Oriented assembly of metal-organic frameworks and deficient TiO₂ nanowires directed by lattice matching for efficient photoreversible color switching

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ABSTRACT The photoreversible color switching system (PCSS) is attracting increasing attention for use in alleviating energy crisis and environmental problems. We report a robust PCSS in which lattice matching enables bottom-up oriented assembly between metal-organic frameworks (MOFs) and inorganic nanocrystals (INCs), two distinct entities that differ drastically in structure and function. Specifically, cubic-phase Prussian blue (PB) of a framework backbone is spontaneously attached to rutile TiO₂ nanowires in a defined orientation triggered by the lattice matching between the (001) plane of TiO₂ and the (222) plane of PB. Ultraviolet light irradiation accelerates the photoelectron transport within the oriented TiO₂/PB system and enables fast photo switching. The derived TiO₂/PB paper can be ranked as one of the best light-printing papers in literature because of its high resolution (~5 μm) and capability to be repeatedly written for >100 times without significant loss of contrast. The ultrathin TiO₂ nanowires are rich in oxygen and Ti vacancies, which allow visible- and sunlight-light printing. Density functional theory calculations suggest that the [Fe(CN)₆]⁴⁻ ligand from the PB attaches preferentially to the (110) surface of TiO₂ to give the ordered TiO₂/PB assembly. The findings demonstrate the strong versatility of particles-mediated assembly in advanced materials design.

Keywords: photoreversible color switching, metal-organic framework, oriented assembly, lattice matching, defects

INTRODUCTION

Development of advanced rewritable paper technologies based on the photoreversible color switching system (PCSS) is actively helping to solve the energy crisis and environmental problems [1–4]. Currently, the appealing PCSS frequently employs light-responsive semiconductors as the electron donor to drive the redox reaction and the color switching reaction of redox-responsive material [5–7]. Over the past decades, Prussian blue (PB), a kind of metal-organic framework (MOF), has been considered as a prominent redox-responsive material [7], since the charge transfer between the mixed-valence transition metals of PB readily renders color switching [8]. Given that the well-known TiO₂ semiconductor can provide photogenerated electrons to enable the charge transfer and discoloration of PB [9],

TiO₂/PB should be one of the most promising candidates for constructing efficient PCSS. However, the key limitation rests in the lack of precise control over the interaction and dispersion of the semiconductor and redox materials, which often causes the sluggish electron transfer kinetics, low color switching rate and poor durability of PCSS [10].

Ultrathin nanowires have a one-dimensional (1D) geometry that promotes charge transport as well as provides large contact area that helps the dispersion of redox-responsive materials [11–13]. Hence, interfacing ultrathin TiO₂ nanowires and nanoscale PB into highly ordered structures may create efficient PCSS. The oriented attachment (OA) of nanocrystals (NCs) is an appealing means for the assembly of nano-units, as it takes advantage of lattice matching to trigger the attachment to assemble adjacent NCs at a specific crystallographic direction [14–17]. The OA of the inorganic semiconductor and MOFs should in theory help to break the constraints of particle-mediated assembly and give novel functional materials. However, researchers have encountered extraordinary challenges in designing the lattice topology of dissimilar building blocks, and the marriage of inorganic semiconductor and MOF *via* defined crystallographic orientation is scarcely reported [18–20].

Herein, we report a spontaneous bottom-up OA of TiO₂ and PB to create OA-TiO₂/PB as a good candidate for highly efficient PCSS. The spontaneous ordered alignment of TiO₂ and PB is directed by the lattice matching of the $d_{\text{TiO}_2(001)}$ spacing (0.297 nm) of TiO₂ and the $d_{\text{PB}(222)}$ spacing (0.292 nm) of PB (Scheme 1). Such ordered architecture accelerates the electron transfer from TiO₂ to PB and ensures fast color switching of PB. The derived ink-free TiO₂-PB rewritable paper can be ranked as one of the best PCSS's in literature because it is responsive to ultraviolet (UV), visible light, and sunlight, and it has high resolution (~5 μm) and high durability (no significant loss of contrast after 100 cycles of writing).

