

Supporting Information

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SI Text

Materials and Methods. All the solvents and chemicals, unless otherwise stated, were obtained from Sigma-Aldrich or its subsidiaries and were used without further purification. Aqueous solutions were prepared with purified water (Millipore Corp., 18.2 M Ω cm at 25 °C). All experiments were performed at room temperature.

Preparation of APCVD hematite electrodes. The photoanodes were prepared according to the atmospheric pressure chemical vapor deposition (APCVD) method previously described (1, 2). In brief, the liquid precursors—iron pentacarbonyl (Fe(CO)₅, Acros, 99.5%) and tetraethoxysilane (TEOS, Aldrich 99.9999%)—are brought to the gas phase by bubbling argon in the corresponding vials. The vapor streams are then mixed and diluted in the carrier gas (dry air), which is targeted at a substrate (FTO, TEC 15, TEC 15, Hartford Glass Co.) heated at ca. 420 °C on a titanium block in a closed chamber. The iron oxide film obtained is formed by the agglomeration of small Fe₂O₃ particles (ca. 5 nm) nucleated in the gas phase, resulting in a cauliflower-like nanostructure.

Preparation of ultrathin USP hematite electrodes. FTO substrates (TEC 15, Hartford Glass Co.) were modified with a monolayer of SiO_x by spraying TEOS (99.999%, Aldrich) 10 vol.% in ethanol. Then, 10 mL of an ethanol solution of 10 mM iron(III) acetylacetonate [Fe(acac)₃, 97%, Aldrich] was sprayed on the substrates placed on a hotplate at 793 K, which produced a conformal hematite layer 20 nm in thickness in typical cases (3).

Deposition of CoO_x overlayer. Electrodeposition of CoO_x overlayers on APCVD hematite photoelectrodes was carried out by modification of procedures published elsewhere (4). A three-electrode setup was employed with hematite as the working electrode, Ag/AgCl/0.3 M NaCl (SSC) as the reference electrode, and Pt gauze as the counter electrode. The electrolyte solution contained 0.5 mM cobalt nitrate hexahydrate solution in 0.1 M phosphate buffer adjusted to pH 7. The working electrode was subjected to 1.0 V vs SSC, controlled by a PGSTAT101 potentiostat (Metrohm Autolab), and the thickness of the CoO_x layer was controlled by changing the time of deposition. For the electrodes reported in this work, the CoO_x layer was obtained with a deposition time of 600 s.

Cobalt treatment. Adsorption of Co²⁺ onto the surface of untreated or treated hematite was achieved by dipping the photoanode in 0.5 mM cobalt nitrate hexahydrate solution in 0.1 M potassium phosphate buffer adjusted to pH 7.

Deposition of Ga₂O₃ overlayer. USP hematite thin films were modified with a Ga₂O₃ overlayer by chemical bath deposition (CBD) (3). The hematite thin films were immersed into 100 mL of water at approximately 348 K. To this solution, 0.418 g of Ga(NO₃)₃·nH₂O and 6.01 g of urea were added successively with an interval of a few minutes under mild stirring. After 15 min of the urea addition, the thin films were rinsed with water and calcined at 773 K for 2 h.

Photoelectrochemical and spectroelectrochemical characterization. Photoelectrochemical studies were carried out in a single-compartment, homemade PEC cell, in a three-electrode configuration with SSC as reference electrode, Pt gauze as counter electrode, and the hematite photoanode as working electrode. The electrolyte solution employed was 0.1 M aqueous NaOH (pH 12.6). Photoanodes were illuminated through the electrolyte-electrode interface (EE) by a 75-W ozone-free Xe lamp (Hamamatsu) adjusted to 1 Sun AM 1.5 simulated sunlight. Potentials were controlled using a PGSTAT101 potentiostat (Metrohm Autolab), and scan rates of 10 mV/s were employed for current density measurements. The same setup (PEC cell and potentiostat) was used for the spectroelectrochemical studies. Here, the PEC cell was incorporated in the sample compartment of a Perkin Elmer (Lambda 25) spectrophotometer, and the optical absorption changes were recorded as a function of applied bias.

Transient absorption spectroscopy. Transient absorption studies on the μ s time scale were obtained using the setup described previously (5). The third harmonic of a Nd:YAG laser (Continuum Surelite I-10, at 355 nm, 6 ns pulse width) as excitation source, with laser intensity of 0.20 ± 0.02 mJ cm⁻² and repetition rate of 0.33 Hz. A 75 W Xe lamp (Hamamatsu) is used as the probe light with monochromators both before and after the sample, and the transmitted light level is measured by a Si PIN photodiode (Hamamatsu) as a function of time following laser excitation of the sample. The transient decay data are the result of averaging between 300 and 1,000 laser shots. Hematite photoanodes were placed in a sealed quartz cuvette filled with electrolyte solution (0.1 M NaOH) for the studies on isolated electrodes (without bias control). For transient measurements under operating conditions (with external electric bias), a two-compartment (not separated by a membrane), homemade, three-electrode PEC cell with borosilicate windows was used. The photoanode was placed in one of the compartments, while the reference (SSC) and counter (Pt gauze) electrodes were placed in the second compartment, shielded from laser and probe lights.

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