

Supporting Information:

Experimental:

1.5 cm x 2.5 cm FTO samples were cleaned ultrasonically for 60 min in a 1:1:1 solution of water, isopropanol and ethanol. For seeding TiO₂ nanoparticles on FTO, the FTO substrate was immersed in 3 ml of 0.05 M TiCl₄ solution at 70 °C for 60 minutes. The FTO samples were removed and rinsed with deionized water to remove remaining precipitants.

For seeding rutile nanorods on FTO the FTO pieces were immersed in a solution of 60 ml water, 60 ml 37% hydrochloric acid and 2 ml Titaniumdiisopropoxide-bis(acetylacetonate), mixed inside a Teflon beaker, with an angle of around 30 ° against the wall of the Teflon beaker in a custom made Teflon holder. The Teflon beaker was placed in a stainless steel autoclave and moved to an oven. The synthesis was conducted at 150 °C for 4 h. After synthesis, the autoclave was cooled down to room temperature under flowing water. The rutile nanorod seeded samples were taken out and rinsed extensively with deionized water to remove precipitants.

For growing tantalum doped rutile nanorods on the pre-seeded samples, a solution of 30 ml water, 30 ml 37% hydrochloric acid was prepared inside a Teflon beaker. 1.2 ml Titaniumdiisopropoxide-bis(acetylacetonate) and 10 μl – 50 μl Tantalum(V) isopropoxide were successively added to the mixture. The pre-seeded samples were immersed into the solution with an angle of around 30 ° against the wall of the Teflon beaker in a custom made Teflon holder. The Teflon beaker was placed in a stainless steel autoclave and moved to an oven. The synthesis was conducted at 200 °C for 4 h and the autoclave was cooled down to room temperature under flowing water after synthesis. The samples were taken out and rinsed extensively with deionized water to remove precipitants. The as grown nanorods were annealed at temperatures from 450°C to 650° C to remove the adsorbed chloride ions.

For IPCE and UV impedance measurements, a standard 3-electrode electrochemical cell with a 0.5 cm x 0.5 cm Pt plate counter electrode, an Ag/AgCl reference electrode (3M KCl) and a 0.1 M Na₂SO₄ electrolyte were used and a standard bias of +500 mV against Ag/AgCl reference electrode was applied. UV impedance spectrums were measured with an IM5ex by Zahner Elektrik with a wavelength of 360 nm and three different light intensities. The photoactive electrode is exposed to flux of photons Φ, with an energy, higher than the bandgap energy of the investigated material and an intensity $I(t)=I_0+\delta I_0 \sin(\omega t)$, I_0 being a constant background illumination and $\delta I_0 \sin(\omega t)$ being the superimposed sinusoidal perturbation of amplitude with $\delta=10\%$. This variation in the intensity creates a varying photocurrent $\Delta i(\omega)$ of singular frequency ω . The complex ratio of $\Delta i(\omega)$ to the variation in the photon flux Φ is measured to give the optoelectrical admittance $[\Delta i(\omega)/\Delta \Phi(\omega)]$ magnitude and phase angle. The electron transport time constant τ_c was calculated by the equation $\tau_c = 1/\omega_{min}$, where ω_{min} is the angular frequency where the magnitude of the imaginary component of the optoelectrical admittance is at maximum, and therefore, $\text{Im}[\Delta i(\omega)/\Delta \Phi(\omega)]$ is at minimum.

For Mott-Schottky measurements, a standard 3-electrode electrochemical cell with a 0.5 cm x 0.5 cm Pt plate counter electrode, an Ag/AgCl reference electrode (3M KCl) and a 0.1 M Na₂SO₄ electrolyte were used and donor density was calculated using:

$$N_D = \frac{2}{\epsilon_r \epsilon_0 q S} \quad [1]$$

where k is the Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-14} \text{ F cm}^{-1}$), q is the elementary charge ($1.6 \times 10^{-19} \text{ C}$), ϵ_r is the relative dielectric constant of rutile (assumed to be 100)^[S1], S is the potential slope of the Mott-Schottky plot shown in figure S3 a) and N_D is the apparent donor density (per cubic centimeters) calculated as 9.11×10^{19} , 5.59×10^{20} and 3.44×10^{21} for the undoped, best and highly doped samples respectively.

Electrochemical impedance spectroscopy (EIS) was carried out using an electrochemical interface (Zahner, IM6). EIS measurements were performed between 100 kHz to 0.01 Hz with a 10 mV rms sinusoidal modulation at open circuit potential in 0.1 M H₂SO₄ solution.

SEM pictures were taken by a Hitachi S4800. In figure S1a, one can see, additionally to some agglomerations of bigger nanoparticles (lower left), that the whole surface is covered by a network of small nanoparticles (lower right).