EXPERIMENTAL SECTION

Chemicals and materials

Potassium hexacyanoferrate(II) trihydrate (K₄Fe(CN)₆·3H₂O), hydrochloric acid (HCl), titanium sulfate (Ti(SO₄)₂) and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP, K30, M_w ~40,000), commercial rutile TiO₂ and hydroxyethyl cellulose

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Scheme 1 Schematic illustration of the lattice matching and the ordered assembly of TiO₂ and PB along a specific direction.

(HEC) were purchased from Sigma-Aldrich. All chemicals used in the experiments were of analytical grade and used without further purification. Deionized (DI) water was used for all experiments.

Synthesis of OA-TiO₂/PB

In a typical procedure, PVP (3.8 g) and K₄Fe(CN)₆·3H₂O (0.12 g) were successively added into aqueous HCl (0.1 mol L⁻¹, 50 mL) under magnetic stirring. The mixture was stirred for 30 min before the addition of Ti(SO₄)₂ (0.0682 g), then ultrasonicated for another 30 min, and finally heated at 80°C for 24 h. The product was collected by centrifugation, washed with DI water for three times, washed with ethanol for another three times, and then dried at 60°C in an oven to give OA-TiO₂/PB hedgehogs. The control sample of pure PB was prepared by repeating the procedure without adding Ti(SO₄)₂.

Preparation of rewritable paper

Typically, the dispersion of OA-PB/TiO₂ in H₂O (15 mg mL⁻¹, 4 mL), the stock solution of HEC (5 mL), and EG (4 mL) were mixed and sonicated to form a homogenous solution. The solution was dropcast directly on a piece of traditional paper (40 mm × 40 mm) that was then dried in an oven at 40°C for 48 h to form the OA-PB-TiO₂/HEC rewritable paper. The films of the control samples in the photo-printing test were prepared under the same conditions. In a control experiment, HEC was dropcast on top of the solid composite film to form an additional HEC layer.

Photoirradiation

Photoirradiation was performed using a 300-W Xenon lamp. The UV-Visible (UV-Vis) absorption spectra of the solid films were recorded on a UV-Vis spectrophotometer. For the photo-printing process, letters and patterns were photo-printed by irradiating the rewritable paper through a photomask made from a plastic transparency sheet prepared by ink-jet printing using a commercial printer.

Photoelectrochemical testing

The photoelectrochemical measurement was performed using a standard three-electrode quartz cell. The working electrode was fluorine-doped tin oxide (FTO) conductive glass coated with the photocatalyst, and Pt and Ag/AgCl were the counter electrode and reference electrode, respectively. The area that the sample

covered was 0.25 cm². Mott-Schottky tests were carried out in Na₂SO₄ solution (0.1 mol L⁻¹) on a ParSTAT MC electrochemical workstation (Princeton Applied Research, Co.). Electrochemical impedance spectra (EIS) were recorded in mixed aqueous solution of 5 mol L⁻¹ K₃[Fe(CN)₆]/5 mol L⁻¹ K₄[Fe(CN)₆]/0.1 mol L⁻¹ KCl on a ParSTAT MC electrochemical workstation. Transient photocurrent response was measured in Na₂SO₄ solution on a CHI660E electrochemical analyser with a Xenon lamp for irradiation.

