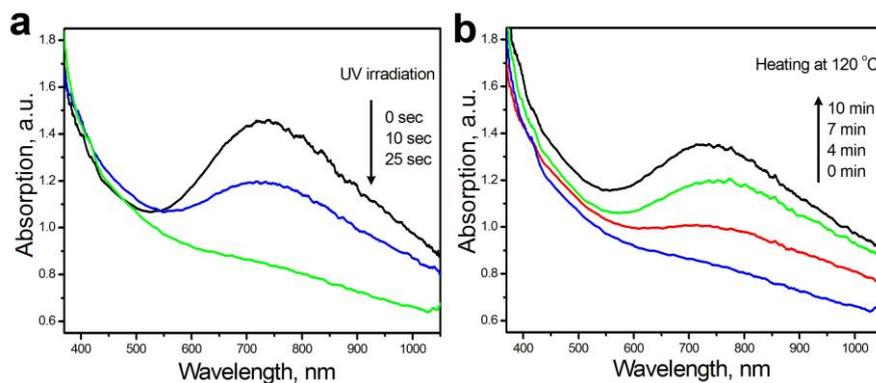


Figure S7. Photo-colour switching and stability of the PB/TiO₂ solid films. (a) UV-vis spectra showing the decolouration process under UV irradiation; and (b) UV-vis spectra showing the recolouration process on heating at 120 °C in air.

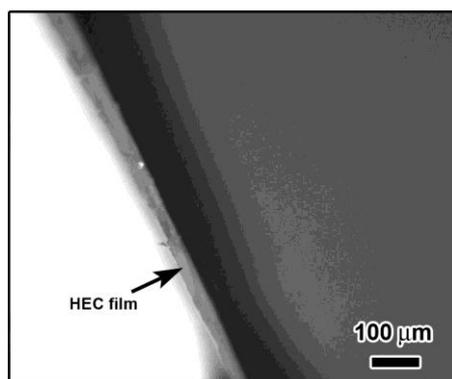


Figure S8. A typical optical microscopy image of fracture surface of the HEC film. The thickness of the film is about $\sim 35 \mu\text{m}$.

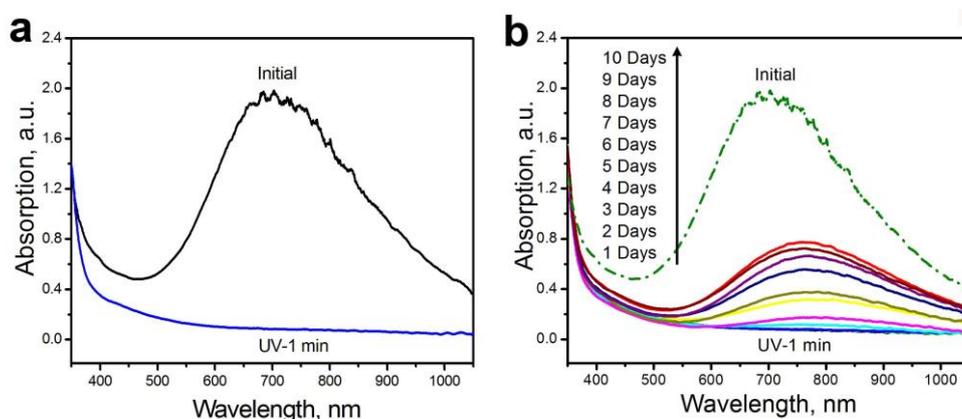


Figure S9. Reversible colour switching of PB/TiO₂/HEC/HEC solid film. (a) UV-vis spectra showing the decolouration process under UV irradiation; (b) UV-vis spectra showing the recoloration process at room temperature under ambient air.

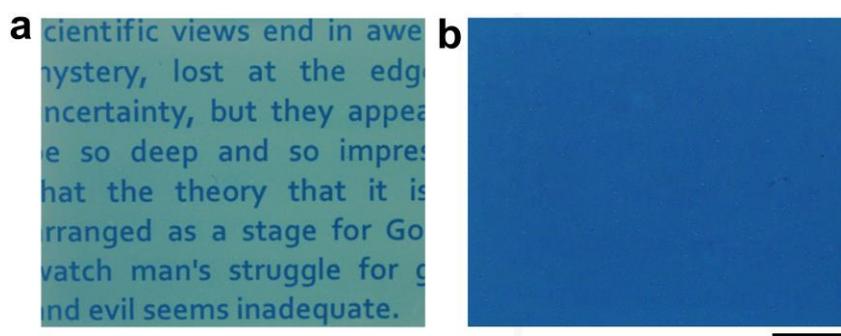


Figure S10. Digital images of photo-printed rewritable paper maintaining at ambient conditions for different times. (a) 4 days, and (b) 10 days. Scale bar: 1 cm. The rewritable paper was still legible even after 4 days although the background gradually turned to light blue, while the rewritable paper recovered its colour after 10 days. The printed text is a quote by Richard Feynman.

