Binary dopant segregation enables hematite-based heterostructures for highly efficient solar H$_2$O$_2$ synthesis

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Dopant segregation, frequently observed in ionic oxides, is useful for engineering materials and devices. However, due to the poor driving force for ion migration and/or the presence of substantial grain boundaries, dopants are mostly confined within a nanoscale region. Herein, we demonstrate that core–shell heterostructures are formed by oriented self-segregation using one-step thermal annealing of metal-doped hematite mesocrystals at relatively low temperatures in air. The sintering of highly ordered interfaces between the nanocrystal subunits inside the mesocrystal eliminates grain boundaries, leaving numerous oxygen vacancies in the bulk. This results in the efficient segregation of dopants (~90%) on the external surface, which forms their oxide overlayers. The optimized photoanode based on hematite mesocrystals with oxide overlayers containing Sn and Ti dopants realises high activity (~0.8 $\mu$mol min$^{-1}$ cm$^{-2}$) and selectivity (~90%) for photoelectrochemical H$_2$O$_2$ production, which provides a wide range of application for the proposed concept.
Ionic oxide heterostructures have attracted significant attention in diverse fields ranging from catalysis to (magneto) optoelectronics owing to their tunable optical, electrical, and magnetic properties by precisely controlling the concentration and location of elements. These heterostructures are mostly fabricated by vacuum technologies, such as atomic layer deposition and chemical vapor deposition. They rely on high-precision equipment and specialized precursor reagents, which limit their large-scale application for production in industries.

Dopant segregation is another approach. It usually occurs in ionic solids containing aliovalent dopant ions and is driven by elastic and/or electrostatic interactions. In many cases, only small amounts of dopants can reach the external surface of polycrystalline or nanocrystalline materials under elevated temperatures owing to the limited ion migration that results from poor driving forces or grain boundaries (GBs). Extrinsic or intrinsic defects in the crystals yield space charge regions that modify a local electrostatic potential, but often lead to inhomogeneous properties and inevitably degrade their performance. Thus, it is challenging to build the heterostructures by dopant segregation. External segregation may be promoted by removing the GBs from doped materials and adding excess space charges; however, these actions are incompatible. The concept of mesocrystal (MC), which is an ordered assembly of nanocrystals via oriented attachment, provides a solution to this problem. We recently discovered that thermal treatment at relatively lower temperatures (e.g., 700 °C for hematite MCs) induces the sintering of an interface (i.e., GB elimination) and creates numerous interfacial oxygen vacancies (VO), which facilitate the oriented migration of dopant ions as well as photogenerated charges.

Charge transfer efficiency and catalytic activity of semiconducting materials are highly influenced by their bulk electronic and surface structures. For example, hematite MCs with thin rutile TiO2 overlayers exhibit excellent performance in photoelectrochemical (PEC) water oxidation to obtain O2 owing to the suppressed surface recombination of photogenerated electrons and holes. H2O2.

**Fig. 1** Space charge-induced dopant segregation. **a** Distribution of dopants and electrostatic potential (donor-doping case) in ionic oxides based on the space charge theory (Supplementary Fig. 1 for acceptor-doping case). Strong segregation of dopants in the space charge layers is induced to compensate the excess charges on the crystal surfaces and bulk GBs (Supplementary Fig. 2). See Supplementary Note 1 for more details on the space charge theory. **b** Schematic illustration of the dopant segregation in different types of ionic oxide crystals: (I) Crystal with numerous GBs: dopants tend to segregate at the surface and GBs. (II) Disordered nanocrystals: a small number of dopants tend to segregate on the surface due to the lack of driving force even at high temperatures. (III) Ordered nanocrystals with highly aligned interfaces: a large number of dopants segregate on the outer surface because of interface sintering (GB elimination), creating numerous interfacial VO and narrowing the space charge layer to drive the charge migration.
which is another product of the water oxidation, exceeds O₂ owing to its usefulness as a green oxidant for industrial chemistry and environmental purification, as well as a clean energy source for fuel cells.

The PEC H₂O₂ production has been mostly realized by two-electron pathway from water oxidation using BiVO₄-based photoanodes; however, these photoanodes are still unstable for practical use due to the dissolution of V⁵⁺ that arises from anodic photocorrosion.

