Supporting Information for

Blue/red light-triggered reversible color switching based on CeO_{2-x} nanodots for constructing rewritable smart fabrics†

Sharjeel Ahmed,[#a] Daniel K. Macharia,[#a] Bo Zhu,[a] Xiaoling Ren,[b] Nuo Yu,[a] Liyun Chen,[*a] Zhigang Chen[*a]

[a]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, International Joint Laboratory for Advanced Fiber and Low-dimension Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.

[*] E-mail address: 06family@dhu.edu.cn (L.Y. Chen); zgchen@dhu.edu.cn (Z.G. Chen)

[b]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

1 Characterization details

The samples were characterized by using high–resolution transmission electron microscopy (HR-TEM, FEI Talos F200S) equipped with energy dispersive spectroscopy (EDS), powder X–ray diffractometer (XRD, Bruker D4), X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI–5400). UV–vis–NIR diffuse spectra were measured by a UV–vis–NIR spectrophotometer (Shimadzu UV–3600) and a white standard of BaSO4 was used as a reference.

[#] These authors contributed equally to the work.

2 Figures

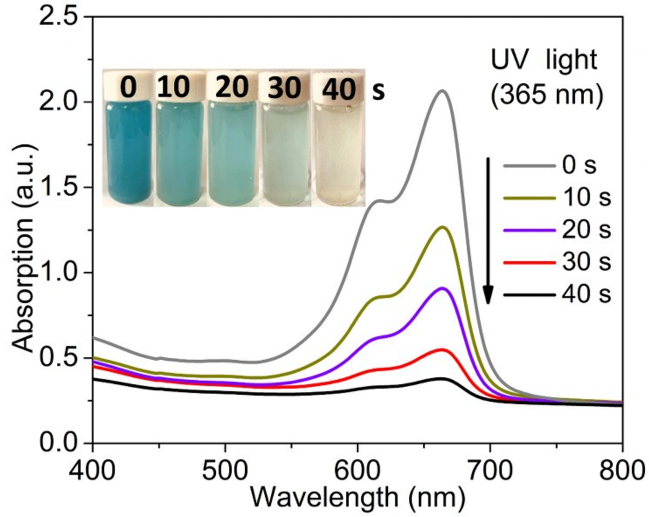

Fig. S1 UV-vis spectra of CeO_{2-x}/Dye/H_2O PCSS during the discoloration process under UV light (365 nm) irradiation for different times (0−40 s)

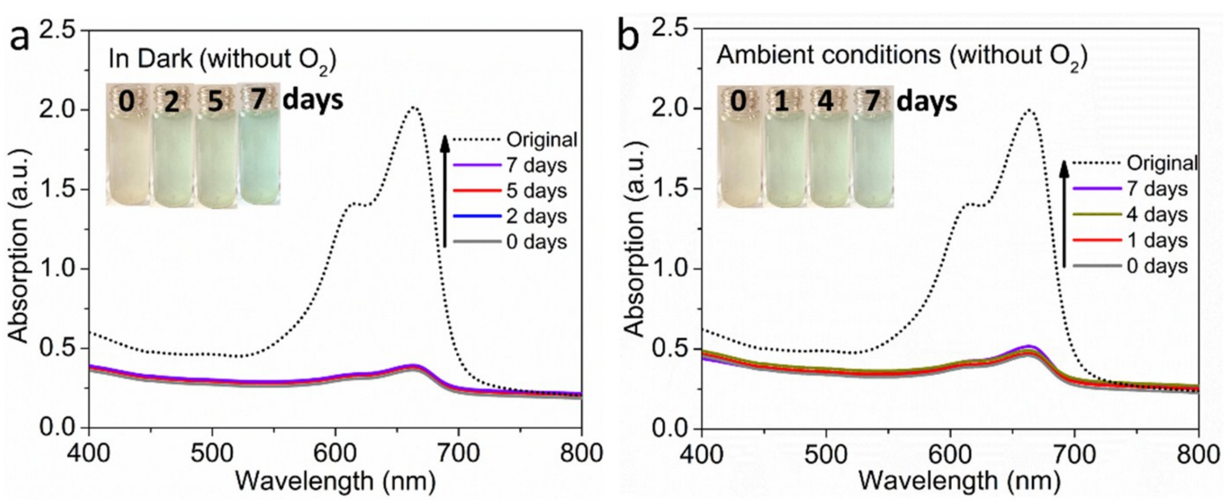

Fig. S2 UV-vis spectra of CeO_{2-x}/Dye/H_2O PCSS during recoloration (a) in darkness without O_2 and (b) in ambient conditions without O_2 for different times (0−7 days)

