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The Fine Characterization and Potential Photocatalytic Effect of Semiconducting Metal **Minerals in Danxia Landforms**

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Abstract: The Danxia landform is representative of the Cretaceous continental red sediment. The careful identification and potential environmental effects of minerals in Danxia red beds have yet to be clearly reported. In this work, reddish sandstone samples were collected from Lang Mountain Danxia landform in Xinning, Hunan province, China, and their mineral phases, element distribution, microstructure, and the spatial relationship of different minerals were investigated using polarizing optical microscope, environmental scanning electron microscopy, energy-dispersive X-ray analysis, electron probe microanalysis, micro-Raman spectra, micro-X-ray diffraction, X-ray fluorescence spectroscopy, and high-resolution transmission electron microscopy. The results revealed that iron oxide (mainly hematite) and titanium oxide (mainly anatase) were the dominant minerals in Danxia red layers. Microcrystalline hematite was suggested as being the coloring mineral. Anatase, reported here for the first time in Danxia red beds, constituted the content of titanium in the red layer (0.17–0.57%) and was present in a significantly higher amount than the adjacent limestone formation (0.13%). Over 95% of Fe/Ti oxides served as a cementation agent along the framework of coarse-grain minerals (quartz and feldspar). The hematite and anatase were visible-light-responsive semiconductors, with a band gap of 2.01 eV and 3.05 eV, respectively. Photoelectrochemical experiments were performed on synthetic hematite, anatase, and their coupled material. The inactive hematite displayed an enhanced 23-fold photocurrent at 0.8 V (vs. Ag/AgCl) when coupled with anatase. Furthermore, in a photodegradation experiment using methyl orange dye under simulated sunlight, the coupled material showed decolorizing efficiency 2.4 times that of hematite. The anatase, therefore, prominently improved the photocatalytic activities of hematite. It is proposed that these semiconducting minerals in red beds produce oxygen reactive species and have significant environmental effects, which is of great importance.

Keywords: Danxia landform; hematite; anatase; photocatalysis; environmental effect

1. Introduction

The Danxia landform, covering approximately 8.6% of the total land mass of China, is a unique type of petrographic geomorphology [1–4]. With vast red-colored sandstones and conglomerates, which were mainly deposited in the Cretaceous period (145-65 million years ago), these spectacular red cliffs and erosional landforms joined the World Heritage List in 2010 due to their classic geomorphological and biogeographic features [5]. The uniqueness of the Danxia landform is attributed not only to its magnificent reddish geomorphology but also to its great value in scientific research as an



important part of the critical zone on Earth's surface [4,6,7]. These red stratified sediments, or red beds, could be used to deduce depositional environments, such as paleomagnetism [8], atmospheric oxygen content [9], paleoceanography and paleoclimate [10], etc. Furthermore, as a significant component of the surface ecosystem and environment on Earth, red beds maintain interactions among minerals, microorganism, water, light, organics, and other substances [7,8,11,12].

Previous researches on the Danxia landform have mainly focused on its developing mechanism, erosion rate, topography, environmental ecology, and petrostratigraphy using macroscopical, traditional, and qualitative methods, such as field study, remote sensing observation, taxonomy, and description [2–4,6,7]. Aside from these, the Danxia red beds cover such a large continental area that their environment effects are of great interest. For conducting intensive studies, minerals are powerful probes to further investigate about Danxia red beds. For example, through SEM microanalysis of the biotite occurring in the red sandstone rock of the northern Scotland Devonian, the mechanical disintegration effect of the alluvial plain during the process of redeposition was thought to turn biotite into hematite, with the latter reddening the rock [11]. A high-resolution transmission electron microscope was used on hematite collected from red beds in the Vispi Quarry section of central Italy, and the results suggested that the hematite with nanograins were authigenic in oxic or suboxic conditions [12]. Batches of adsorption experiments of Cu, Pb, Zn, Co, Ni, and Ag on goethite and hematite were conducted to clarify the metallogenic mechanism and the environmental effect of red beds [13]. Furthermore, the chemical solubility of hematite and goethite was studied via experiments and simulated calculations, which indicated the phase transformation from goethite to hematite during the diagenesis of red beds [14]. Microtechniques and simulated experiments applied to minerals can thus help shed light on the red beds as well as their effects on the surrounding environment in microscale and nanoscale. However, they have seldom been reported in the research of the Danxia landform so far.

