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Charge Transport in $SrTiO_3$:Rh Nanoparticle Photocatalysts for Z-Scheme Water Splitting

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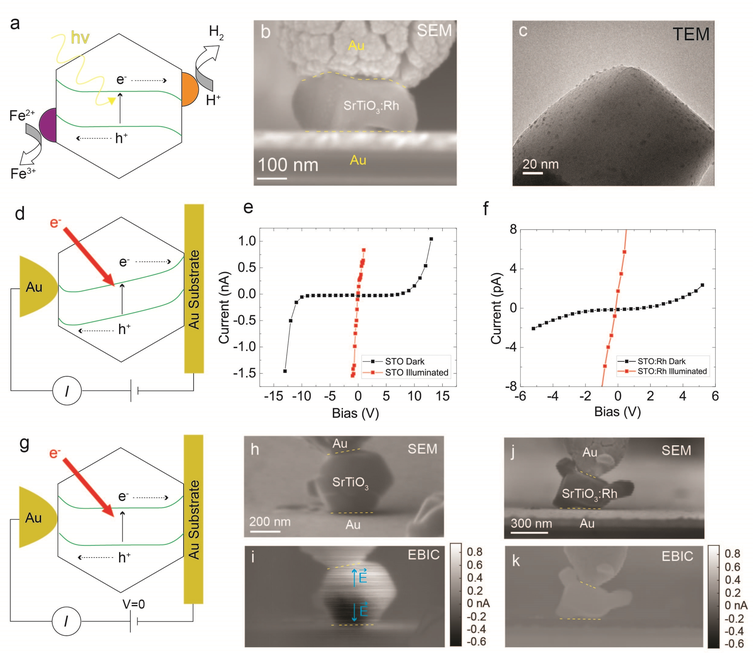
Abstract

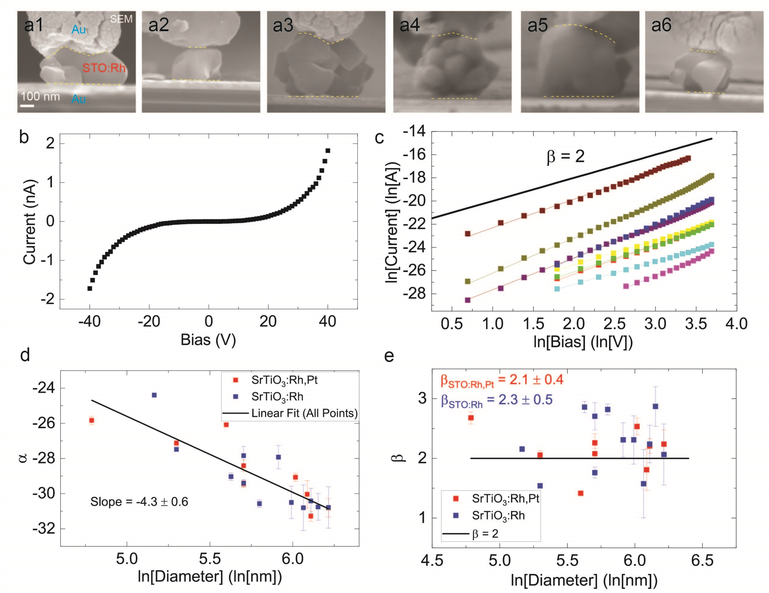
Solar-powered photochemical water splitting using suspensions of photocatalyst nanoparticles is an attractive route for economical production of green hydrogen. $STiO_3$-based photocatalysts have been intensely investigated due to their stability and recently demonstrated[1] near-100% EQY for water splitting using wavelengths below 400 nm. To extend the optical absorption into the visible, $SrTiO_3$ nanoparticles have been doped with various transition metals. Here we demonstrate that doping $SrTiO_3$ nanoparticles with 1% Rh introduces mid-gap acceptor states which reduce the free electron concentration by five orders of magnitude. With the $SrTiO_3$:Rh particles depleted of free carriers, the charge transport mechanism evolves from band to trap-limited conduction, and built-in potential needed for efficient charge separation are dramatically reduced to less than 1 mV. Rhodium states also function as recombination centers, reducing the photocarrier lifetime by nearly two orders of magnitude, and the maximum achievable EQY to 10%, independent of light wavelength. Furthermore, the absence of built-in electric fields within Rh-doped $SrTiO_3$ nanoparticles suggests that modest e-h separation can be achieved by exploiting a difference in mobility between electrons and holes.