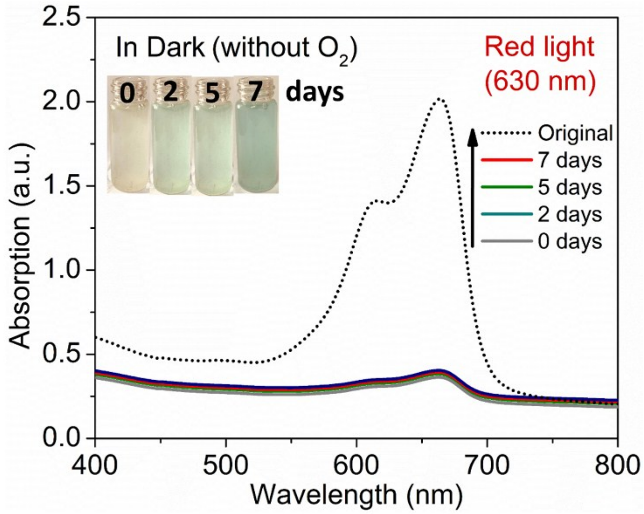

Fig. S3 UV-vis spectra of CeO_{2-x}/Dye/H_2O PCSS during the recoloration process in darkness without O_2 under the irradiation of red (630 nm) light for different times (0−7 days).

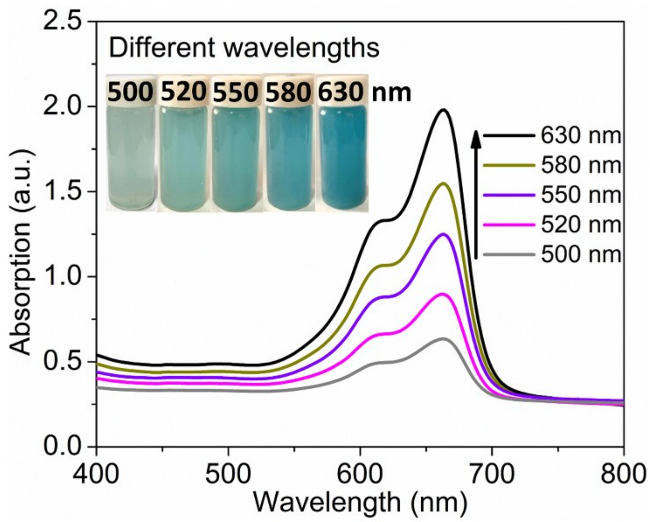

Fig. S4 UV-vis spectra of CeO_{2-x}/Dye/H_2O PCSS during the recoloration process under the irradiation of visible light with different wavelengths (using cut-off filters).