Herein, we present MC-based dopant segregation to easily and effectively modify the surface of hematite MCs for highly efficient and selective solar-driven H₂O₂ production. Hematite (α-Fe₂O₃) is naturally abundant with good stability and suitable bandgap (~2.1 eV) for sunlight absorption and has been extensively studied for solar-driven water oxidation to obtain O₂. The energy-dispersive X-ray (EDX) maps (Fig. 2d) and corresponding EDX spectra (Supplementary Fig. 6) suggest that the specimen is composed of crystallographically aligned nanocrystals. The specific structure of the MC is further featured by single crystal-like diffraction spots obtained from the adjacent nanocrystals (Supplementary Fig. 5d), indicating that the as-synthesized particle is composed of crystallographically aligned nanocrystals. The specific structure of the MC is further featured by single crystal-like diffraction spots obtained from the adjacent nanocrystals (Supplementary Fig. 5d), indicating that the as-synthesized particle is composed of crystallographically aligned nanocrystals.

**Results**

**Structures of hematite-based MCs.** The as-synthesized Sn, Ti-codoped Fe₂O₃ (SnTi–Fe₂O₃) MCs (Supplementary Fig. 3), which cause self-segregation during heating, exhibit uniform cuboid-like morphology (~150 nm, width = ~110 nm, and height = ~90 nm) assembled with closely stacked nanocrystal subunits (~20 nm), as observed from the field-emission scanning electron microscopy (FE-SEM) (Supplementary Fig. 4) and transmission electron microscopy (TEM) images (Fig. 2a, Supplementary Fig. 5). A coherent crystal lattice of hematite (104) is seen with adjacent nanocrystals and intimate interfaces (Fig. 2b and Supplementary Fig. 5c), indicating that the as-synthesized particle is composed of crystallographically aligned nanocrystals. The specific structure of the MC is further featured by single crystal-like diffraction spots obtained from the adjacent nanocrystals (Supplementary Fig. 5d), indicating that the as-synthesized particle is composed of crystallographically aligned nanocrystals. The specific structure of the MC is further featured by single crystal-like diffraction spots obtained from the adjacent nanocrystals (Supplementary Fig. 5d), indicating that the as-synthesized particle is composed of crystallographically aligned nanocrystals.

**Heterostructures formed by dopant segregation.** All doped hematite MCs are composed of a hematite phase, as deduced from the powder X-ray diffraction (XRD) patterns (Supplementary Fig. 9). However, owing to the lattice expansion via the replacement of smaller Fe³⁺ ions (0.55 Å) with larger Sn²⁺ (0.999 Å) and/or Ti⁴⁺ ions (0.605 Å) ions, the peak positions of the hematite diffraction lines shifted towards smaller angles (solid lines in Fig. 3a). The corresponding lattice d(104) space values increased from 2.709 to 2.730 Å with an increase in total dopant concentration from 0 to 30 mol% (Supplementary Fig. 10), confirming the uniform incorporation of Sn and/or Ti ions in the hematite lattice owing to the replacement with Fe³⁺ ions. After thermal treatment, the diffraction peak positions (dashed lines in Fig. 3a) and d values of the doped samples exhibited the same level of undoped Fe₂O₃ (Fig. 3b), suggesting that most of the doped Sn²⁺ and/or Ti⁴⁺ ions (~90%) were diffused out from the hematite lattice. We observed a broad diffraction peak located at 27° (and 26.5°) for the annealed Ti–Fe₂O₃ sample, which shifted towards smaller angles (solid lines in Fig. 3a). The corresponding lattice d(104) space values increased from 2.709 to 2.730 Å with an increase in total dopant concentration from 0 to 30 mol% (Supplementary Fig. 10), confirming the uniform incorporation of Sn and/or Ti ions in the hematite lattice owing to the replacement with Fe³⁺ ions.

The synchrotron-based X-ray total scattering measurements and pair distribution function (PDF) analysis are powerful methods to characterize disordered or amorphous structures. The as-synthesized SnTi–Fe₂O₃ sample shows a peak shift, along with the broadening of the peaks, towards a larger interatomic distance (r) compared to the undoped Fe₂O₃ (Fig. 3d) and Supplementary Fig. 11), suggesting an expansion of the hematite lattice by the replacement of Sn²⁺ sites with larger-sized Sn²⁺ and Ti⁴⁺ ions. The thermal treatment leads to a lattice rearrangement in the bulk as indicated by the peak shifts toward the r values of the undoped Fe₂O₃. Considering that the length of corner-sharing Ti–Sn (and Sn–Sn) bond of rutile TiO₂ (and SnO₂) is 3.55 Å (and 3.68 Å) along with the corresponding PDFs (Supplementary Fig. 12), an increase in amplitude at 3.5–3.7 Å implies the formation of the dopant oxide overlayers. A new peak with a Q value of 1.872 Å⁻¹ (1.916 Å⁻¹) for the annealed Sn–Fe₂O₃ (Ti–Fe₂O₃) is assigned to SnO₂ (rutile TiO₂) (Supplementary Fig. 12), implying a weak and broad scattering peak located between that of SnO₂ and TiO₂. Meanwhile, only a weak and broad scattering peak was detected, probably due to the disordered structure of the overlayer, as indicated by the HRTEM image.

