Optimized FTO seeding enables the growth of high efficient Ta-doped TiO$_2$ nanorod photoanodes

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Tantalum doped rutile nanorods were hydrothermally grown on FTO substrates using a new seeding approach. This approach allows the incorporation of high concentrations of up to 4.8 at% tantalum as active doping and results in a significant enhancement of photoelectrochemical water splitting rate (1.8 mA/cm² at a potential of +1.5 V vs RHE) which corresponds to ~1% photocurrent conversion efficiency under AM 1.5, 100 mW/cm² simulated sunlight irradiation.

Since the first reports by Fujishima and Honda, titanium oxide is well known for its ability to serve as a semiconductor for the photoelectrolysis of water into H₂ and O₂. In spite of inherent drawbacks (large band-gap of 3.0 eV that allows only UV light absorption), TiO₂ is still considered as one of the most promising candidates as a photoanode for water splitting, due to its strong optical UV absorption, high chemical stability and low cost. One-dimensional morphologies of TiO₂ such as nanotubes or nanorods offer direct electrical pathways for photogenerated electrons which is considered a key beneficial feature for an enhancement of the performance of photoelectrochemical devices. Lately, hydrothermally grown rutile nanorods have attracted much attention because of their comparably high photoconversion efficiencies due to their single crystalline and 1D nature. These nanorods are typically grown on FTO, as the small lattice mismatch of 2 % between FTO and rutile crystal structure enables the direct hydrothermal growth onto this substrate. To improve the PEC activity of the rods, various seeding strategies on FTO that not only enables the successful growth but also the nature of the seeds (upper left) and TiO₂ splitting curves for pure and tantalum doped rutile nanorods grown on rutile nanorod seeded FTO substrate, and c) PEC water splitting curves for Ta-doped rutile nanorods with different doping ratios grown onto Ru-Nr seed FTO annealed at 500 °C, and d) PEC water splitting curves for pure and tantalum doped rutile nanorods grown on rutile nanorod and TiO₂ nanoparticle seeded samples respectively, annealed at 450 °C and photocurrent conversion efficiencies calculated for pure and doped samples with NR seeding (upper left).

Therefore we explored alternate seeding strategies for direct hydrothermal tantalum doped nanorod growth. The by far most successful attempt turned out to be the use of small undoped rutile nanorods. Figure 1b) shows an SEM image of an FTO surface with these non-doped seeding rods. For the seeding process, the FTO substrate was immersed in a titanium precursor solution with lower concentration and treated at a lower temperature of 150 °C for 4h. From these seeds, the tantalum doped nanorods can start growing successfully into single crystalline tantalum doped rutile nanorods as shown in Figure 1a. To investigate the influence of the doping process on the PEC activity of the rods, PEC water splitting experiments were conducted, as outlined in the experimental procedure on the PEC activity of the rods, PEC water splitting experiments were conducted, as outlined in the experimental
section, in 1 M KOH using AM 1.5 conditions at 100mW/cm². To screen for an optimized doping concentration, we varied the ratio of Ta/Ti precursor. In Figure 1c the maximum photocurrent for various doping ratios is shown. Clearly at a Ta/Ti precursor ratio of 0.008 a maximum photocurrent is observed. With higher doping ratios, the maximum photocurrent decreases, due to the increasing numbers of recombination centers. For further characterization, we used the best performing Ta/Ti = 0.008 sample. The I-V characteristics of these optimally performing rutile nanorod seeded, tantalum doped nanorods reach a maximum photocurrent of ~1.8 mA/cm²− this is far superior to the non-doped TiO₂ rods that only reach around 0.8 mA/cm² (the TiCl₄ seeded tantalum doped samples perform even worse). If the tantalum content in a TiCl₄ seeded sample and a rutile seeded sample, grown under identical hydrothermal conditions are compared, one finds over 8 times more tantalum for the rutile seeded samples (calculated from Figure 2e and Figure S2b).