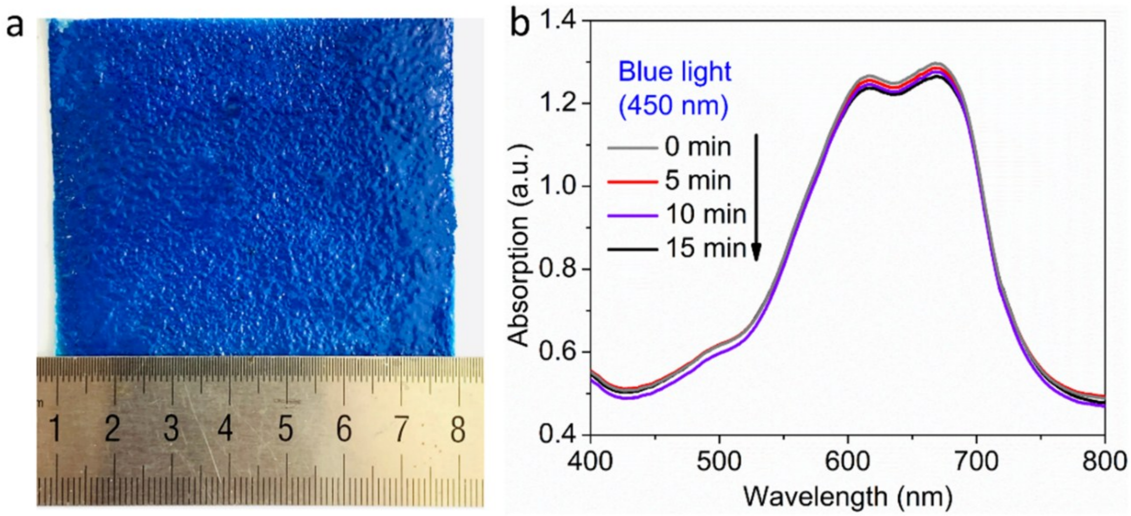

Fig. S5 (a) Photo of the CeO_2 /MB/HEC-coated fabric after 15 min of blue (450 nm) light irradiation, (b) the evolution of the UV-vis spectra of same fabric during blue (450 nm) light irradiation for 15 min. This indicates that CeO_2 nanorods without enough oxygen vacancies cannot confer the discoloration of the fabric.

Table S1 Color fastness to water laundering test for CeO_{2-x}/MB/HEC-coated fabric

No. of Samples	Color Staining					
	Acetate	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**
Sample 1	3	2–3	2	3–4	3–4	2–3
Sample 2	2–3	2	2–3	3	3	2
Sample 3	2–3	2	2	2–3	2–3	2

Note: The grading of grey scale for staining (5 = excellent, 4 = good, 3 = average, 2 = moderate, 1 = poor)

The color fastness to water laundering test was performed according to the ISO 105-C06 standard in a water bath (HZ-0037) containing a rotateable shaft under normal agitation. The sample size of CeO_{2-x}/MB/HEC-coated fabric with adjacent multifiber strip were tailored to be 100 × 40 ± 2 mm. The specimens were placed in containers (diameter 75 ± 5 mm, height of 125 ± 10 mm and capacity of 550 ± 50 mL) containing standard detergent solution (A09, 150 mL). The laundering speed was set at 40 ± 2 rotations/min and a temperature at 40 °C for 30 min. Then, the sample was placed in conditioned atmosphere 21 ± 1 °C, 65 ± 2% RH overnight for evaluation. The color fastness was determined by using grey scale for staning. For instance, the average grade for staining of cotton is 2 on the grey scale (Table S1), which indicates that the colorfastness to water laundering is moderate (neither too good nor too bad). CeO_{2-x}/MB/HEC-coated fabric exhibits the moderate resistance to laundering due to the hydrogen bonding between the abundant -OH groups in HEC and chemical groups of dyes (such as $-N(CH_3)_2$ groups in MB and LMB). Hydrogen bonding between these fuctional groups results in the fixing of the dye molecules on the surface of the fabric. We intend to use dye linkers to improve the water laundering fastness in our next project.