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interfaces (GB elimination) by annealing, interfacial \( V_O \) with a positive charge(s) (i.e., \( V^* \) in the Kröger–Vink notation) are formed, which can create the space charge regions (Supplementary Fig. 13 and Supplementary Table 1) and yield a repulsive force against the dopant cations. This effectively drives the oriented self-segregation of larger-sized dopants to the external surface in addition to the elastic energy (EE) induced by the size mismatch between the dopant and host ions without any significant dopant accumulation in the GB regions (see Supplementary Note 1 for details).

**Formation of composite oxide overlayers.** To elucidate the local structures of the overlayers, X-ray absorption spectroscopy (XAS) at Fe, Ti, and Sn K-edges was performed. The normalized Fe K-edge XANES spectra (Supplementary Fig. 14) of all the hematite-based samples are close to the standard \( \alpha \)-Fe\(_2\)O\(_3\), indicating that the doping and annealing treatments have negligibly affected the valence and coordination states of the iron cation. The normalized Ti K-edge XANES spectra of the Ti-containing samples are shown in Fig. 4a. For transition metals in oxides, the threshold energy position of the spectra is very sensitive to their oxidation states, while the shapes of the peaks give information about the local structural environments of the absorbing elements\(^{39}\). The peak shapes of the annealed Ti–Fe\(_2\)O\(_3\) MCs in pre- and post-edge regions are similar to those of rutile TiO\(_2\), but the line position is located between those of rutile and FeTiO\(_3\). These results are consistent with the fact that the rutile overlayer with the FeTiO\(_3\) intermediate layer is seen in the HRTEM image.
For the annealed SnTi–Fe₂O₃ sample, the characteristic peak of rutile in the pre-edge (indicated by the black arrow) did not appear. Moreover, the peak shape and position are different from those of reference TiO₂ and annealed Ti–Fe₂O₃, indicating that no rutile TiO₂ phase was formed as the main product in this sample. The annealed SnTi–Fe₂O₃ sample also has a similar strongest absorption peak with FeTiO₃ at the post-edge region; thus, the oxidation state of Ti ions is similar to that of FeTiO₃. Besides, a much stronger first post-edge peak may indicate the Sn–Ti coordination. This was further supported by the comparison of the ex situ Ti K-edge XAS profile measured in transmission and CEY modes (Supplementary Fig. 15).

Figure 4b depicts in situ Ti K-edge XANES spectra of as-synthesized SnTi–Fe₂O₃ MCs. When the temperature increased from 40 to 700 °C, a negligible change in the peak shape and position was observed. No characteristic peak of the rutile phase was observed during heating, whereas the two post-edge peaks shifted to the higher energy and became smooth with an increase in the first post-edge peak at 700 °C due to the formation of binary Sn–Ti oxides. For the Ti–Fe₂O₃ sample, the rutile phase was formed at 700 °C (Supplementary Fig. 16).

Ex and in situ Sn K-edge FT-EXAFS measurements enhanced the investigation of the dynamics of dopant segregation (Figs. 2i and 4c, and Supplementary Figs. 17 and 18). The peak position of the Sn–Sn bond for annealed Sn–Fe₂O₃ sample is close to that of the reference SnO₂ (Fig. 2i and Supplementary Fig. 17), proving the formation of SnO₂ overlayers. For the annealed SnTi–Fe₂O₃ sample, the second main shell has a shorter radial distance than that of SnO₂ owing to the formation of Sn–Ti coordination (i.e., SnTiO₃)³⁰,³¹. The peak intensity of the Sn–Fe coordination shell
gradually decreases as the temperature increases from 48 to 700 °C (Fig. 4c) because the Sn–coordination becomes disordered due to the diffusion of Sn ions from the hematite lattice. A second Sn–Sn coordination peak is formed and grows when the temperature rises to ~450 °C (Supplementary Fig. 19). Meanwhile, the Sn–Ti coordination peak appears at 700 °C and becomes stronger during the heat preservation and cooling stages, which agrees with the Ti K-edge XANES result (Fig. 4b). The growth of the Sn–Sn and Sn–Ti coordination peaks during the cooling stage indicates ordered Sn-coordinations by suppressed oscillation or diffusion of the elements at lower temperatures. For Sn–Fe₂O₃ sample, the SnO₂ phase is formed, as indicated by the increase in the Sn–Sn coordination at ~550 °C (Supplementary Fig. 18). Based on these results, it is concluded that Sn²⁺ ions migrate from the hematite lattice before Ti⁴⁺ ions owing to their larger radius (i.e., larger EE), and segregate on the surface to form the SnO₂ (or SnO) phase at ~450 °C. The deficient SnTiOₓ overlayers are then formed when Ti⁴⁺ ions segregate at the surface and react with SnO₂ at 700 °C (Fig. 4d). In addition, a very small amount of SnO₂ remained at the outer surface during the annealing treatment at 700 °C.