As with other natural red beds worldwide, oxidized iron (Fe^{3+}) in the Danxia regions are thought to be the dominant coloring element. Furthermore, hematite (Fe₂O₃) and goethite (α -FeOOH) have been suggested as the main hosted minerals of Fe^{3+} in those red beds, which dye the rock a reddish color [13–15]. In particular, hematite has been thought to be the most common and stable mineral in red beds and is regarded as the terminally oxidation state of Fe-bearing minerals, e.g., green rust, ferrihydrite, goethite, lepidocrocite, and magnetite [16]. Furthermore, hematite is one of the most abundant minerals in soil, especially fertile red soil exposed in southern China and some regions of South America and the tropics [17]. One of the environmental effects of hematite, as well as other widely distributed minerals such as goethite, anatase, and rutile, derives from their brilliant semiconducting and photon-responsive properties by which these minerals can convert solar energy into chemical energy and nourish microorganisms [18,19]. Specifically, when the incident light energy is greater than the threshold value (i.e., band gap) between the valence band and the conduction band of these minerals, electron-hole pairs can be generated, and some redox reactions are triggered with the release of energy [20,21]. Such vital redox reactions, the so-call photocatalytic effect, which occurs among light, minerals, water, organics, and microbes, could play a significant role in the geochemical cycle of elements, materials, and energy in Earth's critical zone [22,23]. Danxia red beds develop exposed cliff and outcrops under continuous solar light, which merits further investigation to find out whether the inside minerals could exert their photon-absorption property in sunlight and catalyze some reactions.

In this work, a series of measurements, such as X-ray fluorescent (XRF), electron microprobe Analysis (EMPA), polarizing optical microscope (POM), environmental scanning electron microscopy (ESEM), energy-dispersive X-ray analysis (EDX), micro-Raman spectra, micro- X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM), were used to characterize the composition of elements and the distribution and morphology of the mineral phases in the red bed samples collected from Lang Mountain in southern China. To shed light on the environmental effect of the semiconducting minerals found in red beds, some photoelectrochemical experiments were

conducted on synthetic metal oxides. Subsequently, the potential impact of vast Danxia landforms on the special ecology and environment of southern China may be clarified from a microscopic perspective.

2. Materials and Methods

2.1. Sample Preparation

The collection of sandstone samples took place at Lang Mountain, Hunan province, China (Figure 1). Seven sampling sites were chosen around the Lang Mountain; these locations are shown in Figure S1 and Table S1 (in Supplementary Materials). The loose and fragile sandstone samples were separated into two parts. One was glued with resin and then air-dried, followed by cutting along the vertical direction and burnishing into 30-µm-thick thin sections for the in situ observation of POM and SEM and the measurements of EPMA, XRD, and Raman spectrum. The other part was ground into fine powder (particles less than 36 µm) for the XRF and TEM measurements.



Figure 1. (a) Distribution of Danxia landforms in China, modified from Peng et al. [4]. (b) The full view of Lang Mountain with a typical Danxia landform. (c) The reddish sandstone in Lang Mountain; inset: mineral particles (in microscale) separated from the sandstone.

According to the analytic results of the field samples, a series of simulation experiments focusing on the photoelectrochemical activities of detected semiconductor minerals were conducted in the lab. Fe_2O_3 (hematite phase) and TiO_2 (anatase phase) were deposited onto fluorine-doped tin oxide conductive glasses (abbreviated as FTO, South China Xiang Science & Technology Company Limited, Shenzhen, China) and manufactured into electrodes, while the FTO glass was washed with acetone, ethanol, and deionized water (in that order) in advance. The preparation of the TiO_2 electrode was realized with the sol-gel method. The mixture containing 10 mL ethanol, 1.26 mL deionized water, and 1 mL concentrated nitric acid was added into the other mixture with 6 g tetrabutyl titanate, 40 mL ethanol, and 1 mL acetylacetone. After one day, the precursor in yellow was extracted and spread onto the FTO glass evenly, followed by calcination in a furnace in air at 400 °C for 24 h with a heating rate of 10 °C/min. The deposition of Fe₂O₃ used the hydrothermal method. A Teflon-lined stainless steel autoclave containing 0.15 mol/L FeCl₃, 1 mol/L NaNO₃, and a piece of FTO glass was sealed and then heated at 94 °C for 4 h with a heating rate of 15 °C/min. After natural cooling, the FTO glass was taken out and washed with deionized water, and it was finally calcined in the furnace in air at 550 °C for 2 h with a heating rate of 10 °C/min. The Fe₂O₃ electrode was well prepared when it cooled down. A coupled Fe₂O₃-TiO₂ material was synthesized according to the abovementioned methods in which Fe₂O₃ was covered onto the as-prepared TiO₂ directly.