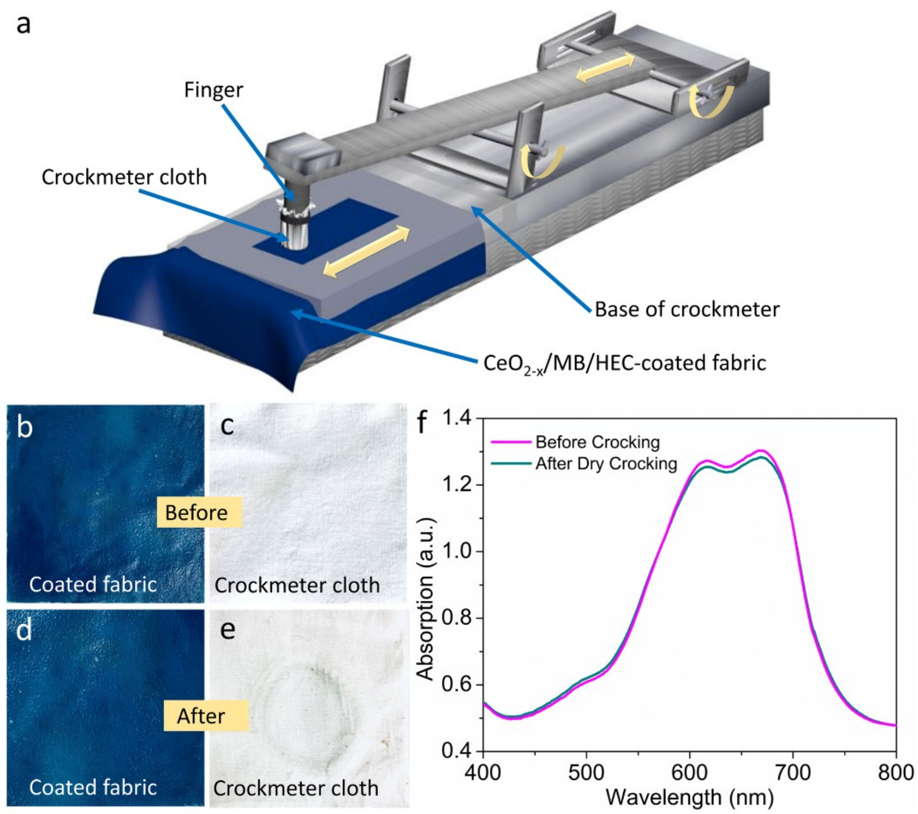

Fig. S6 Schematic illustration of crocking process of CeO_{2-x}/Dye/HEC-coated fabric (a). Photos of CeO_{2-x}/Dye/HEC-coated fabric and crockmeter cloth before (b,c) and after (d,e) dry crocking. (f) UV-Vis-NIR spectra of CeO_{2-x}/Dye/HEC-coated fabric before and after crocking.

The color fastness to crocking test was performed according to the AATCC 8 standard by rubbing the surface of CeO_{2-x}/MB/HEC-coated fabric using an electronic crockmeter (Y571B) (Fig. S6a). Prior to testing, the coated fabric specimens were tailored to have the dimensions of 50 × 130 mm and the crockmeter cloth was 50 mm^2. The specimens were pre-conditioned at 21 ± 1 °C, 65 ± 2% RH for 4 h. The test specimens were placed on the base of crockmeter and dry crockmeter cloth was mounted over the finger, lowered onto the specimen and cranked for 10 complete turns at rate of 1 turn/s. Then, the crockmeter cloth was removed for evaluation. Before dry crocking, the CeO_{2-x}/MB/HEC-coated fabric is blue (Fig. S6b) and dry crockmeter cloth is white (Fig. S6c). After dry crocking, there is no color change on both CeO_{2-x}/MB/HEC-coated fabric and the crockmeter cloth (Fig. S6d,e). The grading number of the color on the cloth was found to be 5 according to the grey scale for staining, which implies excellent color fastness to dry crocking. Furthermore, the photoabsorption properties were also monitored before and after dry crocking of CeO_{2-x}/MB/HEC-coated fabric. UV-vis-NIR spectra of the CeO_{2-x}/MB/HEC-coated fabric confirms that there is almost no decrease in photoabsorption after dry crocking (Fig. S6f), confirming excellent color fastness.