Characterization

The crystalline phase of the samples was examined on an X-ray diffractometer (XRD, PANalytical X'pert MPD). The morphology, size, and elemental energy-dispersive spectroscopy (EDS) of the samples were investigated using a scanning electron microscope (SEM, Philips XL30) and a transmission electron microscope (TEM, FEI Tecnai G2 F20). Atomic-resolution spherical-aberration-corrected TEM (ACTEM) was tested on an FEI Tecnai F30 microscope at 300 kV. X-ray photoelectron spectra (XPS) were recorded on a PHI 5000 VersaProbe spectrometer. Fourier transform infrared (FT-IR) spectra were collected using a Nicolet 5700 spectrometer. UV-Vis diffuse reflectance spectra (DRS) of powder samples were obtained using a Varian Cary 500 UV-Vis-near infrared (NIR) spectrometer equipped with an integrating sphere and BaSO₄ was used as the reference. UV-Vis DRS of the film samples were performed on a Hitachi UV-3010 UV-Vis spectrophotometer. Brunauer-Emmett-Teller (BET) surface area was measured with an ASAP2020 M apparatus (Micromeritics Instrument Corp.). An HP LaserJet P110 printer was used to make the photomask. Electron paramagnetic resonance (ESR) spectra were collected on a Bruker A300 spectrometer (Germany). Laser confocal Raman spectroscopy was measured with a DXR2Xi apparatus (Thermo Fisher Scientific).

DFT calculation

To investigate the assembly mechanism of OA-TiO₂/PB, density functional theory (DFT) calculations were run using the Vienna *ab initio* simulation package (VASP) [21]. Spin-polarized DFT calculations were performed using Dmol³ with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional [22]. Three layers of rutile TiO₂ were chosen as the periodic slabs for both (110) and (001) surfaces. All core electrons were treated with DFT Semi-core Pseudopotentials, and the double numerical basis plus d class

extended orbital was used. A vacuum of 15 Å was built to construct both the rutile $\text{TiO}_2(110)$ and $\text{TiO}_2(001)$ surfaces. Atoms were fully relaxed in all thorough calculations. The optimization of structures was done when the force tolerance was $<0.005 \text{ Ha Å}$ and the energy difference was $<10^{-5} \text{ Ha}$. The surface energy of rutile TiO_2 facet was calculated as follows:

$$\gamma = (E_{\text{total}} - nE_{\text{bulk}}) / 2A, \quad (1)$$

where γ is the surface energy of rutile TiO_2 facet, E_{total} is the total energy of the relaxed rutile TiO_2 surface slab, E_{bulk} is the total energy of rutile TiO_2 bulk unit cell, n is the number of the bulk rutile TiO_2 units in the slab, and A is the surface area of the slab model. In addition, the adsorption energy of $\text{Fe}(\text{CN})_6^{4-}$ (E_{ads}) on either $\text{TiO}_2(001)$ or $\text{TiO}_2(110)$ was calculated as follows:

$$E_{\text{ads}} = E_{\text{Fe}(\text{CN})_6^{4-}/\text{R-TiO}_2} - (E_{\text{Fe}(\text{CN})_6^{4-}} + E_{\text{R-TiO}_2}), \quad (2)$$

where $E_{\text{Fe}(\text{CN})_6^{4-}/\text{R-TiO}_2}$ is the total energy of water adsorbed on the rutile TiO_2 surface, $E_{\text{Fe}(\text{CN})_6^{4-}}$ is the energy of $\text{Fe}(\text{CN})_6^{4-}$, and $E_{\text{R-TiO}_2}$ is the energy of the clean rutile TiO_2 surface.

RESULTS AND DISCUSSION

Bottom-up self-assembly of TiO_2 and PB

A facile one-pot synthesis of OA- TiO_2 /PB, i.e., hydrothermal growth using $\text{Ti}(\text{SO}_4)_2$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, and PVP in distilled water at 80°C , was adopted to accomplish the spontaneous oriented assembly of TiO_2 and PB. The XRD patterns (Fig. 1a) verify that the OA- TiO_2 /PB consists of rutile TiO_2 (JCPDS No. 21-1276) and cubic PB (JCPDS No. 73-0687). The FT-IR spectra (Fig. S1a in the Supplementary information) have the Ti-O stretching vibration of TiO_2 and the C-N stretching vibration