**Performance of PEC H₂O₂ synthesis.** Next, we demonstrate an outstanding ability of the hematite-based heterostructure as a photocatalyst for PEC H₂O₂ synthesis (Fig. 5a). Figure 5b shows the current density–voltage curves of photoanodes, which were followed by the same thermal treatment as mentioned earlier, operated in the dark or under simulated sunlight illumination. The photocurrent density obtained for the optimized SnTi−Fe₂O₃ photoanode at 1.23 V vs. RHE was approximately 1.1 mA cm⁻², which is much higher than those of Fe₂O₃ (0.37 mA cm⁻²), Ti–Fe₂O₃ (0.83 mA cm⁻²), and Sn–Fe₂O₃ (0.23 mA cm⁻²). This improved performance may result from the reduced electron transfer resistances in the bulk and at the interfaces of hematite/FTO and hematite/electrolyte by the surface passivation with overlayers and n-type conductivity arising from the interfacial VO₂ in addition to interparticle sintering and necking, as suggested by the electrochemical impedance spectroscopy (EIS) (Supplementary Fig. 20) and Mott–Schottky plots (Supplementary Fig. 13 and Supplementary Table 1).

We quantitatively analyzed the H₂O₂ generation by the N,N-diethyl-1,4-phenylenediamine (DPD) method (Supplementary Fig. 21). The number of H₂O₂ produced from the SnTi−Fe₂O₃ photoanode increased almost linearly with the illumination time, which is much more active than Ti–Fe₂O₃, Sn–Fe₂O₃, and Fe₂O₃ (Fig. 5c). No H₂O₂ was generated without light irradiation or from the Pt cathode under the operating conditions (Supplementary Fig. 22a). The Sn–Fe₂O₃ photoanode (i.e., the SnO₂ overlayer) showed a much lower photocurrent but a higher Faradaic efficiency (FE) of H₂O₂, whereas the Ti–Fe₂O₃ photoanode (i.e., the TiO₂ overlayer) exhibited an opposite trend (Fig. 5d). No gaseous oxygen was detected by the gas chromatography (GC) analysis, possibly due to the low concentration of evolved O₂, whereas the amount of H₂ (with FE over 90%) linearly increased with the illumination time (Supplementary Fig. 22b, c).

Furthermore, the co-doping of Sn and Ti significantly enhanced the generation of both photocurrent (i.e., H₂) without any notable decrease over 90 min and H₂O₂ with high FEs (>90%) in the range of 1.0–1.8 V vs. RHE (Supplementary Fig. 23). The optimized SnTi−Fe₂O₃ photoanode realized an H₂O₂ generation rate of ~0.8 μmol min⁻¹ cm⁻², which is comparable to those of the active BiVO₄-based photoanodes (Supplementary Fig. 24). To the best of our knowledge, this is the first example of a hematite-based PEC water-splitting system that

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**Fig. 4 In situ observation of dopant segregation. a** Ex situ Ti K-edge XANES spectra of annealed Ti-containing samples and reference samples. **b** In situ Ti K-edge XANES spectra of as-synthesized SnTi−Fe₂O₃ measured with the similar heating procedure used for electrodes preparation. The spectra are shifted along the y-axis for the sake of better clarity. **c** In situ FT-EXAFS spectra of as-synthesized SnTi−Fe₂O₃ measured with the similar heating procedure used for electrodes preparation. **d** Schematic illustration of the binary dopant segregation enabling the heterostructures during thermal treatment of as-synthesized SnTi−Fe₂O₃ MC.
achieves a high FE for H₂O₂ generation with a good H₂/HSO₄ co-production capability. At higher voltages (>1.8 V vs. RHE), dark currents are more significant owing to the EC oxidation of water for obtaining O₂ (Fig. 5b)²⁰, leading to the decreased FE of H₂O₂ to H₂O oxidation. The electrocatalytic nature of SnO₂ (site #1), the OH adsorption was significantly enhanced, leading to a poor H₂O₂ evolution activity. The two electrons are delocalized over neighboring Sn⁴⁺ ions, which are probably oxidized with VO (Supplementary Fig. 28, and Supplementary Table 3). They also reported that an oxidized passivation layer (~2 nm thickness) that resembles SnO₂ formed at the top surface of SnTiO₃. We thus modeled various rutile SnO₂ structures possessing VO, where subsurface VO mimics the Sn²⁺ structure suitable for H₂O₂ generation.