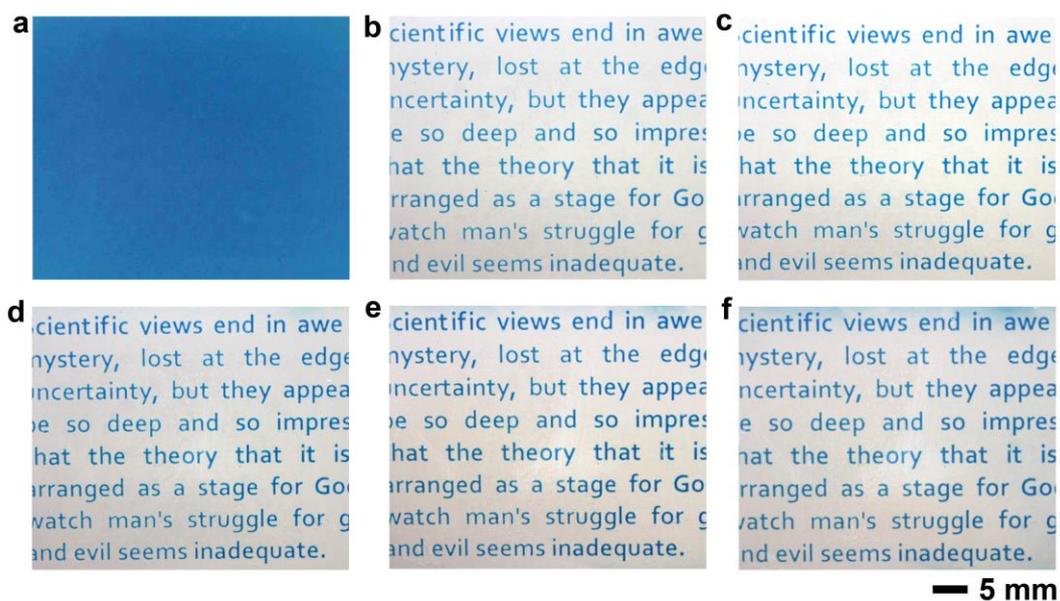


Figure S11. Legibility of letters on the rewritable paper. (a) Digital image of original rewritable paper, (b-f) digital images of rewritable paper maintain in ambient air after writing of (b) 1 day, (c) 2 day, (d) 3 days, (e) 4 days, (f) 5 days. The printed text is a quote by Richard Feynman.

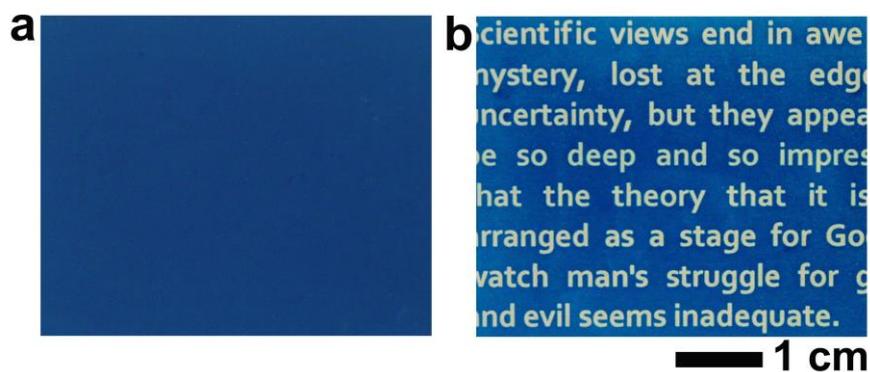


Figure S12. Reverse printing of letters and patterns on the rewritable paper. Digital images of (a) original rewritable paper and (b) printed text quoted from Richard Feynman.