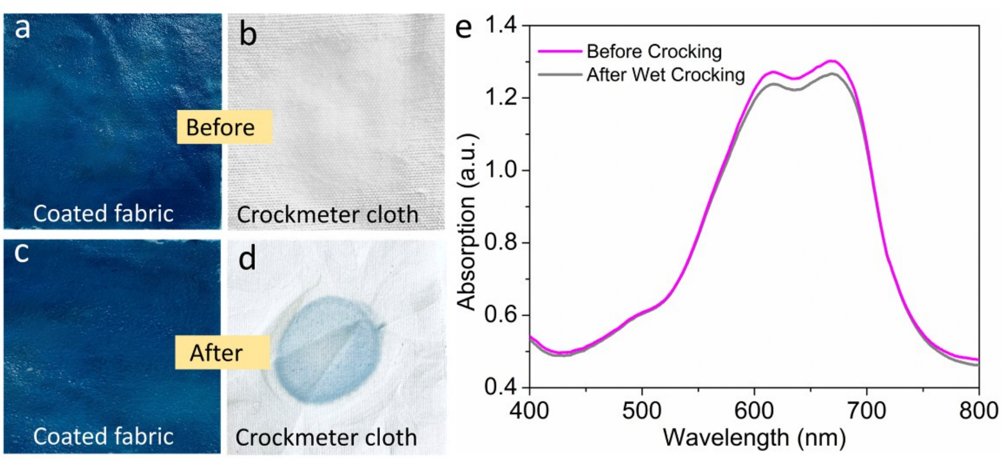

Fig. S7 Photos of CeO_{2-x}/Dye/HEC-coated fabric and crockmeter cloth before (a,b) and after (c,d) wet crocking. (e) UV-Vis-NIR spectra of CeO_{2-x}/Dye/HEC-coated fabric before and after the crocking process.

Wet crocking was performed according to the AATCC 8 standard. Firstly, the size of CeO_{2-x}/MB/HEC-coated fabric specimen and crockmeter cloth were tailored to have sizes similar to the dry crocking test above. The crockmeter cloth was wetted to 65% to its weight and 10 crocking cycles performed similar to the dry crocking process (Fig.6a). Before wet crocking, the CeO_{2-x}/MB/HEC-coated fabric is blue (Fig. S7a) and dry crockmeter cloth is white (Fig. S7b). After crocking, there is no apparent change in the color of CeO_{2-x}/MB/HEC-coated fabric (Fig. S7c), but the wet crockmeter cloth exhibits a light blue color (Fig. S7d). According to the grey scale for staining, the grading number was found to be 3 indicating average colorfastness to wet crocking. Furthermore, the photoabsorption properties were also monitored. UV-vis-NIR spectra of the CeO_{2-x}/MB/HEC-coated fabric confirms that there is slight decrease in photoabsorption after wet crocking (Fig. S7e), due to the relatively weak nature of the hydrogen bonds which can break in the presence of water. Therefore, the CeO_{2-x}/MB/HEC-coated fabric has relatively good color fastness to wet crocking.

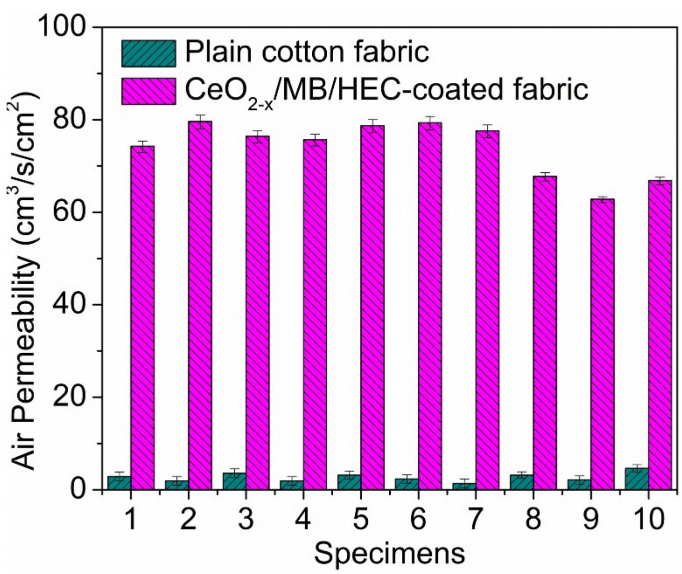

Fig. S8 Air permeability of both plain cotton fabric and CeO_{2-x}/MB/HEC-coated fabric