Imaging Internal E Fields within Invididual $SrTiO_3$ Nanoparticles



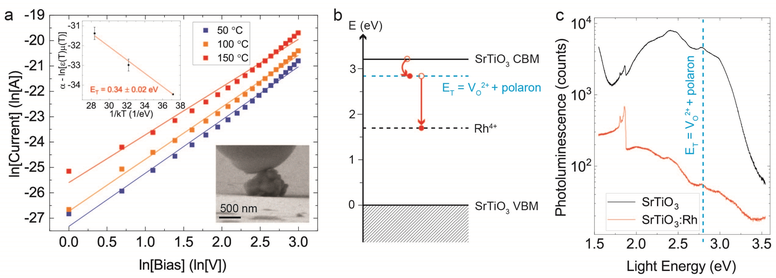
(a) A cartoon of a photocatalytic nanoparticle with band-bending (green lines) that separates charge to evolve hydrogen gas and oxidize a redox mediator in solution. (b) A gold nanoprobe makes electrical contact with an $SrTiO_3$:Rh nanoparticle within the SEM. (c) A high-magnification TEM image of an $SrTiO_3$:Rh particle resolves 5~nm Pt co-catalysts on its surface. (d) Electrons injected by the primary electron beam create e-h pairs analogously to irradiation by light. I-V curves become linear in both unintentionally doped (e) $SrTiO_3$ and Rh-doped $SrTiO_3$ (f) under e-beam illumination, and the photocarrier lifetimes of 70 ps and 1 ps, respectively, are extracted assuming ideal betaconduction. (g) Absent applied bias, EBIC acquired (i) from the same $SrTiO_3$ particle as (e,h) reveals strong built-in E fields at both Au-$SrTiO_3$ interfaces. Conversely, EBIC acquired (k) from the Rh-doped $SrTiO_3$ particle of (f,j) no built-in E field due to a lack of free carriers. Dashed-yellow lines are drawn on the SEM and EBIC images to mark the Au-$SrTiO_3$ interfaces.

Space-Charge Limited Transport



(a1-a6) SEM micrographs of representative $SrTiO_3$:Rh photocatalyst particles of varying sizes, with (a1-a3) and without Pt co-catalysts (a4-a6). Dashed-yellow lines are drawn on the SEM images to mark the Au-\$SrTiO_3$:Rh interfaces. (b) In dark conditions, I-V data is nonlinear, indicative of non-Ohmic transport. (c) Transport data from 9 nanoparticles can be linearized on a log-log scale, in agreement with SCLC conduction[2], $I = 9A\varepsilon_r\varepsilon_0V^2N_cExp[E_T/kT]/8D^3N_t$. (d) Constant-field conductivity ($\alpha = \ln[9A\varepsilon_r\varepsilon_0V^2N_c/8D^3N_t] - E_T/kT$) exhibits a strong dependence on particle diameter, independent of the presence of a Pt co-catalyst. (e) Variable-field conductivity (β) is, within its error bar, equal to the ideal value of 2 for both platinized and bare nanoparticles.

Rhodium Dopants Trap Free Electrons



(a) Temperature-dependent conduction in a single $SrTiO_3$:Rh nanoparticle. A trap energy of 0.34 ± 0.02 eV is extracted, corresponding to an oxygen vacancy bound with a polaron[3]. (b) Energy band diagram for $SrTiO_3$:Rh with oxygen vacancy and Rh trap levels. Rhodium atoms form an acceptor state which traps the free electrons donated by oxygen vacancies, transforming conduction to SCLC. (c) PL taken from unintentionally doped and $SrTiO_3$:Rh nanoparticles confirms the presence of an oxygen vanacy trap at 2.8 eV above the valence band (marked with dashed-blue line). The PL intensity of $SrTiO_3$:Rh is 84 times lower, presumably due to non-radiative recombination via rhodium states.

[1] Takata et al. "Photocatalytic Water Splitting with a Quantum Efficiency of Almost Unity". Nature **2020**, *581*, 411-414
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[3] Janotti et al. "Vacancies and Small Polarons in $SrTiO_3$" Physical Review B. **2014**, *90*, 085202

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