DFT calculations of adsorption energies. To identify reaction active sites, we calculated the adsorption energies of relevant intermediates O* and OH* for various structures, including pure hematite (Fig. 5e), using density functional theory (DFT) based on the computational hydrogen electrode model⁴¹,⁴². We then calculated free energy changes of OH* and O* (ΔG_{OH*} and ΔG_{O*}) to construct activity volcano plots for two-electron oxidation to H₂O₂.

As shown in Fig. 5f, bare hematite (110) surface is not suitable for H₂O₂ evolution, but it is for O₂ evolution (Supplementary Figs. 25 and 26, Supplementary Table 2, and Supplementary Note 3), judging from the calculated ΔG_{OH*} (1.33 eV) and ΔG_{O*} (3.45 eV), which are deviated from the preferred range for H₂O₂ evolution (1.6 eV < ΔG_{OH*} < 2.4 eV, ΔG_{O*} < 3.5 eV)⁹,¹⁹. We also point out that a simple doping treatment cannot improve the reaction selectivity, according to the fact that the ΔG_{OH*} values calculated for two local structures, Sn⁴⁺-doped TiO₂ (Sn-TiO₂) and Ti⁴⁺-doped SnO₂ (Ti-SnO₂), where the dopants are considered as the surface active sites, are comparable to those of SnO₂ and TiO₂, respectively (Fig. 5f, Supplementary Fig. 27, and Supplementary Table 3).

Recently, Diehl et al. reported an ilmenite-type SnTiO₃ structure where each Sn²⁺ possesses a lone pair, forming layers separated by a van der Waals gap⁴⁴,⁴⁵. This finding inspired us to explore local structures of SnTiO₃ overlayers, but our calculations revealed that the ideal SnTiO₃ (0001) surface has a ΔG_{OH*} of 1.24 eV (ΔG_{O*} of 3.04 eV), which is not suitable for H₂O₂ evolution (Fig. 5f, Supplementary Fig. 28, and Supplementary Table 3). They also reported that an oxidized passivation layer (~2 nm thickness) that resembles SnO₂ formed at the top surface of SnTiO₃. We thus modeled various rutile SnO₂ structures possessing VO, where subsurface VO mimics the Sn²⁺ support from SnTiO₃ and examined their possibility as a catalytic site on the annealed SnTi-Fe₂O₃. As demonstrated in Fig. 5e and f, when VO was introduced near the surface of SnO₂ (site #1), the OH adsorption was significantly enhanced, leading to a poor H₂O₂ evolution activity. The two electrons are left behind when a neutral VO is formed and these electrons are delocalized over neighboring Sn¹⁺. An increase in electron density on the Sn ions alters their coordination from 6- to 5-fold coordination. This local under-coordination increases the electronegativity of Sn and reduces the reorganization energy required to distort Sn–O bonds for OH adsorption. Meanwhile, when VO is present in deeper positions, the ΔG_{OH*} value shifts toward the volcano peak where the catalyst is optimal for H₂O₂ production according to Sabatier’s principle (Fig. 5f, Supplementary Fig. 29, and Supplementary Table 4)⁴⁶. We also found a similar tendency for rutile-type Sn₃xTi₅O₁₆ₓ with VO (Supplementary Fig. 30 and Supplementary Table 5)³⁰.

Discussion
The activity of heterogeneous photocatalysts is strongly influenced by their ability to exhibit chemisorption on reactants and intermediates. Since the surface Sn²⁺ ions are probably oxidized to Sn⁴⁺ during the annealing treatment in the air (Supplementary Fig. 29, and Supplementary Table 4)⁴⁶.
Fig. 8d), partially amorphized SnO2 (or Sn0.5Ti0.5O2) (below 2 nm thickness) could form at the outer surface of disordered SnTiOx overlayers. Such a heterostructure could be realized by successive binary dopant segregation through nanoparticle networks in the MCs (Fig. 4d). Among the structures utilized in the DFT calculations, the prospective ones are SnO2 or Sn0.1Ti0.9O2 with V0 at depths of 1.2–1.7 nm (e.g., site #5 in Fig. 5e, f, and Supplementary Fig. 29), which are structurally analogous to the Sn5+ species on the disordered SnTiOx overlayers. Our calculations further point out the importance of the V0 concentration in controlling the selectivity of the water oxidation reaction (Fig. 5i). It was reported that surface V0 can lower the H2O2 evolution activity by promoting water dissociation to form intermediates for O2 evolution on BiVO4, but the V0-position dependence of H2O2 evolution has been overlooked so far.