2.2. Characteristic Methods

The polished thin sections of rock samples were first observed by a polarizing optical microscope (LV100POL, Nikon, Tokyo, Japan). In particular, metallic minerals were relucent under reflected light, whose positions were located accurately for follow-up tests. EMPA was carried out on an electron microprobe analyzer (EPMA-1720, Shimadzu, Kyoto, Japan) to measure the composition and concentration of elements. When the selected regions were fixed (backscattered mode), mapping patterns were obtained under 15 kV operating voltage and 10 nA operating current, with a spot size of 1 μ m. Rock thin sections and prepared electrodes were sprayed with a film of thin gold due to its poor conductivity before being observed by a SEM (Quanta 650FEG, FEI, Hillsboro, OR, USA) equipped with an EDX detector. The compositions of major elements in powder samples were investigated using an XRF spectrometer (Advant'XP+, Thermo ARL, Écublens, Switzerland) on the basis of the weight fractions of the equivalent oxides. Prior to this, the powder was made into glass disks by melting at 1100 °C for 4 min in lithium tetraborate and lithium metaborate. The loss on ignition was the calculated weight difference before and after calcination at 980 °C for 20 min.

The phases of metallic minerals found in the polarizing optical microscope on the rock thin section were in situ identified by micro-XRD (Rapid IIR, Rigaku, Tokyo, Japan). The data were collected at 40 kV operating voltage and 250 nA operating current with 1°/s step size. Micro-Raman spectra were recorded by a Renishaw inVia Reflex Raman microscope equipped with a 532 nm laser. The beam was through a 65 μ m slit and a 50× objective with 50 mW power. Each spectrum was captured at 30 s and averaged by 10 successive scans with $\pm 1 \text{ cm}^{-1}$ resolution. Before TEM measurement, the solution containing powder samples was dropped onto a holey carbon film supported by a Cu grid. After air-drying, the prepared sample was loaded into the holder of TEM (TECNAIF 20, FEI, Hillsboro, OR, USA) equipped with an EDX detector at 200 kV. Digital micrograph version 3.6.5 (Gantan Ltd., Pleasanton, CA, USA) was applied for the image processing.

The ultraviolet-visible diffuse reflection spectrum (UV-vis DRS) of synthetic samples in 300-1000 nm was detected on a spectrometer (UV-3600 Plus, Shimadzu, Japan) equipped with a diffuse integrating sphere attachment. BaSO₄ was used as a reference. The slit width of the incident light was 2.00 nm.

2.3. Photoelectrochemical and Photocatalytic Experiments

Photoelectrochemical measurements were carried out in a quartz glass reactor with a three-electrode configuration using CHI 660C electrochemical apparatus (Chenhua, Shanghai, China). The oxide electrode covering on the FTO glass was set as working electrode, a platinum sheet $(1 \times 1 \text{ cm})$ was used as the counter electrode, and the reference electrode was Ag/AgCl (3 mol/L KCl). The electrolyte composition was 0.5 mol/L Na₂SO₄ and 0.5 mol/L ethanol. An externally simulated solar light came from a 500 W high-voltage light-emitting diode (LED) lamp ($\lambda > 400 \text{ nm}, 130 \text{ mW/cm}^2$), straight irradiating the backface of the working electrode (the side without oxide covering). The linear sweep voltammetry (LSV) method was used from 0 V to 1.6 V (vs. Ag/AgCl) to separately record the current under light-on and light-off conditions. A potential of 0.8 V (vs. Ag/AgCl) was applied in the photocurrent response measurement. The on and off conditions of light were controlled by the shielding separator in the same time period (60 s).

The photocatalytic experiment was performed to the degradation of methyl orange (MO) dye. The oxide electrode was placed in the quartz glass reactor, which contained 90 mL MO solution with 3.2 mg/L initial concentration and pH value of 4.4. The light source configuration was the same as the above photoelectrochemical measurements. After a certain period of irradiation (1 h), 1.0 mL suspension was extracted to measure the adsorption spectra of MO at 476 nm by UV-vis spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA).