from the cyanide group of PB. The co-existence of PB and TiO_2 was confirmed by the Raman spectra and XPS spectra (Fig. S1). In TEM (Fig. 1b) and SEM (Fig. S2) images, the OA- TiO_2 /PB appears as $\sim 500 \text{ nm}$ monodisperse hedgehog-like particles, with several branches growing from the center. The elemental mapping images (Fig. 1c and Fig. S3) show homogeneous distribution of Fe, C, N, Ti, and O in OA- TiO_2 /PB, revealing the good dispersion of PB and TiO_2 . The relative mass ratio of TiO_2 (Ti as the indicator) to PB (Fe as the indicator) is approximately 2.28:1 according to the energy dispersive X-ray spectroscopy (EDX) (Fig. S4). In addition, the OA- TiO_2 /PB demonstrates high surface area ($45.83 \text{ m}^2 \text{ g}^{-1}$) from the BET measurement (Fig. S5).

In OA- TiO_2 /PB, each branch of the hedgehog particle is an array of nanowires about hundreds of nanometers in length and 2–6 nm in diameter (Fig. S6). When PB is selectively removed from the OA- TiO_2 /PB by chemical etching (Fig. S7), the residual material becomes pure OA- TiO_2 that inherits the hedgehog morphology from the assembly of aligned nanowires (Fig. 2a, e, and Fig. S8). The ACTEM image (Fig. 1d) reveals the fine structure of the ultra-small nanowires at atomic scale. The OA- TiO_2 nanowires have an ultrathin diameter ($\sim 2 \text{ nm}$) and abundant Ti vacancies within the lattices. The lattice fringes of the TiO_2 nanowires (Fig. S9) show 45° interfacial angle as well as 0.226- and 0.331-nm spacings that can be attributed to the (200) and (110) facets of rutile TiO_2 , respectively. It can be calculated from the crystal structure that the nanowires grow along the [001] direction. Of note, the elongated nanowires are aligned orderly side by side on the (110) facets in the large-scale TEM image (Fig. S10).

Oriented assembly of dissimilar materials to form a mesocrystal

The PB particles incorporated within the TiO_2 framework have a

Figure 1 (a) XRD pattern, (b) TEM image, and (c) dark-field TEM image and corresponding elemental mapping images of OA- TiO_2 /PB; (d) ACTEM image of OA- TiO_2 .

Figure 2 (a) TEM image, (b) SAED pattern, (c) HRTEM image, and (d) simulated diffraction pattern of OA-TiO₂/PB; (e) TEM image, (f) SAED pattern, (g) HRTEM image, and (h) simulated diffraction pattern of TiO₂.

lattice fringe spacing of $d = 0.301$ nm corresponding to the (222) facets of PB (Fig. 2c). Intriguingly, the TEM images show that the spatially separated PB particles basically have a uniform orientation globally (Fig. S11), with the (222) plane of PB particles perpendicular to the (110) plane of TiO₂. Clearly, these PB particles are assembled and distributed within the TiO₂ matrix orderly.

Selected area electron diffraction (SAED) patterns were analyzed to assess the crystallographic correlation of OA-TiO₂/PB. As depicted in Fig. 2a–c, each branch of OA-TiO₂/PB has a spot-like SAED pattern that is normally observed from single crystal [23]. The spot-like SAED pattern can be divided into two distinct sets of patterns of TiO₂ and PB, and the set of diffraction pattern of PB disappears after removal of PB by chemical etching (Fig. 2e–g). The spot-like SAED patterns thus verify that both TiO₂ and PB are orderly assembled, sharing the same orientation as identified from HRTEM (Fig. 2c). Furthermore, the (222) facets of PB are perpendicular to the (110) facets of TiO₂ (Fig. 2c). In other words, the (222) facets of PB are parallel to the (001) facets of TiO₂ (Scheme 1), and along this direction they show similar standard d spacing, i.e., $d_{\text{TiO}_2(001)} = 0.297$ nm and $d_{\text{PB}(222)} = 0.292$ nm.