For PEC H2O2 synthesis, several mechanisms have been proposed (Supplementary Note 4). In particular, the presence of HCO3- is significant to accelerate the water oxidation to H2O2. Bakhshi et al. also demonstrated that the tuning of ΔGOH by doping of Gd ions to BiVO4 significantly improves the activity and selectivity of PEC H2O2 synthesis; in 2 M KHCO3 electrolyte. In our system, the oxidized layers supported on SnTiOx serve as a bifunctional catalyst to adequately adsorb water molecules (i.e., OH*) and facilitate HCO3- mediated interfacial transfer of photo-holes from excited hematite core for efficient H2O2 evolution. In the future, detailed analyses of reaction intermediates using operando spectroscopic methods will be important to refine the mechanism of H2O2 formation.

In summary, we developed MC-based binary dopant segregation to construct heterostructures with preferential properties for solar H2O2 synthesis. The oxidized surface Sn5+ species on the disordered SnTiOx overlayers are potential active sites for efficient H2O2 generation. The composite overlayers on the hematite can be modified to further improve the PEC performance for practical use and fit specific other sustainable reactions like CO2 reduction. Moreover, other types of overlayers, such as nitrides and hydrides, may be fabricated by varying the synthesis conditions (e.g., annealing in N2 or H2 atmosphere) for emerging functionalities.

Methods

Synthesis of hematite-based MCs. The hematite MCs containing Sn2+ (6.5 mol%) and Ti4+ (6.5 mol%) dopants (SnTi–Fe2O3) were synthesized via a simple surfactant-free solvothermal method (Supplementary Fig. 3). Briefly, a mixed metal precursor of 1 mmol of Fe(NO3)3·9H2O (FUJIFILM Wako Pure Chemical, 99.5%), 0.0575 mmol of TiCl4 (Sigma-Aldrich), and 0.075 mmol of SnCl2 (FUJIFILM Wako Pure Chemical, 97.0 %) were dissolved in a mixed solvent of 40 mL of N,N-dimethylformamide (FUJIFILM Wako Pure Chemical, 99.0 + %) and 10 mL of methanol (FUJIFILM Wako Pure Chemical, 99.8 + %). The above solution was then treated at 180 °C for 24 h in a 100 mL Teflon-lined autoclave reactor. After naturally cooling, the resulting solid product was thoroughly washed with water and ethanol and dried at 60 °C (8 h). The hematite MCs with individual dopants of Sn2+ (Sn–Fe2O3) and Ti4+ (Ti–Fe2O3), and undoped hematite (Fe2O3) MCs were synthesized via the same method by varying the dopant precursors. The doping levels of Sn2+ and Ti4+ were controlled by varying the amounts of Sn2+ and Ti4+ in the precursor solution.

Fabrication of hematite MC-based photoanodes. The hematite MC-based films were prepared by multiple spin-coating (3000 rpm) of an ethanol solution containing the highly dispersed hematite-based MCs (10 mg mL−1) on a piece of cleaned fluorine-doped tin oxide (FTO)-coated glass (2.5 × 1.7 cm). To obtain the stable films, the above-prepared electrodes were annealed in a furnace at 700 °C for 20 min in the air with a heating rate of 20 °C min−1 and collected for further use after naturally cooling. This annealing treatment is also a key step for the formation of dopant oxide overlayers by accelerating the dopant segregation to the hematite surface.

Characterizations. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) measurements were performed on a Dimension Icon (Bruker) using a silicon nitride probe (Bruker, PFQNE-AL). FE-SEM observations were performed on JSM-7100F (JEOL). TEM observations were performed on JEM-2100F (JEOL) operated at 200 kV. EDX mapping and HAADF-STEM images were collected with a FEI Tecnai F20 G2. EELS analysis was performed on a JEOL ARM200F cold field emission (JEOL) microscope operated at 200 kV. The powder XRD patterns were recorded on a Rigaku Ultima IV diffractometer with Cu Ka radiation (λ = 1.5418 Å) at a voltage of 40 kV and a current of 40 mA. The XPS measurements were performed on a PHI X-ray photoelectron spectrometer (ULVAC-PHI). The spectra were calibrated by the reference of the C1s peak at 284.8 eV. Synchrontron-based X-ray total scattering measurements with a synchrotron beam (HELIG) were performed at the Greek beamline of the ECLIPSE 16.4.1 (9.44 Å) and 14.1.1 (8.3 Å) at the Advanced Light Source (ALS, beamline 6.0.8). A xenon light source (Asahi Spectra, LAX-C100) equipped with an AM 1.5 filter with the light intensity of 100 mW cm−2 was used to illuminate the electrodes (CS-30) on the backside (through the FTO glass) with a working area of 0.72 cm2. The current–voltage curves were obtained by cyclic voltammetry at a scan rate of 20 mV s−1. All the applied potentials have been converted into the potential vs. RHE via the Nernst equation (ERHE = ERHEAg/AgCl + 0.359 × pH + 0.1995). The EIS measurements were performed at 123 V vs. RHE with frequencies between 0.5 Hz and 10 kHz under back illumination with the simulated sunlight. The Mott–Schottky plots were measured in the dark at a frequency of 10 kHz.