All the reagents used for the experiments (such as acetone, ethanol, nitric acid, tetrabutyl titanate, acetylacetone, methyl orange, FeCl₃, NaNO₃, and Na₂SO₄) were analytically pure (>99.99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The water was distilled deionized water (18 M Ω ·cm).

3. Results and Discussion

3.1. The Mineralogical Identification of Fe Oxides and Ti Oxides

Some mineral particles with microscale separated from the sandstone in Lang Mountain (Figure 1c) showed that the reddish substance was just like a coated material, while the interior particle with light color had more light penetration. Under the microscope with reflected light (Figure 2a,b), some dim grains with hundreds of micrometers were encircled by numerous particles, which presented a bright white color and dozens of micrometers or smaller. The central particles were further identified as silicate minerals in transmitted light (Figure 2c,d). This indicated that some metallic minerals, acting as cement, were almost uniformly distributed around some nonmetallic minerals. Elementary composition results determined by XRF (Table S2) showed that the red beds, compared to local siltstone in grey, were enriched in Fe and Ti by 2.6 and 2.2 times on average, respectively. The abundance of Fe in red beds has always been reported to be high, but the enrichment of Ti has never been reported before. Moreover, EPMA was used to obtain elementary mapping of Fe and Ti on a silicate particle, which was coated by a thin (several microns) ant dense metallic shell (Figure 3a,b). Notably, the distribution of Fe and Ti fell exactly into the region containing metallic minerals, with some regions enriched with both Fe and Ti, as shown in Figure 3c,d.



Figure 2. (**a**,**b**) Rock thin section in optical microscope with reflected light. (**c**) Plane polarized light and (**d**) perpendicular polarized light. Panels (**b**–**d**) show the same mineral particle. "Kfs" refers to K-feldspar.





Figure 3. In the rock thin section, a silicate particle surrounded by metallic shell structure enriched with Fe and Ti. Images from (**a**) optical microscope, (**b**) backscattered mode of electron microprobe analyzer, (**c**) Fe elementary distribution map, and (**d**) Ti elementary distribution map.

From a more microscopic perspective using SEM, some crystal granules that were enriched in Fe were found to display rhombohedral form, as shown in Figure 4a,b. According to the element composition and crystal morphology, these particles distributed among silicate minerals were probably hematite (α -Fe₂O₃). Another mineral aggregation consisted of several tetragonal crystals and contained considerable Ti (Figure 4c), which could be assigned as Ti oxides. According to their crystal shape, they were probably anatase or rutile, whose chemical formula and crystallographic system are the same. The silicate minerals, by contrast, were mainly made of abundant Si, Al, Mg, and Na (Figure 4d).

Micro-XRD, micro-Raman spectra and HRTEM were used to precisely identify the metallic oxide minerals in this study. The XRD pattern of one rock thin section sample is shown in Figure 5a. Though the spot size ($\sim 100 \ \mu m$) of X-ray in XRD measurement was larger than the metallic oxide particles, the signal from Fe oxide minerals was collected owing to its relatively high concentration (compared with Ti oxide). Quartz was identified as the main component with the three strongest peaks at 20.8°, 26.6°, and 50.1°, corresponding to (100), (011), and (112) planes (JCPDS No. 89-8935), respectively. The secondary mineral phase was designated to hematite (α -Fe₂O₃), whose three strongest peaks at 33.1°, 35.6° and 54.1° were assigned to (104), (110), and (116) lattice planes (JCPDS No. 89-0599), respectively. Figure 5b illustrates the Raman spectra of hematite from different sampling sites as well as the standard pattern from the RRUFF database. The hematite in our case contained all the above Raman modes, whose active Raman modes of trigonal hematite include seven optical vibration modes $(2A_{1g} + 5E_g)$, located at about 225, 498 cm⁻¹ and 247, 293, 299, 412, 613 cm⁻¹, respectively [24]. Furthermore, high-resolution TEM image (Figure 5c,d) showed the interplanar distances of (012) and (01-2) planes of α -Fe₂O₃. The fast Fourier transform pattern (Figure 5d) also supported this conclusion with the [400] zone axis and angle of 86° , which was identical to the theoretical value. Given the above, the occurrence of α -Fe₂O₃ was confirmed in samples collected from the red beds of Danxia, as reported in previous studies [13,15]. Surprisingly, the existence of TiO₂ was found by micro-Raman as the mineral phase of anatase in samples collected from different sedimentary layers of all sampling