Theoretical analyses

It is likely that lattice matching drives the oriented alignments of TiO₂ and PB. To verify this speculation, free-standing oriented TiO₂/PB superlattice (Fig. S12) was built by establishing a vacuum layer in the [110] direction of TiO₂ to connect to the [222] direction of PB. The simulated crystal diffraction patterns are consistent with the actual experimental findings (Fig. 2d). Hence, the attachment of PB and TiO₂ takes place *via* the perpendicular connection of the (222) plane of PB to the (110) plane of TiO₂. Moreover, when the TiO₂ supercell without PB was simulated, the diffraction patterns of the (222) plane of PB disappeared (Fig. 2h), which agrees with the experimental disappearance of the diffraction pattern of OA-TiO₂ after the removal of PB from OA-TiO₂/PB (Fig. 2f, g). Hence, lattice matching indeed drives the oriented growth of PB on TiO₂/PB

into ordered mesocrystals, an intriguing class of big microscale particles built from NCs with good alignment [24]. The long-range structural order may be the key to regulating the structure and functionality of materials [25].

To examine the growth mechanism of OA-TiO₂/PB, we systematically removed individual components from the hydrothermal synthesis while keeping other variables unchanged. The results show that the formation of OA-TiO₂/PB relies on [Fe(CN)₆]^{4−} instead of PVP. Specifically, when [Fe(CN)₆]^{4−} is absent but PVP exists in the starting materials, only big TiO₂ microspheres are obtained (Fig. 3a). In contrast, when PVP is absent but [Fe(CN)₆]^{4−} remains, TiO₂ assembles into a hedgehog structure (Fig. 3b), and with increasing concentration of [Fe(CN)₆]^{4−}, fewer nanospheres are formed and nanowires emerge (Fig. 3c–f). The time-dependent XRD patterns of the samples show that PB and TiO₂ grow at the same time (Fig. S13). DFT calculations show that [Fe(CN)₆]^{4−} tend to adsorb on the (110) planes of TiO₂, as the adsorption of [Fe(CN)₆]^{4−} is more energetically favourable on the (110) plane of TiO₂ (−7.175 eV) than on the (001) plane of TiO₂ (−4.195 eV) (Fig. 3g).

In this way, the preferential adsorption of [Fe(CN)₆]^{4−} on the (110) surface of TiO₂ may bridge the alignments of two TiO₂ nanowires during crystal growth. That is, the synergy between the oriented adsorption of [Fe(CN)₆]^{4−} and the growth of TiO₂ nanowires drives the confined growth of TiO₂ and the spontaneous ordered assembly of TiO₂ and PB (Fig. 3h).

Rapid electron transport in OA-TiO₂/PB for light printing

PB has a cubic framework with Fe²⁺ and Fe³⁺ cations bridged by linear cyanide anions (Fig. S14). In principle, PB can be reversibly converted to Prussian white (PW) *via* the following reaction [26]:

This reversible transformation makes PB a good candidate as light-printing material [9,27]. Meanwhile, TiO₂ is one of the most promising catalysts to afford photo-generated electrons upon irradiation by light [28]. Because the edge of the con-

Figure 3 SEM images and models of the products (a) without $[\text{Fe}(\text{CN})_6]^{4-}$ and (b) without PVP; SEM images of the products prepared by adding (c) 0, (d) 0.06, (e) 0.09, and (f) 0.12 g $[\text{Fe}(\text{CN})_6]^{4-}$, respectively; (g) the adsorption energy of the TiO_2 (110) and TiO_2 (001) facets for $[\text{Fe}(\text{CN})_6]^{4-}$; (h) the formation mechanism of OA- TiO_2 /PB.

duction band of rutile TiO_2 (ca. -0.57 eV vs. standard hydrogen electrode (SHE)) is above the redox potentials of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ (ca. 0.36 eV vs. SHE) and $\text{Fe}^{2+}/\text{Fe}^{3+}$ (ca. 0.77 eV vs. SHE) (Fig. S15), PB can be reduced by the photogenerated electrons of TiO_2 [9,29]. This electron transfer is visualized by the color change between blue (PB) and white (PW) [5]. We can then exploit the electron transfer between TiO_2 and PB in an ordered architecture for repeated ink-free light printing as an alternative to conventional papermaking [30].

