**Supplementary Information**

**Ge-doped Hematite for an Unassisted Water Splitting System with Enhanced Efficiency**

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**Supplementary Fig. 1 | SEM and TEM images of FeOOH and Ge doped FeOOH.** The top-view (a-1 and b-1) and cross-sectional (a-2 and b-2) SEM images and a TEM image (a-3 and b-3) of **a,** FeOOH nanorod and **b,** Ge-doped FeOOH nanorod.

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**Supplementary Fig. 2 | TEM image of GeO2/FeOOH. a,** STEM image of the entire GeO2/FeOOH nanorod and the corresponding elemental mapping image of **b,** Fe, **c,** O, **d,** Ge, **e,** Sn and **f,** C.

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**Supplementary Fig. 3 | Sn diffusion process.** Illustration of Sn diffusion **a,** without the GeO2 layer (H and Ge-H) and **b,** with the GeO2 layer (Ge-PH).



**Supplementary Fig. 4 | BET analysis for surface area.** SEM images of powder type hematite for BET measurements. **a,** H, **b,** Ge-H and **c,** Ge-PH. **d,** N2 adsorption-desorption isotherms of H, Ge-H and Ge-PH. The BET surface area of each sample is around 2 m2/g (H and Ge-H) and 10 m2/g (Ge-PH). **e,** The pore distribution in H, Ge-H and Ge-PH. **f,** The calculated ECSA values of each photoanode.

For the BET measurement, we collected each precipitate prepared with the same process as the hematite nanorods on the FTO substrate to ensure sufficient quantity of the samples (0.5 g). The morphology of these precipitates is very similar to the nanostructure grown on the FTO substrate as shown in Supplementary Figs.4a-c. As shown in Supplementary Figs.4d and 4e, the surface area of porous hematite (Ge-PH, 10 m2/g) is higher than that of nonporous hematite (H and Ge-H, 2 m2/g). We also carried out the electrochemically active surface area (ECSA) from cyclic voltammetry CV curves as shown in Supplementary Fig. 4f. The ECSA results of Ge-H and Ge-PH were improved by Ge doping and the highest values of Ge-PH were obtained.



**Supplementary Fig. 5 | PEC performance and hematite crystallinity of various dopants in hematite.** SEM images of **a,** Sn-doped, **b,** Ti-doped and **c,** Si-doped porous hematite. **d,** J-V curves of each photoanode. **e,** XRD patterns of hematite with different dopants and **f,** the zoomed image in e showing the (110) and (300) plane.

We created a porous structure with Sn, Ti, Si doping based on previous studies, by dipping in SnCl4, TiCl4 or APTMS solutions as shown in Supplementary Fig. 5a-c. Supplementary Fig. 5d shows that Ge-doped hematite had the best performance. In the case of Si-doping, particularly, the PEC performance decreased significantly. This is probably because to be doped in hematite, Si requires a high enthalpy energy of formation during thermal diffusion. This result is consistent with the calculated formation energies. For Si-doped Fe2O3, most fabrication systems were achieved using ultrasonic spray pyrolysis (USP) or atmospheric pressure chemical vapor deposition (APCVD). These approaches involve nonequilibrium processes. Therefore, considering formation energy, structural evolution is essential for doping through an overlayer. This is consistent with the results for crystallinity shown in Supplementary Figs. 5e and 5f. Although most peaks of hematite’s crystallinity were overlapped by the peaks of FTO substrate, it can be seen that Ge-doped hematite has the best crystallinity in the (110) and (300) plane. This well matches the calculated formation energies for dopant solubility in hematite.

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**Supplementary Fig. 6** **|** Onset potential of various photoanodes in our experiments.

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**Supplementary Fig. 7** **|** The photoelectrochemical performance of Ge-H according to the amount ofdifferent Ge precursors in 100 ml of 150 mM FeCl3.

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**Supplementary Fig. 8 |** The depth profiles of (Sn+Ge)/Fe ratio.

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**Supplementary Fig. 9 | The PEC performance by different light illumination.** **a,** Schematic representation of electron/hole transport in a hematite photoanode under front and backside illumination. LSV curves of **b,** Ge-H and **c,** Ge-PH under front and backside illumination.



**Supplementary Fig. 10 |** J-V curve of perovskite solar cell under illumination.

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**Supplementary Fig. 11 |** Stability of NiFeOx/Ge-PH at 1.23VRHE for an extended period.

**Supplementary Table 1.** Recent reports on single hematite-based photoanodes with representative dopants (Si, Ti, Sn and Ge). The photocurrent density of all reports at 1.00VRHE was confirmed approximately.

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**Supplementary Table 2.** Recent reports on single hematite-based photoanodes for unassisted solar water splitting systems.

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