sites (Figure 5e). The optical phonons at Brillouin zone of anatase conform to the following irreducible representation: $\Gamma = A_{1g} + A_{1u} + 2B_{1g} + B_{2u} + 3E_g + 2E_u$, where A_{1g} (513 cm⁻¹), B_{1g} (399, 519 cm⁻¹) and E_g (144, 197, 639 cm⁻¹) are Raman-active [25]. The above modes were all included in our measurement, providing solid evidence for the universality of anatase-phase TiO₂ in the red beds of Danxia. To the best of our knowledge, this is the first time the anatase-phase TiO₂ in Danxia has been discovered, as it is a vital but easily overlooked mineral. Notably, it was hard to find rutile or brookite—the other two titanium oxides in the samples—while some other Fe oxides, such as goethite, maghemite, and ilmenite, were all nanominerals and therefore identified by HRTEM (Figures S2–S4).



Figure 4. Backscattered electron images in SEM of (**a**) silicate and Fe oxide particles, (**b**) hematite particles (inset: EDX pattern), (**c**) silicate and Ti oxide particles (inset: EDX pattern), and (**d**) EDX pattern of silicate mineral.

According to the EPMA mapping results (Figure 3), the elements Fe and Ti could coexist in some regions, which imply that anatase and hematite might be close in spatial scale. In some samples collected from different sites, it was found that anatase and hematite could be very close in the spatial distribution (Figure 6). The micro-Raman focused on the area in microscale (several microns), whose peaks could be assigned to anatase and hematite as well as quartz (Figure 6a). Furthermore, EDX in TEM confirmed that two small individual nanoparticles were enriched in Fe and Ti, respectively, and their particle sizes were just below 150 nm (Figure 6b and Figure S5). Specifically, the clear resolved d-spacings of 0.270 and 0.252 nm in the region denoted as "c" corresponded to the lattice fringes of (104) and (110) facets in α -Fe₂O₃ (Figure 6c), and two planes highlighted spots in the corresponding simulated fast Fourier transform pattern (inset of Figure 6c) that were well indexed to the [-441] zone axis. The high-resolution TEM image and selected area electron diffraction pattern indicated that the particle marked with a green color in Figure 6b was anatase, whose interplanar spacings were 0.168 nm and 0.482 nm, corresponding to (21–1) and (002) facets with the [-240] zone axis, respectively (Figure 6d).



Figure 5. (a) XRD pattern of the selected sample as well as the standard quartz and hematite as reference. (b) The Raman spectra of hematite collected from all sampling sites. (c) A hematite particle in TEM image. (d) The high-resolution TEM image and simulated fast Fourier transform pattern (inset) of the hematite particle. (e) The Raman spectra of anatase collected from all sampling sites. The location and full names of these sampling sites are shown in Figure S1 and Table S1, respectively.



Figure 6. (a) Raman spectra of samples in several different sampling sites. The dash lines in red, blue, and green mark the Raman modes of anatase, hematite, and quartz, respectively. The location and full names of these sampling sites are shown in Figure S1 and Table S1, respectively. (b) EDX elementary mapping of Si, Fe, and Ti using TEM. (c) High-resolution TEM image captured from the Fe-enriched region in (b). Inset: simulated fast Fourier transform pattern and its identification. (d) High-resolution TEM image captured from the Ti-enriched region in (b). Inset: selected area electron diffraction pattern and its identification.