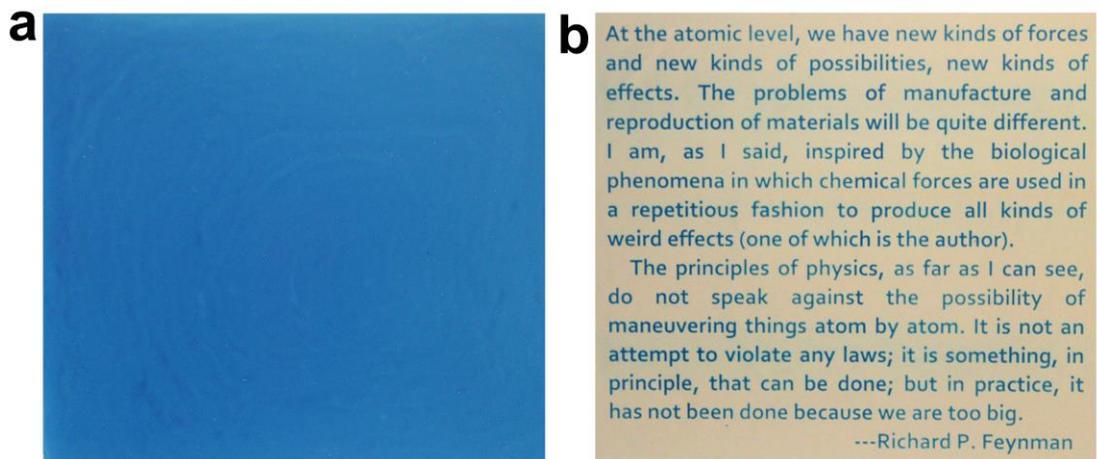


Figure S13. Printing of letters on the rewritable paper with large size. Digital images of (a) original rewritable paper and (b) photo-printed letters on the rewritable paper. Scale bar: 1 cm. The printed text is a quote by Richard Feynman.

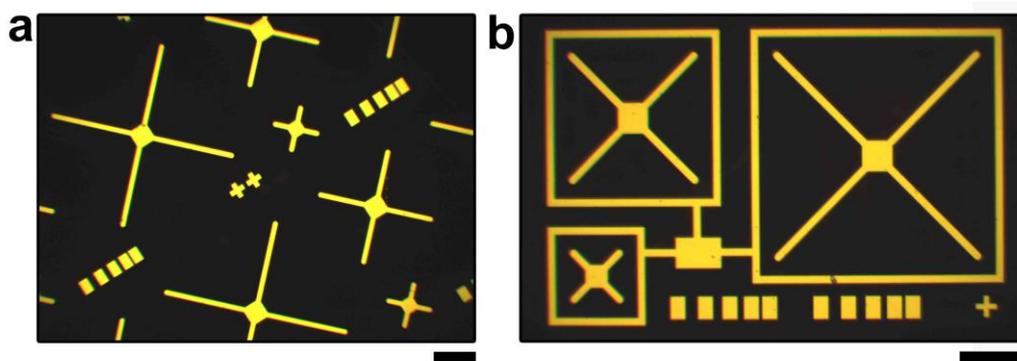


Figure S14. (a, b) Optical microscopy images of microscale patterns on the original chrome photomask. Scale bar: 200 μm .

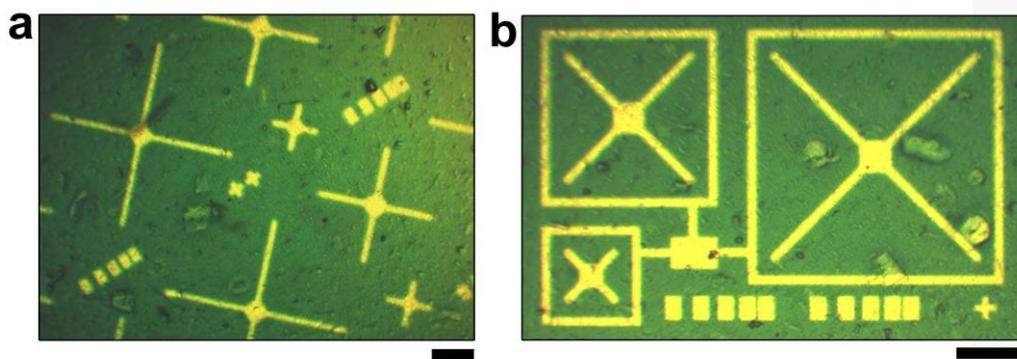


Figure S15. High resolution photo-printing on the rewritable paper. Both (a) and (b) are showing optical microscopy images of microscale patterns. The sharp edges of the microscale patterns demonstrate high resolution printing. Scale bars: 200 μm .