The air permeability was analyzed by measuring the rate of airflow passing perpendicularly through CeO_{2-x}/MB/HEC-coated fabric and plain cotton fabric (11.4 cm^2) under air pressure (125 Pa) using air permeability tester (Optima 2100DV). The test was performed according to ASTM D737-96 standard. Prior to testing, the 10 specimens for each fabric were pre-conditioned at 21 ± 1 °C, 65 ± 2% RH for 24 h. After, the specimens were clamped on the column to ensure that the fabric covers the entire opening. Then, the control valves were closed to ensure that the manometer indicated zero. Further, the pressure valves were opened to achieve the required pressure (125 Pa) and the air permeability recorded. The average air permeability of plain cotton fabric is found to be 73.9 ± 1.2 $cm^3/s/cm^2$ (Fig. S8). Interestingly, the average air permeability of CeO_{2-x}/MB/HEC-coated fabric is measured to be 2.7 ± 0.6 $cm^3/s/cm^2$, indicating that small amount of air can permeate even after coating of the fabric.

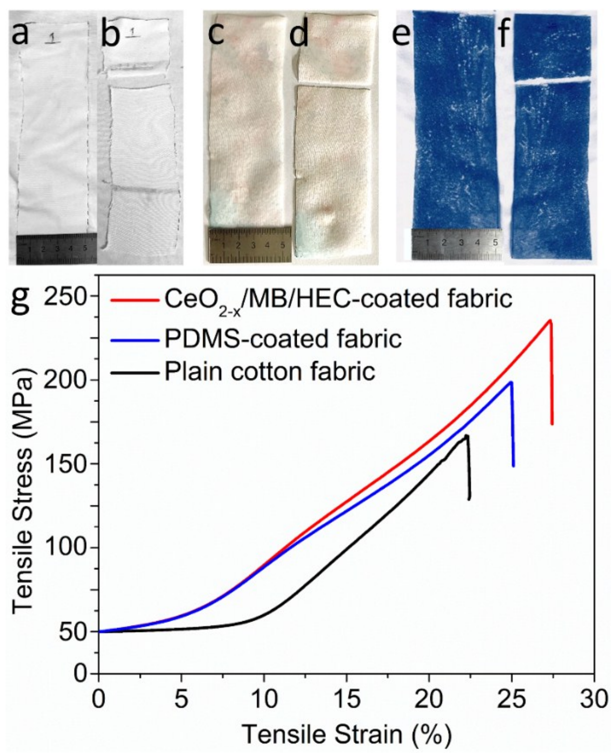

Fig. S9 Photos of plain cotton fabric (a, b), PDMS-coated cotton fabric (c,d) and CeO_{2-x}/MB/HEC-coated fabric (e,f) before and after the mechanical test. (g) Curves of tensile stress versus tensile strain from different fabrics.

The mechanical properties were investigated before and after the coating of PDMS or CeO_{2-x}/MB/HEC PCCS layer by using tensile stress/strain curves. The mechanical properties were determined according to ASTM D5035 standard. Three kinds of fabrics (plain cotton fabric (Fig. S9a), PDMS-coated cotton fabric (Fig. S9c) and PCSS-coated fabric (Fig. S9e)) were tailored to have the sizes of 5 cm × 20 cm, and each kind has three samples. Under 250 kg load with a load rate of 500±10 mm per min and gauge distance of 100 mm, all the fabrics break (Fig. S9b, d and f). The plain cotton fabric has a breaking stress of 167±15 MPa, and a breaking stress of PDMS-coated cotton fabric is 198±19 MPa (Fig. S9g). Importantly, the breaking stress of CeO_{2-x}/MB/HEC-coated fabric goes up to 238±24 MPa, which is the highest and reveals that CeO_{2-x}/MB/HEC-coating can improve the strength. Therefore, CeO_{2-x}/MB/HEC-coated fabric has high strength due to the coating.

3 Videos

Video 1. The video showing the writing process on the smart fabric by blue (450 nm) light.

Video 2. The video showing the erasing process on the smart fabric by red (630 nm) light.