3.2. Simulated Photoelectrochemical Experiments of Fe Oxides and Ti Oxides

Anatase-phase TiO₂ and hematite-phase Fe₂O₃ are well-known semiconducting materials, thus they can harvest and convert solar light into electric energy and chemical energy. In terms of this study, the first discovery of anatase and its concomitance with hematite in Danxia red beds begs the question of whether these widespread minerals in sun exposure have some potential effects on the local environment. To investigate this, some synthetic Fe₂O₃, TiO₂. and coupled Fe₂O₃–TiO₂ samples were used to measure their photoelectrochemical properties and photocatalytic performance. XRD (Figure 7a) and micro-Raman spectra methods (Figure 7b) confirmed that pure hematite-phase Fe₂O₃–TiO₂ sample contained all the spectroscopic features of each component. The diffraction peaks of TiO₂ were wider than Fe₂O₃, implying the smaller crystalline size of the former. Based on Scherrer's equation, the crystalline size of TiO₂ was estimated as approximately 20 nm, according to the full width at half maximum (FWHM) value of peak assigned as (011) plane. Under the scanning

electron microscope, the as-prepared Fe₂O₃ exhibited as rod-like, which was at most 1 μ m in length and hundreds of nanometers in diameter (Figure 7c); the plate-like TiO₂ with a smooth surface showed crisscross fissuring, probably due to the considerable contraction when cooling (Figure 7d). While depositing Fe₂O₃ on the as-prepared TiO₂, rod-like Fe₂O₃ particles assembled on the surface of TiO₂ and filled in the fissuring between the plate-like TiO₂ (Figure 7e). The coupled Fe₂O₃–TiO₂ sample in this case was just like those natural samples found in the Danxia red beds; the close contact between the two components made their interaction possible. EDX elementary mappings for the synthesized Fe₂O₃–TiO₂ sample are shown in Figure S6. The distribution of Fe was found to overlap with that of Ti, inferring the close contact of hematite and anatase.



Figure 7. The spectroscopic identification of Fe_2O_3 , TiO_2 , and coupled Fe_2O_3 – TiO_2 using (**a**) XRD and (**b**) Raman spectrum. Secondary electron images of (**c**) Fe_2O_3 , (**d**) TiO_2 , and (**e**) coupled Fe_2O_3 – TiO_2 in SEM.

The photoresponsive properties and optical band gap values (E_g) of the as-prepared oxides were determined by UV-vis DRS and Tauc's plot [26]. The direct transition of photogenerated carriers between the valence band and conduction band is described by the Tauc model:

$$(Ahv)^2 = K(hv - E_g) \tag{1}$$

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$$Ahv = 0, \qquad E_{g} = hv \tag{2}$$

where *K* is a proportionality constant, *hv* is the incident photon energy, and A is the absorbance measured by UV-vis DRS. The Tauc plot is presented as the change of $(Ahv)^2$ versus *hv*; therefore, it is used to determine the direct optical E_g through linear extrapolation. The results, as well as actual photos of synthetic electrodes, are shown in Figure 8. The pure TiO₂ was UV-light active and its band gap was estimated as 3.05 eV (Figure 8a,b), resulting in its off-white color due to limited absorption in solar light (Figure 8d). In contrast, Fe₂O₃ exhibited a reddish color and strong absorption below 600 nm (Figure 8a,d), and its band gap value was approximately 2.01 eV (Figure 8c). The coupled Fe₂O₃–TiO₂ sample, interestingly, presented as orange and an almost similar absorption feature as Fe₂O₃ (Figure 8d). This indicated that the light absorption property of Fe₂O₃–TiO₂ coupled sample must have been mainly determined by Fe₂O₃; in other words, the incorporation of moderate TiO₂ would not considerably change the photoresponsive property of Fe₂O₃. The E_g of semiconducting minerals determines their longest absorbed wavelength of light, thus indicating the utilization efficiency of sunlight. The smaller the E_g of the semiconducting minerals, the more flux of light would be absorbed by them, which helps improve the production of oxidizing photogenerated holes and reductive photogenerated electrons. As such, naturally occurring hematite and anatase can evoke redox reactions under solar light.



Figure 8. (a) UV-vis diffuse reflection spectrum (DRS) of Fe_2O_3 , TiO_2 , and coupled Fe_2O_3 – TiO_2 . Optical band gap estimated from Tauc's plots of (b) TiO_2 and (c) Fe_2O_3 . (d) Actual photos of three synthetic electrodes.