PEC measurements. The PEC measurements were conducted in a typical three-electrode system in 1.0 M NaHCO3 aqueous solution (pH = 8.3) with the fabricated hematite MC-based film as a working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode with saturated KCl solution as the reference electrode. The electrodes with photoanode and cathode were separated with a membrane (Sigma-Aldrich). All the EIS data were recorded and analyzed on an electrochemical workstation (ALS, model 605E). A xenon light source (Asahi Spectra, LAX-C100) equipped with an AM 1.5 filter with the light intensity of 100 mW cm−2 was used to illuminate the electrodes (CS-30) on the backside (through the FTO glass) with a working area of 0.72 cm2. The current–voltage curves were obtained by cyclic voltammetry at a scan rate of 20 mV s−1. All the applied potentials have been converted into the potential vs. RHE via the Nernst equation (ERHE = ERHEAg/AgCl + 0.359 × pH + 0.1995). The EIS measurements were performed at 123 V vs. RHE with frequencies between 0.5 Hz and 10 kHz under back illumination with the simulated sunlight. The Mott–Schottky plots were measured in the dark at a frequency of 10 kHz.

Product analysis. The evolved gas from the PEC cell was analyzed by a GC (Shimadzu, GC-8A) equipped with an MS-5A column and a thermal conductivity detector. To remove air in the reactor, the electrolyte solutions in well-sealed working and counter electrode cells were collected by the Naion membrane were bubbled with Ar gas for at least 30 min before the measurements. To minimize the influence of air leaks, the analysis of gas products was carried out independently using the same electrode under the same conditions. A relatively large amount of gas sample (50 mL) from the working electrode cell was measured every time for O2 detection. 20 μL of gas sample from the counter electrode cell was collected and measured for H2 evolution. The GC was calibrated by injecting various concentrations of pure O2 and H2 gases (Supplementary Fig. 3). In addition, the gases (O2 and H2)olutions were prepared using N,N-dicyclohexyl-1,4-phenylenediamine (DPD) sulfate. Typically, 200 μL sample aliquots collected with a syringe during irradiation were mixed with 200 μL potassium phosphate buffer solution (pH = 7), 2 mL water, 20 μL DPD solution (0.1 g DPD in a 10 mL 0.05 M H2SO4 solution), and 20 μL freshly prepared peroxidase (POD) solution (3 mg POD in 3 mL deionized water), and the mixture was shaken for 120 s. The above solutions were analyzed by UV–vis spectroscopy (JASCO, V-700). The H2O2 concentrations were calibrated with standard H2O2 solutions. The concentration of dissolved O2 in the electrolyte was evaluated using a free radical analyzer (World Precision Instruments, TBR4100), which is based on an electrochemical (amperometric) detection, with an ISO-OX-2 oxygen sensor (World Precision Instruments). The detected currents were converted to O2 concentrations using the obtained calibration curve.

DFT calculations. All the calculations reported in this work were carried out using the revised version of Perdew-Burke-Ernzerhof exchange-correlation functional97 and the projector-augmented wave method as implemented in Vienna Ab Initio Simulation Package. The spin-polarization effect and dipole correction were considered (through the FTO glass) with a working area of 0.72 cm2. To perform the geometry optimization of the anti-ferromagnetic bulk system with a cut-off energy of 520 eV and Monkhorst–Pack k-point meshes of 4 × 4 × 4 to determine the lattice constants, and then by using 4 Fe-layers with a vacuum of 15 Å and 4 × 4 × 1 Monkhorst–Pack k-points. For the calculations of OH* and O*, several coverage patterns have been considered, from 1/12 to 0.5, corresponding to 1 and 6 adsorbates per cell. For Fe3O4, a Hubbard U value of 4.3 eV was employed. The computational hydrogen electrode was employed, for which the Gibbs free energy of 1/2 H2 = 0 + 2 e− is set to zero. The charging energy was computed as ΔG = ΔE + AZPE − TAS, where traditionally reported values are used for the zero-point energy and entropy to compute AZPE − TAS at standard temperature.
conditions, since they are known to be very similar between different oxides. For the calculations of SnO$_2$... the same procedure as Fe$_2$O$_3$ was employed, except that the cut-off energy used was 400 eV and the (110) slab model consisted of 1 x 2 super-cell with 8 Sn-layers. The adsorption energies were computed with one adsorbate for each of the 8 Sn-layers. The VD$_{2}$O$_{3}$ dependence of the volcano plot was investigated with changing vacancy sites (Supplementary Fig. 28).