PECWS experiments were done in a in a three electrode electrochemical cell with a 0.5 cm x 0.5 cm platinum counter electrode and an Ag/AgCl reference electrode under 1.5 G simulated sunlight at 100 mW/cm² in 1M KOH solution by chopping the light off and on at predetermined values to measure the J-V curves in light and dark. This approach only deviates negligibly from carrying out the experiment by continuous sweep under light and in the dark as shown in Figure S3. When using the differently seeded samples in one reaction vessel, a drastic difference in water splitting activity can be seen (Figure S1b). The

rutile nanorod seeded sample reaches a maximum photocurrent of around 1.0 mA/cm², whereas the TiCl₄ seeded sample only achieves a maximum photocurrent of around 0.5 mA/cm².

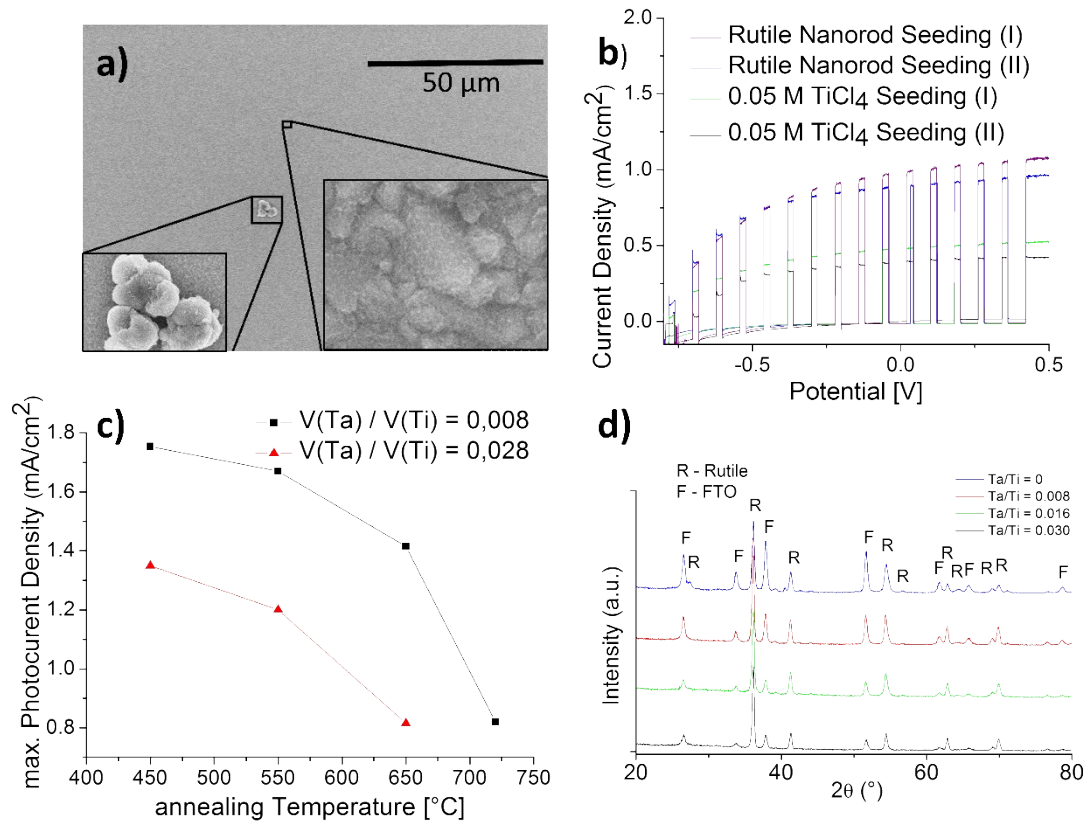


Figure S1 a) SEM image of a TiO₂ nanoparticle seeded FTO substrate b) PEC watersplitting curves, showing the influence of seeding on tantalum doped rutile nanorods with a tantalum to titanium precursor volume ratio of (I) 0.037 and (II) 0.042 grown on rutile nanorod and TiCl₄ seeded FTO annealed at 450 °C c) dependency of maximum photocurrent at +500 mV vs. Ag/AgCl to annealing temperature with two different precursor volume ratios d) XRD of tantalum doped TiO₂ nanorods for different precursor ratios of Ti/Ta