The ability to convert light into electricity was verified by photoelectrochemical measurements. The current-voltage characteristics are shown in Figure 9a. Compared with the smaller yield of current in the dark, strong dependences of the photocurrent density on light were observed, indicating that light (simulated sunlight) indeed facilitated the formation of extra electrons from semiconducting hematite and anatase. In addition, the three oxide materials showed different performances. The hematite-phase Fe_2O_3 , the foremost concern in this work due to its dominant

concentration, showed the worst photoelectric conversion capacity compared with its two counterparts. Notably, when Fe_2O_3 was coupled with TiO_2 , a remarkable enhancement of photocurrent density was observed, which must be ascribed to the assistance of anatase-phase TiO_2 with brilliant photoelectric conversion capacity. Furthermore, when the bias was fixed at 0.8 V (vs. Ag/AgCl), the current density was obtained under alternant dark and simulated sunlight, as shown in Figure 9b. The dark currents in all cases were negligible, while enhanced, sensitive, and stable current signals were captured when photons were incident. In particular coupled Fe_2O_2 -TiO₂ produced a stable

captured when photons were incident. In particular, coupled Fe₂O₃–TiO₂ produced a stable photocurrent density of about 42 μ A/cm² under this condition, preponderating 23 times over pure Fe₂O₃. The highest photocurrent density was assigned to pure TiO₂ (inset), whose photocurrent density reached almost 300 μ A/cm². With its narrower absorption range of solar light, the better photoelectrochemical performance of TiO₂ than Fe₂O₃ could likely be attributed to its nanoscale particles, which decreased migration distance and the probability of recombination of photogenerated carriers [27]. Based on these results, it is suggested that even with a low concentration of TiO₂ in red beds, their extraordinary photoelectric conversion capacity should make a difference. More importantly, once TiO₂ is involved, the massive but inferior Fe₂O₃ in red beds could significantly improve their photoelectric conversion performance.



Figure 9. Photoelectrochemical measurements of the three oxide electrodes in $0.5 \text{ mol/L Na}_2SO_4$ and ethanol. (a) Current density vs. bias curves and (b) current density vs. time curves at 0.8 V (vs. Ag/AgCl). Inset: TiO₂ case.

Methyl orange (MO) dye is a model compound to measure the photocatalytic activity of photocatalyst, which was used in this case to compare the photocatalysis-related redox reaction rate of the three as-prepared oxides. The results are presented in Figure 10. In simulated solar light, MO molecules were under slight photolysis with a 19% removal rate after 12 h irradiation time. When a photocatalyst was added, as expected, the photodegradation efficiencies were enhanced at different levels. The change of absorption spectra of MO in the presence of coupled Fe_2O_3 -TiO₂ is illustrated in Figure S7 (the spectra in other photocatalyst cases were similar and are not shown). The absorption peak at $\lambda = 476$ nm declined gradually and presented a slight blue shift with increasing irradiation time, suggesting the progressive decolorization of the MO during the reaction. Specifically, only 27% of MO molecules were removed in the case of Fe₂O₃, while a 48% removal rate was reached for coupled Fe₂O₃–TiO₂ after 12 h. The pure TiO₂, surprisingly, degraded MO by 75% within the same time (inset in Figure 10a). The photocatalytic performance of the three materials above were extremely similar to their photoelectrochemical measurements (Figure 9), indicating that passivated Fe₂O₃ could become active when coupled with superior TiO_2 . Notably, in Figure 10a, the drastic decrease in MO concentration in the first hour could most likely be attributed to the strong physical adsorption, followed by the slow photocatalytic degradation for the rest of the reaction time. Thus, the removal rate by 20% of TiO₂ in the first hour might be due to its nanoscale particle size, huge specific surface area, and strong absorption capability. Figure 10b demonstrates the photocatalytic degradation of

MO following the pseudo-first-order law, with an apparent rate constant of $k = 0.019 h^{-1}$, 0.046 h^{-1} , and 0.103 h^{-1} for Fe₂O₃, coupled Fe₂O₃-TiO₂, and TiO₂, respectively. Based on this, the coupled Fe₂O₃-TiO₂ exhibited a removal efficiency of MO 2.42 times that of inactive Fe₂O₃, which highlighted the assistance effect of TiO₂.



Figure 10. (a) Change in relative MO concentration under irradiation for Fe_2O_3 and coupled Fe_2O_3 -TiO₂ as well as the situation without photocatalyst. Inset: TiO₂ case. (b) The variation of ln (C_t/C_0) of MO against irradiation time and linear fitting for Fe_2O_3 and coupled Fe_2O_3 -TiO₂. The linear fitting was not involved in the first data point to exclude the factor of physical absorption. Inset: TiO₂ case.