Hence, we fabricated a prototype of rewritable paper (see experimental details) by dropcasting an aqueous mixture of OA- TiO_2 /PB, HEC, and EG on a piece of regular paper. Three control samples were prepared additionally for comparison, i.e., broken OA- TiO_2 /PB (Fig. S16) in which the assembly structure was abraded by rigorous grinding (referred to as broken OA- TiO_2 /PB), a mechanical mixture of OA- TiO_2 and pre-synthesized PB (referred to as OA- TiO_2 +PB), and a mechanical mixture of commercial TiO_2 and pre-synthesized PB (referred to as C- TiO_2 +PB). All samples were firstly subjected to UV irradiation to test their photo switching behavior. After UV irradiation, the exposed regions gradually became colorless while the unexposed regions remained dark green (Fig. S17). In the case of OA- TiO_2 /PB, the reduction of PB to PW took place after only 5 s (Fig. 4a), as was observed both from the disappearance of the UV-Vis absorption band of PB at ~ 685 nm and a significant shift of the absorption edge (~ 3 eV) in XPS toward lower energy (Fig. S18) [31]. That is, we can start with a blue paper and write patterns in white or do the reverse with the help of a photo-mask. In contrast, the analogous photo-conversion required 20 s for both OA- TiO_2 +PB and C- TiO_2 +PB (Fig. 3b and Fig. S19). The speed of electron transfer between TiO_2 and PB can be observed by naked eye from the color change in a highly straightforward manner (Fig. 4c, d). The fast light printing speed (5 s) makes the OA- TiO_2 /PB film one of the most excellent light-printing papers at present (Table S1).

The electron transfer capability of the samples was examined using the EIS spectra and through photocurrent analysis (Fig. S20). Compared with OA- TiO_2 /PB and OA- TiO_2 +PB, the OA- TiO_2 /PB favors charge transfer, rendering faster transport and separation of photo-induced charges, and thus gives a smaller semicircle in the Nyquist plot. The photocurrent is smaller in OA- TiO_2 /PB than OA- TiO_2 +PB because the photo-generated electrons are more quickly captured [32]. In addition, the broken OA- TiO_2 /PB shows a sharp increase of impedance than OA- TiO_2 /PB in EIS. Thus, the orderly alignment of TiO_2 and PB in OA- TiO_2 /PB accelerates the electron transfer and improves the printing speed.

Other features of OA- TiO_2 /PB that result from the ordered architecture include the following.

(1) High resolution: the photo-printed patterns on the rewritable paper have high resolution. Complex patterns contrasting dark green and white can be printed successfully with very high resolution (~ 5 μm , Fig. 5a) on the rewritable paper by light irradiation, thanks to the high level of dispersion of PB within the TiO_2 matrix that resulted from the ordered assembly.

(2) High durability: the printing process is highly reversible and the coloration medium is highly durable. Oxidation in air for 12 h returns the PW in the colorless form to the PB in the starting state (Figs S21 and S22). In real application scenarios, the retention time of the light-printed pattern can be tuned by adjusting the dose and thickness of the HEC film on the paper that protects PW from oxidation (Figs S23 and S24). The color reversal *via* oxidation in air can also be accelerated from 12 h at ambient temperature to 30 min at 120°C (Fig. S25). It is worth remarking that after 100 consecutive cycles of photo-switching, the rewritable paper still maintains its behavior without notable loss of performance, as can be seen from the UV-Vis spectra (Fig. 5b).

(3) Visible and sunlight printing: whereas many developed systems using TiO_2 and redox dyes (such as methylene blue)

Figure 4 UV-Vis spectra showing the decoloration process of (a) OA-TiO₂/PB film and (b) OA-TiO₂+PB film under UV irradiation. After UV irradiation, the solid film of (c) OA-TiO₂/PB and (d) OA-TiO₂+PB gradually turned colorless.

