

強誘電体の可視光起電力効果 —光誘起逐次酸化還元—

Visible-light ferrophotovoltaics — Light-induced successive redox reactions —

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In this presentation, I report *successive-redox* mediated ferrophotovoltaics, where two gap states enable e^-h^+ pair formation in a wide photon-energy ($h\nu$) range. Our approach is based on acceptor and donor states that act as scaffolds for generating photoinduced carriers. A single transition-metal dopant with two different valence states in the ground state introduces these gap states and thereby provides successive redox cycles under illumination. This is, in principle, capable of activating a PV response at small $h\nu$ without being restricted by material bandgap. Our experimental and theoretical study on a prototypical ferroelectric BaTiO₃ demonstrates that the 3d orbitals of iron derive donor and acceptor states in the Fe²⁺-Fe³⁺ coexisting state and also that e^-h^+ pairs injected by two sequential Fe³⁺/Fe²⁺ reactions deliver a robust PV effect not only under visible light but also at $h\nu$ greater than E_g .

Figure 1b indicates the current density (J) vs. bias voltage (V) properties under light with $h\nu = 3.1$ eV of BaTiO₃ single crystals in the single domain state. The oxidized sample (Fe³⁺) exhibits a short-circuit J (J_{sc}) of -32 nA/cm² and an open-circuit voltage (V_{oc}) of 5.9 V. I note that the reduced sample (Fe²⁺-Fe³⁺) show a markedly large response: a J_{sc} of -520 nA/cm² is over one order of magnitude larger and an V_{oc} of 35 V is approximately six times as large as that of the oxidized one. Figure 1e shows the normalized current I/I_{opt} as a function of photon energy ($h\nu$). The reduced sample (Fe²⁺-Fe³⁺) exhibits a much higher I/I_{opt} in a wide $h\nu$ range. The first onset is estimated at ~ 1.6 eV, which agrees well with 1.5 eV of the difference of the CBM – Fe-3d_{z²} for Fe²⁺-V_O^{••}. The second onset was found at ~ 2.0 eV, which is in quantitative agreement with the difference between the VBM and the empty states for Fe³⁺ and Fe³⁺-V_O^{••}. I found that the third onset appears at ~ 2.3 eV, which accords with the gap for the CBM – the filled Fe-3d_{x²-y²} state for Fe²⁺-V_O^{••}.

1. Noguchi, Y., Taniguchi, Y., Inoue, R. & Miyayama, M. *Nat. Commun.* 11, 1–10 (2020).

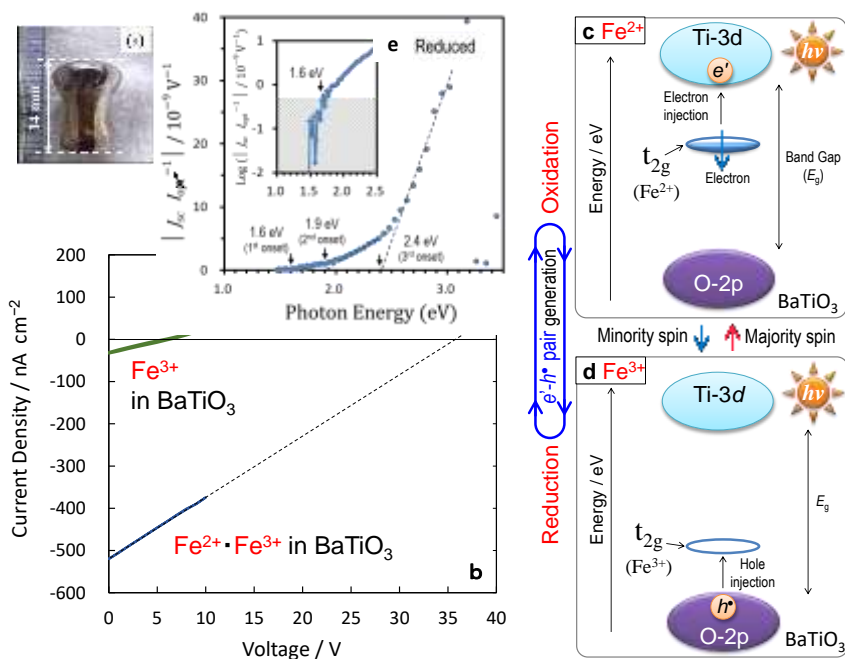


Figure 1 Successive-redox mediated photovoltaic properties of Fe-doped BaTiO₃ single crystals (a) in the single domain state. b Current voltage properties under light with $h\nu = 3.1$ eV of the oxidized sample (Fe³⁺) and the reduced sample (Fe²⁺-Fe³⁺). In the Fe²⁺-Fe³⁺ coexisting state, electron-hole pairs can be generated under visible light through c electron injection induced from the electron-filled Fe²⁺ (d_{z²}) state to the conduction band (Ti-3d) associated with the iron oxidation (Fe²⁺ → Fe³⁺) and d hole injection from the unoccupied Fe³⁺ states (e.g., d_{xy}) to the valence band (O-2p) along with the iron reduction (Fe³⁺ → Fe²⁺). These successive-redox reactions could deliver visible-light photovoltaic effect.