3.3. The Potential Environmental Effect of Fe Oxide and Ti Oxide Minerals on the Danxia Landform

The Danxia landform in southern China is a unique environment, represented as erosional cliffs in which countless minerals assemble and lithify into rock. Semiconducting minerals, represented as hematite and anatase, once formed and exposed in sunlight should be excited and generate reductive electrons and oxidizing holes. The photogenerated electrons from natural minerals have been found to synthesize prebiotic organics and facilitate the growth of microorganisms in soil [28,29]. Furthermore, the photogenerated holes from natural minerals are able to decompose organics and kill bacteria in wastewater [30,31]. In this work, anatase was found for the first time as a mineral in the red beds of Danxia. In addition, with the assistance of anatase, the major species hematite was found to exhibit significant photoelectrical performance and highly efficient photocatalytic activities. According to our simulated experiment, these two minerals could utilize solar light to photocatalytically decompose and destroy organics. In fact, several studies have reported that there are different levels of desertification in the red beds of Danxia, even though this landform is located in the humid region of southern China [32,33]. Many factors are thought to be responsible for the continuous desertification of Danxia, such as lithological features, natural impacts, and human activities, resulting in sparser vegetation and decreased microbial community year on year. Based on this study, another mechanism is proposed with the photocatalytic effects of hematite and anatase on an increasing number of barren red beds. A similar mechanism has been put forward in abiotic Mars and oligotrophic desert, where titanic oxides (anatase and rutile) and iron oxide (mainly hematite) are assumed to produce considerable reactive oxygen species (ROSs) with extreme solar irradiation, and these strong oxidizing agents have the ability to decompose organics and exacerbate desertification [34,35]. On a positive note, the photocatalytic effects of natural semiconducting minerals are suggested as possibly stimulating metabolism and the growth of microorganisms in the soil [29,36], thus promoting internal biodiversity and soil fertility. Hematite and anatase in this case could also exert a similar effect on the Danxia landform. In summary, semiconducting minerals in the red beds of Danxia might simultaneously play reconstructive and constructive roles in the environment. Though such effects of every mineral particle remain minimal, the considerable distribution of all semiconducting minerals and the long history of solar irradiation could lead to a great accumulation and make a significant difference. This study provides a completely new perspective to understand the minerals in the Danxia landform. Moreover, it should be noted that semiconducting minerals, such as hematite and anatase, are widespread on the surface of Earth, thus the photocatalytic performance and the environmental effects of semiconducting minerals in the critical zone of Earth should be highly regarded.

4. Conclusions

The Danxia landform, which developed mainly from terrestrial coarse clastic rocks, constitutes a special red bed geomorphology in China. However, the fine identification of its environmentally functional minerals has received little attention. In this study, the Lang Mountain Danxia landform served as a case study to investigate the phase, distribution, as well as the microstructural and spatial relationship, of these minerals. Hematite and anatase were verified as being the main metallic minerals. The first reported anatase found in the Danxia landform could keep a close contact with hematite, whose configuration was shown to be beneficial to their interaction. The brilliant semiconducting and photoelectric properties of hematite, anatase, and their coupled product were examined on synthetic materials. When coupled with anatase, the inactive hematite demonstrated enhanced photoelectric conversion capacity and photocatalytic efficiency of degrading methyl orange in sunlight. Therefore, these natural semiconducting minerals could play a potential role in the destruction of the organic network in vast red beds, most likely resulting in the desertification of the Danxia landform. Other positive effects of these minerals on microorganisms are also proposed. This study reconsiders the environmental functions of minerals in red beds and offers a new perspective to understand the interaction among light, mineral, and organic materials in a long-term geohistory.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/8/12/554/ s1. Figure S1: The distribution map of sampling sites in Lang mountain geopark, Figure S2: The TEM images of some mineral nanoparticles (a) and the identification of goethite through its interplanar spacing of (010) (b), Figure S3: The TEM images of a well-crystalline maghemite particle (a) and its lattice fringes (b). Inset: selected area electron diffraction pattern and its identification, Figure S4: The TEM images of ilmenite (a) and its lattice fringes (b). Inset: simulated fast Fourier transform pattern and its identification, Figure S5: The change of absorption spectra of MO with irradiated time in the presence of coupled Fe₂O₃-TiO₂, Table S1: The location of sampling sites, Table S2: The concentration of major elements of sandstone samples through XRF method (wt %).

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