

Local structures of hematite-mesocrystal-based photoanodes for efficient and selective solar water splitting

Hydrogen peroxide (H_2O_2) has attracted considerable interest owing to its usefulness as a green oxidant for applications in industrial chemistry and environmental purification, as well as a clean energy source for fuel cells. Solar-driven photoelectrochemical (PEC) water splitting is one of the ideal strategies for the on-site production of H_2O_2 and CO_2 -free H_2 gas [1]. PEC H_2O_2 production has been mostly realized by a two-electron pathway of water oxidation using BiVO_4 -based photoanodes, but these photoanodes are expensive and have low stability. Alternatively, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is naturally abundant with good stability and a suitable bandgap (~ 2.1 eV) for the absorption of sunlight, and has been extensively studied for use in solar-driven water oxidation to generate O_2 . However, there are no reports on hematite-based photoanodes for water oxidation to obtain H_2O_2 , probably because of their unfavorable surface properties.

A mesocrystal (MC) is an ordered assembly of nanoparticles via oriented attachment and has been applied as a photocatalyst [2]. We have recently discovered that the thermal treatment of hematite MCs at high temperatures (e.g., 700°C) induces the sintering of the interface, which creates numerous interfacial oxygen vacancies (V_O) for the enhanced separation of photogenerated electrons and holes [3,4].

Herein, we present MC-based dopant segregation to effectively modify the hematite MCs surface for highly efficient and selective solar-driven H_2O_2 production (Fig. 1) [5]. The sintering of highly ordered interfaces between the nanocrystal subunits inside the MC eliminates substantial grain boundaries, leading to the efficient segregation of dopants on the external surface, which results in the formation of deficient SnTiO_x overlayers for H_2O_2 production.

The synchrotron-based X-ray total scattering with pair distribution function (PDF) analysis, which is a powerful method of characterizing disordered or amorphous structures, was performed with the incident X-ray energy of 61.4 keV at SPing-8 **BL04B2**. Data were collected using the hybrid detectors of Ge and CdTe. The reduced PDF $G(r)$ was obtained by the conventional Fourier transform (FT) of the Faber–Ziman structure factor $S(Q)$ extracted from the collected data. The as-synthesized Sn- and Ti-doped hematite ($\text{SnTi-Fe}_2\text{O}_3$) sample shows a peak shift, along with the broadening of the peaks, towards a larger interatomic distance (r) than the undoped Fe_2O_3 sample (Fig. 2), suggesting the expansion of the hematite lattice due to the replacement of Fe^{3+} sites by the larger Sn and Ti atoms. The thermal treatment at 700°C in air for 20 min leads to a lattice rearrangement in the bulk, as indicated by the peak shifts toward the profile of the undoped Fe_2O_3 sample. Considering that the length of the corner-sharing Ti–Ti (and Sn–Sn) bond of rutile TiO_2 (and SnO_2) is 3.55 Å (and 3.68 Å), the increase in amplitude at 3.5–3.7 Å implies the formation of the dopant oxide overlayers.

To elucidate the local structures of the overlayers, X-ray absorption spectra (XAS) at Ti and Sn K -edges were collected at SPing-8 **BL01B1**. The samples were prepared by pelletizing the uniform mixtures of hematite-based MCs or reference samples with dehydrated boron nitride powders. Figure 3(a) shows the normalized Ti K -edge XANES spectra of the Ti-containing samples. For transition metals in oxides, the threshold energy position of the spectrum is sensitive to their oxidation states, while the shapes of the peaks give information about the local structural environments of the absorbing elements. The peak shapes of the annealed Ti-doped hematite ($\text{Ti-Fe}_2\text{O}_3$)

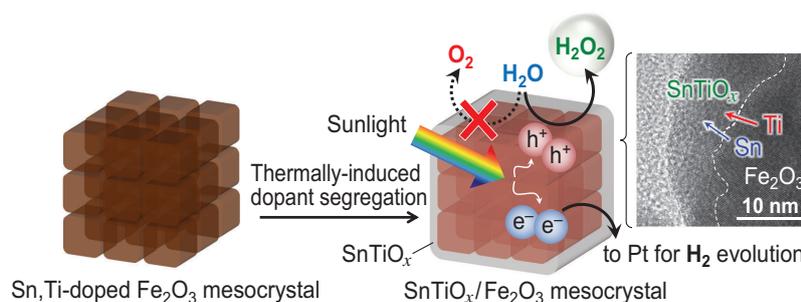


Fig. 1. Hematite-mesocrystal-based photocatalyst for solar H_2O_2 production. A hematite mesocrystal is a superstructure of particles, each around 20 nm in size. The segregation of Sn and Ti atoms doped in the mesocrystal was thermally induced to form a composite oxide (SnTiO_x) layer. A transmission electron microscopy image is also shown.