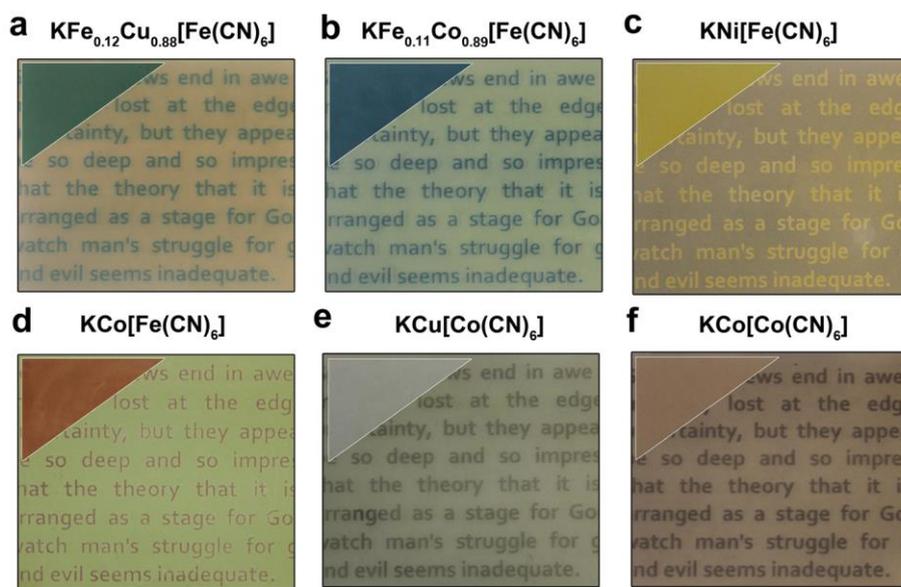


Figure S16. Rewritable paper with various working colors by using different PBA NPs as imaging media. (a) $\text{KFe}^{2+}_{0.12}\text{Cu}^{2+}_{0.88}[\text{Fe}^{3+}(\text{CN})_6]$, (b) $\text{KFe}^{2+}_{0.11}\text{Co}^{2+}_{0.89}[\text{Fe}^{3+}(\text{CN})_6]$, (c) $\text{KNi}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$, (d) $\text{KCo}^{2+}[\text{Fe}^{3+}(\text{CN})_6]$, (e) $\text{KCu}^{2+}[\text{Co}^{3+}(\text{CN})_6]$ and (f) $\text{KCo}^{2+}[\text{Co}^{3+}(\text{CN})_6]$. Insets are the original color of the corresponding rewritable film. Scale bar: 5 mm. The printed text is a quote by Richard Feynman.

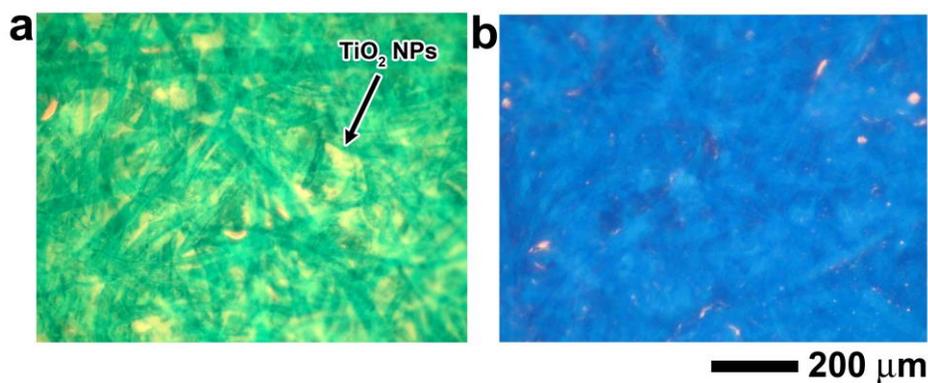


Figure S17. Optical microscopy images of rewritable paper by incorporating a mixture of imaging media, TiO_2 nanoparticles and HEC into paper substrate. (a) Methylene blue, and (b) Prussian blue nanoparticles.