Figure 5 (a) Sunlight-driven printing and legibility of letters and patterns on the rewritable paper; (b) reversible color switching and stability of OA-TiO₂/PB; the XPS spectra of (c) Ti 2p_{3/2} and (d) O 1s of OA-TiO₂ and C-TiO₂; (e) ESR spectrum of OA-TiO₂.

require UV light to initiate the color switching [33], the OA-TiO₂/PB system can simply use visible light. The OA-TiO₂/PB has abundant oxygen vacancies (OVs) in addition to Ti vacancies (Fig. 5c). In the XPS spectra of OA-TiO₂/PB, the Ti 2p_{3/2} peak shifts towards lower binding energy (~0.25 eV) compared with that of C-TiO₂ [34], and the O 1s peak (Fig. 5d) has a binding energy of 531.47 eV that corresponds to the oxygen species adsorbed on OVs [35]. Furthermore, the ESR spectra of OA-TiO₂/PB (Fig. 5e) give a resolved symmetrical ESR signal at $g = 2.003$ that can be attributed to electron trapping at OVs [36]. The presence of both oxygen and Ti vacancies enhances the photo absorption of TiO₂ and extends the absorbance to the visible region [37], as is verified by the UV-Vis spectra and

photocurrent (Fig. S26). Upon irradiation at 450 nm or with sunlight, OA-TiO₂/PB switches from dark green to colorless after 10 and 3 min, respectively (Fig. S27). This visible-light-responsive rewritable paper offers great opportunities for practical applications, as visible light and sunlight are safer than UV light to human.

CONCLUSIONS

We exploited the oriented assembly of TiO₂ and PB driven by lattice matching to fabricate an efficient and reversible rewritable paper whose color switching can be driven by visible light. The OA-TiO₂/PB assembly was prepared by a facile one-pot synthesis, in which PB is attached on the energetically favored facet of

ultrathin TiO₂ nanowires to attain a particular crystallographic orientation. With the oriented assembly, the OA-TiO₂/PB integrates the complementary properties of TiO₂ and PB. Accelerated photoelectron transport within the highly oriented TiO₂/PB system provides the foundation for rapid photo switching. Thanks to the presence of oxygen and Ti vacancies in the ultrathin TiO₂ nanowires, the OA-TiO₂/PB is responsive to visible light and sunlight. The developed rewritable paper allows high resolution (~5 μm) and can be repeatedly written for more than 100 times without significant loss of contrast. Theoretical analyses further shed light on the mechanistic aspects about how lattice matching can induce the self-assembly of the inorganic semiconductor and MOF building blocks, although they are structurally and functionally dissimilar. The present work adds to a growing body of knowledge on the rational design of complex functional materials.

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Supplementary information Supporting data are available in the online version of the paper.

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晶格匹配驱动的二氧化钛纳米线与金属有机框架的定向组装应用于可逆光致变色

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摘要 开发新型光致变色(PCSS)材料, 发展可擦写式光打印技术, 是解决能源和环境问题的重要途径。本文报道了一种高效、可逆光致变色材料, 即一种由富缺陷态超细TiO₂纳米线和金属有机框架材料普鲁士蓝(PB)自发定向组装形成的TiO₂/PB介晶材料。TiO₂和PB具有不同的晶体结构特征, 诱导其定向组装的驱动力在于: TiO₂的(001)晶面和PB的(222)晶面具有相似的晶面间距, 即“晶格匹配”机制。这种有序组装结构促进了TiO₂/PB间的电子传输, 实现了紫外光照射下5秒内的快速光打印。TiO₂/PB光打印纸同时具有高的分辨率 (~5 μm), 在重复打印超过100次仍保持对比度基本不变, 是已报道最好的光打印纸之一。超细TiO₂纳米线同时富含氧空位和钛空位, 可实现可见光和太阳光打印。基于密度泛函理论计算, 我们提出了一种配体介导的金属有机框架材料与无机材料的定向组装机制, 为开发高效PCSS系统及其他先进材料提供了新的思路。