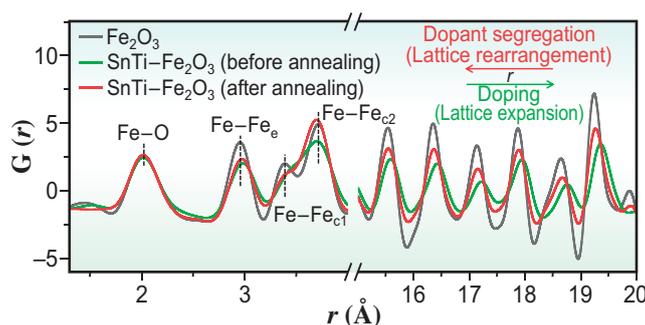


Fig. 2. Synchrotron-based X-ray total scattering measurements with PDF analysis. The peak at approximately 2 Å is composed of shorter Fe–O (1.94 Å) and longer Fe–O (2.12 Å) distances. The peak at approximately 3 Å is composed of the first-neighbor edge-sharing (Fe–Fe_e, 2.95 Å) and face-sharing (Fe–Fe_f, 2.90 Å) Fe–Fe distances. The first- and second-neighbor corner-sharing Fe–Fe pairs are at 3.39 Å (Fe–Fe_{c1}) and 3.72 Å (Fe–Fe_{c2}), respectively.

MCs in pre- and post-edge regions are similar to those of rutile TiO₂, suggesting the formation of the rutile overlayer. For the annealed SnTi–Fe₂O₃ sample, the characteristic peak of rutile TiO₂ in the pre-edge region was not clearly observed.

In situ Sn K-edge FT-EXAFS measurements helped us to gain more information on the dynamics of thermally induced dopant segregation. For the annealed SnTi–Fe₂O₃ sample, as shown in Fig. 3(b), the second main shell has a shorter radial distance than that of SnO₂ owing to the formation of Sn–Ti coordination. The peak intensity of the Sn–Fe coordination shell gradually decreases with increasing temperature from

48 to 700°C because the Sn coordination becomes disordered as a result of the diffusion of Sn atoms from the hematite lattice. On the other hand, the Sn–Ti coordination peak appears at approximately 700°C and becomes stronger during the heat preservation and cooling stages. From these results, we concluded that Sn atoms initially migrate from the hematite lattice owing to their larger radius and segregate on the surface to form the SnO₂ phase. The deficient SnTiO_x overlayers are then formed when Ti atoms segregate at the surface and react with SnO₂ at 700°C (Fig. 1). The composite overlayers on the hematite MCs could act as co-catalysts for highly selective solar H₂O₂ synthesis.

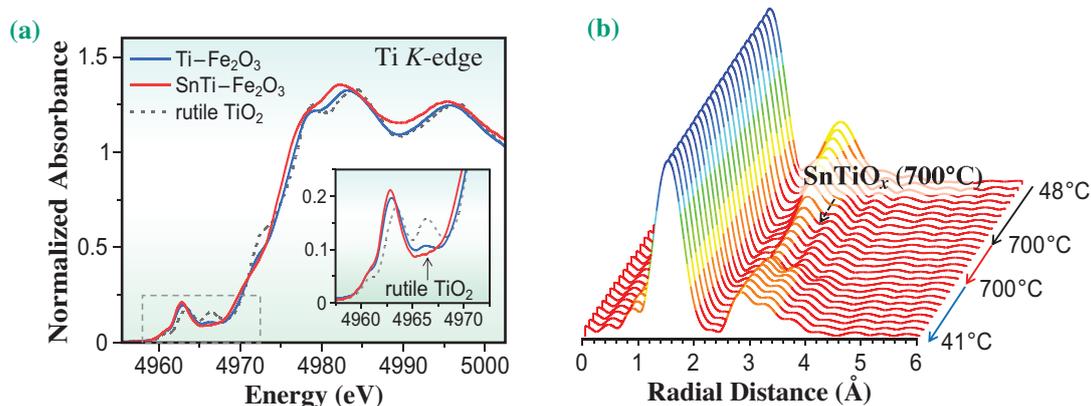


Fig. 3. X-ray absorption spectroscopy (XAS) measurements. (a) *Ex situ* Ti K-edge XANES spectra of annealed Ti-containing samples and reference samples. (b) *In situ* Sn K-edge FT-EXAFS spectra of as-synthesized SnTi–Fe₂O₃ measured with a heating procedure similar to that used for electrode preparation.

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