Data availability
Source data are provided with this paper.

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References
1. Vurgaftman, I., Meyer, J. R. & Ram-Mohan, L. R. Band parameters for III-V compound semiconductor and their alloys. J. Appl. Phys. 89, 5815–5857 (2001).
2. Ahn, C. H. Ferroelectricity at the nanoscale: local polarization in oxide thin films and heterostructures. Science 303, 488–491 (2004).
3. Zhou, P., Yu, J. & Jaroniec, M. All-solid-state Z-scheme photocatalytic systems. Adv. Mater. 26, 4920–4935 (2014).
4. Marichy, C., Bechelany, M. & Pinna, N. Atomic layer deposition of nanoscale films for energy and environmental applications. Adv. Mater. 24, 1017–1032 (2012).
5. Gong, Y. et al. Vertical and in-plane heterostructures from WS$_2$/MoS$_2$ and related materials. Nat. Mater. 13, 1133–1142 (2014).
6. Kliewer, K. L. & Koehler, J. S. Space charge in ionic crystals. I. General theory of the space charge concept. J. Chem. Phys. 3, 5576–5591 (2005).
7. Soares, M. R. S. et al. Unraveling the role of Sn segregation in the electronic transport of polycrystalline hematite: raising the electronic conductivity by lowering the grain-boundary blocking effect. Adv. Electron. Mater. 5, 1900065 (2019).
8. Hwang, S.-L. & Chen, I.-W. Grain size control of tetragonal zirconia polycrystals. J. Am. Ceram. Soc. 87, 3269–3277 (2004).
9. Li, W., Shi, J., Zhang, K. H. L. & Macmanus-Driscoll, J. L. Defects in complex oxide thin films for electronics and energy applications: challenges and opportunities. Mater. Horiz. 7, 2832–2859 (2020).
10. Colfen, H. & Antonietti, M. Mesocrystals: inorganic superstructures made by highly parallel crystallization and controlled alignment. Angew. Chem. Int. Ed. 44, 5576–5591 (2005).
11. Tachikawa, T. & Majima, T. Metal oxide mesocrystals with tailored structures and properties for energy conversion and storage applications. NPG Asia Mater. 6, 1–11 (2014).
12. Sayama, K. Production of high-value-added chemicals on oxide semiconductor photoanodes under visible light for solar chemical-conversion processes. ACS Energy Lett. 3, 1093–1101 (2018).
13. Fuku, K. & Sayama, K. Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/brass oxide heterostructured photoanode. Chem. Commun. 52, 5406–5409 (2016).
14. Shi, X. et al. Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide. Nat. Commun. 8, 701 (2017).
15. Campos-Martin, J. M., Blanco-Brieva, G. & Fierro, J. L. G. Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. Angew. Chem. Int. Ed. 45, 6962–6989 (2006).
16. Hermans, Y., Murcia-López, S., Klein, A. & Jaegermann, W. BiVO$_4$ surface reduction upon water exposure. ACS Energy Lett. 4, 2522–2528 (2019).
17. Sivula, K., Le Formal, F. & Grätzel, M. Solar water splitting: progress using hematite (α-Fe$_2$O$_3$) photoelectrodes. ChemSusChem 4, 432–449 (2011).
18. Shen, S., Lindley, S. A., Chen, X. & Zhang, J. Z. Hematite heterostructures for photoelectrochemical water splitting: rational materials design and charge carrier dynamics. Energy Environ. Sci. 9, 2744–2775 (2016).
60. Zhang, X., Klaver, P., van Santen, R., van de Sanden, M. C. M., & Bieberle-Hütter, A. Oxygen evolution at hematite surfaces: the impact of structure and oxygen vacancies on lowering the overpotential. *J. Phys. Chem. C* **120**, 18201–18208 (2016).

61. Man, I. C. et al. Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159–1165 (2011).

62. Sanson, A., Mathon, O., & Pascarelli, S. Local vibrational dynamics of hematite (α-Fe2O3) studied by extended X-ray absorption fine structure and molecular dynamics. *J. Chem. Phys.* **140**, 1–8 (2014).

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**Author contributions**

Z.Z. and T. Tachikawa wrote the paper with contributions from all co-authors. Z.Z. synthesized the materials and performed most of the experiments. Z.Z. and T. Tachikawa performed the data analysis. T. Tsuchimochi and S.L.T. performed the DFT calculations. T.I. performed the X-ray absorption measurements. Y.K. performed parts of the PEC experiments and data analysis. S.M. performed the STEM/EELS measurements. K.O. and H.Y. performed the X-ray total scattering measurements. T. Tachikawa conceived and supervised the project.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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