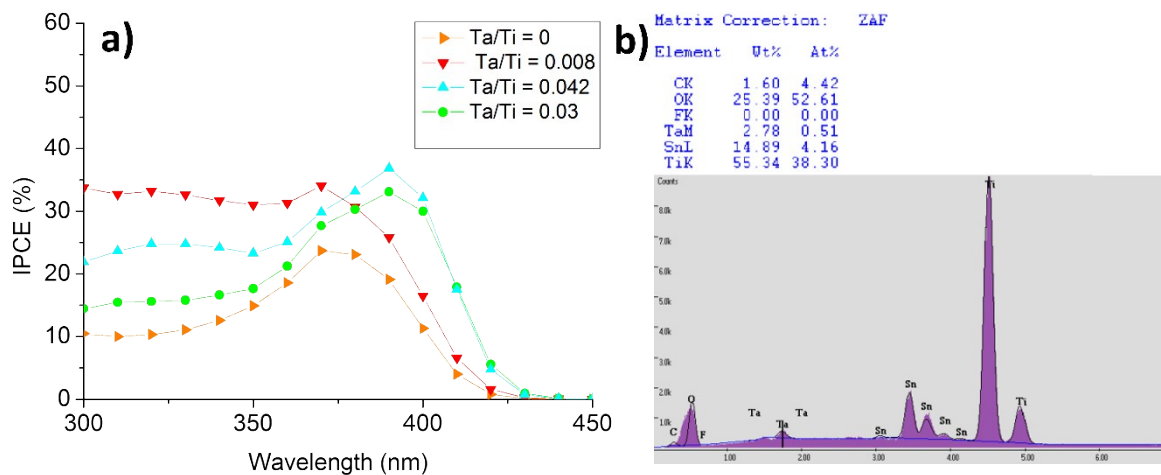


Figure S2 a) IPCE dependency of incoming light wavelength of tantalum doped and undoped rutile nanorods b) EDX analysis of tantalum doped nanorods grown on nanoparticle seeded substrates synthesized in the solution with starting precursor ratio of 0.008.

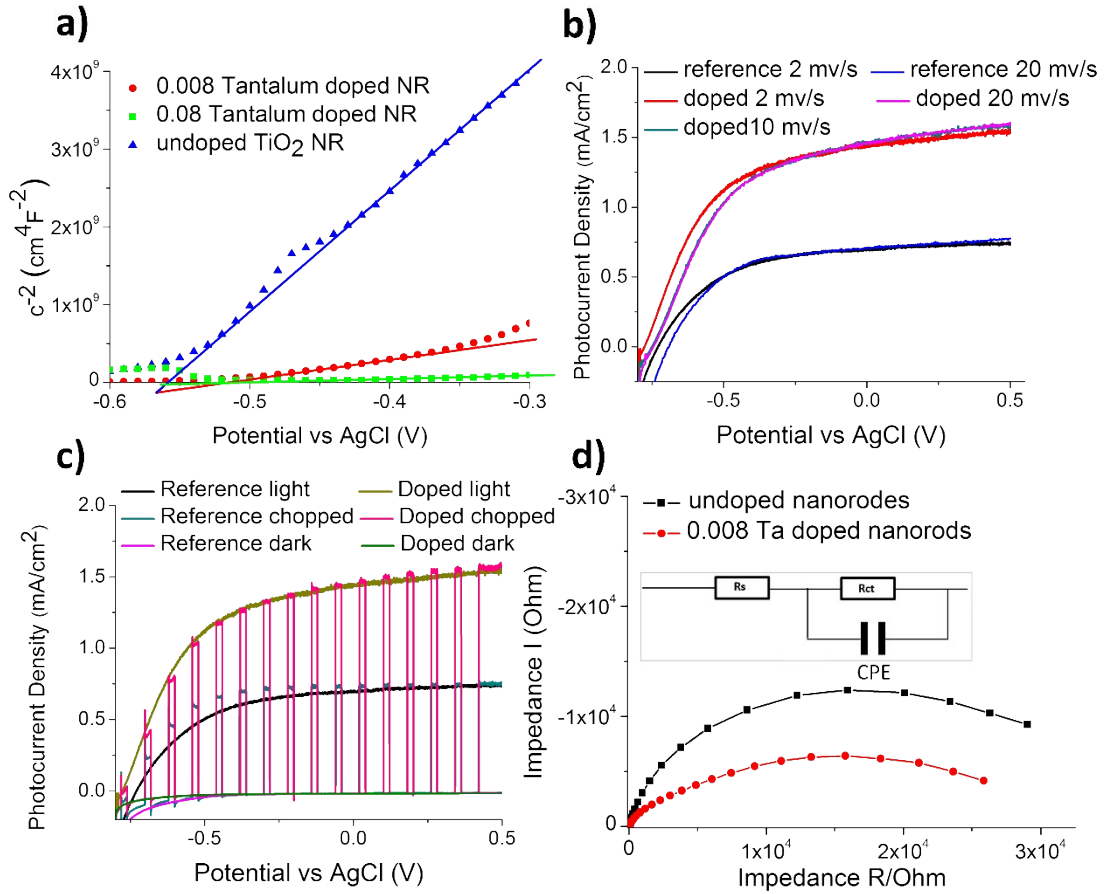


Figure S3 a) Mott-Schottky plots of doped and undoped nanorods b) J-V curves under simulated sunlight for different sweep rates for doped and undoped nanorods c) J-V curves in light, dark and chopped approach for a doped and undoped nanorods d) Nyquist plots of the samples measured at open circuit potential in H_2SO_4 solution and the model circuit used for fitting, demonstrating that the charge transfer resistance for the doped samples is slightly lower than for undoped samples.

Table S1 Calculated value of the equivalent circuit elements by fitting results to the model circuit

Sample	DC potential (V)	R_s (Ohm)	R_{ct} (KOhm)	CPE1-T (uFarad)	CPE1-p (m)
undoped	0.134	22.69	5.25	17.38	908.6
0.008Ta doped	0.148	18.35	3.05	3.052	714.3

Reference:

S1: I. BURN, in "Engineered Materials Handbook", Vol. 4, edited by S. J. Schneider Jr, ASM International, USA, 1991, p. 1112.