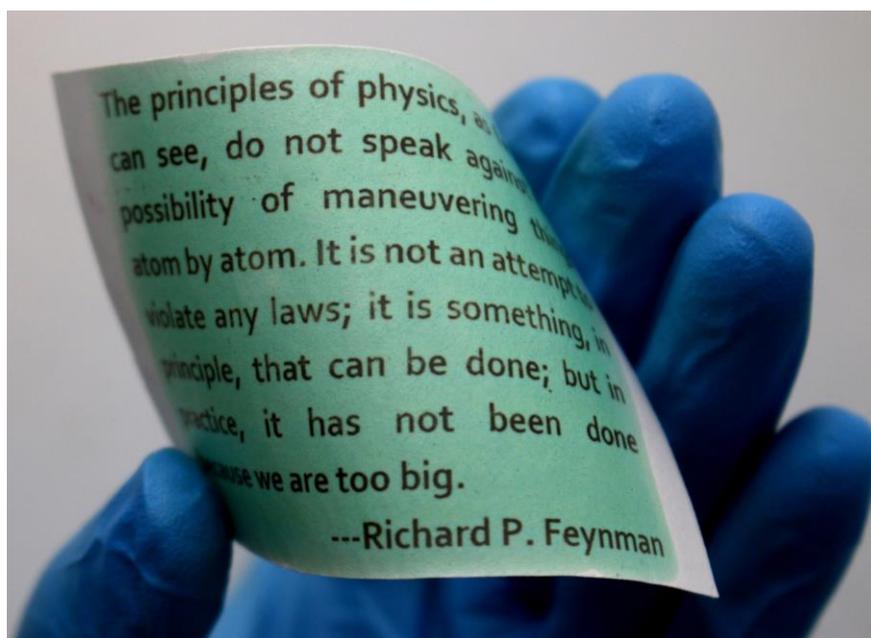


Figure S18. Digital image of a rewritable paper using $\text{KCu}^{2+}[\text{Co}^{3+}(\text{CN})_6]$ nanoparticles as imaging media and paper as substrate. The photo-printed letters show a high resolution for reading purpose. The printed text is a quote by Richard Feynman.

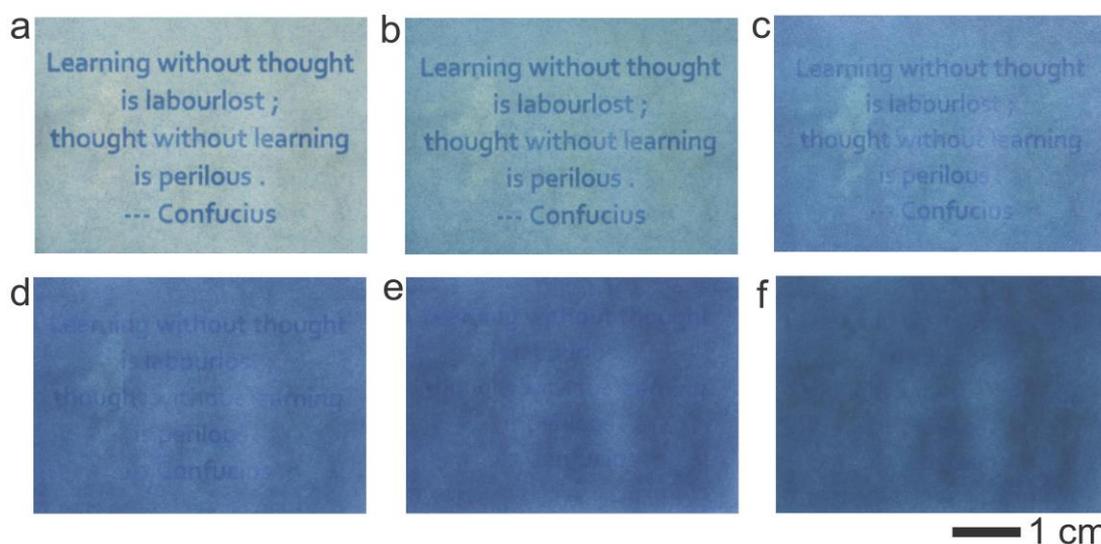


Figure S19. Digital photographs of the light-printed rewritable paper by heating at $150\text{ }^{\circ}\text{C}$ in ambient air for different times. (a) 0 min, (b) 1 min, (c) 5 min, (d) 10 min, (e) 15 min, (f) 20 min. The printed text is a quote by Confucius.