To evaluate the efficiency of PEC hydrogen generation from doped and undoped rutile nanorod samples, the photoconversion efficiency as shown in Figure 1d) was calculated based on the equation, η = (I.23 – VJ)/I11. I is the photocurrent density at the measured potential, V is the applied voltage versus the reversible hydrogen electrode (RHE) and J is the irradiance intensity of 100 mW/cm² (AM 1.5). The reversible hydrogen electrode (RHE) potential can be converted from the Ag/AgCl reference electrode via the Nernst equation5,13. Considering the values for the used (3M KCl) Ag/AgCl reference and the 1M KOH solution this converts to: RHE = V(Ag/AgCl) + 1.04 V. The best sample with the initial volume ratio of V(Ta)/V(Ti) = 0.008 achieved an efficiency of ~1.0% at a bias of ~0.52 V versus Ag/AgCl (0.52 V vs RHE), whereas the undoped sample only achieved ~0.33% at a voltage of ~0.37 V versus Ag/AgCl (0.67 V vs RHE). This present a 200% increase and shows that tantalum doping can significantly increase the maximum photocurrent at lower potentials, which results in a highly improved photocurrent conversion efficiency.

A detailed analysis of the best performing rods used in our investigations with TEM, XPS and EDX are shown in Figure 2. XRD and SAD pattern only show rutile phase to be present and no significant tantalum phase could be detected. There was no significant change in the lattice found after tantalum incorporation as expected due to the comparable ionic radii (with VI coordination) of Ti⁺⁺ (0.061 nm) and Ta⁺⁴ (0.064 nm) ions.13 As can be seen in figure 2f and g, the interplanar d-spacing of (110) planes for the doped tantalum nanorods determined from HRTEM is 0.3155 nm, compared to 0.3167 nm for the undoped TiO₂ nanorods. While the incorporation of tantalum into anatase has some minor effect on XRD spectra14, no changes in the XRD could be observed in case of tantalum doped rutile.8,15. From the TEM shown in Figure 2g, one can see that the (110) plane is parallel to the growth direction of the nanorods as previously reported2 and this is also reflected in the TEM of the non-doped reference sample in Figure 2f). Although others have reported the appearance of a core-shell structure at doping concentrations of 2.6 atomic percent in a solvothermal method9, we did not observe such structures. XPS spectra shown in Figure 2a, b, and c show the Ta4f peaks of Ta₂O₅, the Ti2p peaks and the O1s peaks respectively. The Ta/Ti ratio according to XPS is 1.5%. The EDX measurements seen in Figure 2e show an average tantalum concentration of 3.2 atomic percent which converts to a tantalum concentration of 4.8 atomic percent when corrected for the substrate tin and oxygen content. In the content of the crystal composition it is noteworthy that the average content, measured by EDX is significantly higher than the concentration in solution and on the surface, measured by XPS. This indicates the presence of a concentration gradient (with higher tantalum content at the bottom of the rods). A likely explanation is a difference in decomposition rate of the tantalum and the titanium precursor under hydrothermal conditions. At the end of the synthesis the tantalum precursor is mainly decomposed leading to a decreased tantalum to titanium ration in solution and near the surface. This may also explain the different tantalum concentrations in the differently seeded samples. It is reasonable to assume that the growth speed of the rutile nanorods is different on different surfaces, since in case of the rutile nanowire seeded sample there is no need for the nucleation of small rutile particles and rutile rods can just grow onto the already present rutile wires. In case of the nanoparticle seeded samples, there has to be nucleation of rutile particles or a transformation of the anatase particles to the rutile crystal structure which has been shown to occur under these reaction conditions9. The difference in both, growth and decomposition rate therefore leads to different tantalum concentration in the resulting rods, therefore changing their performance. Different decomposition rates thus can lead to gradients of tantalum concentration in the nanorods. To investigate this, ToF-SIMS sputter depth profiles, as shown in Figure 3a, were acquired. Figure 3b shows the ToF-SIMS spectra, which confirms that tantalum is present in the sample. The sputter depth profiles of Figure 3a show that in all cases, there is an increase in tantalum
concentration with sputter depth, in line with above discussion and gradient formation.

Another factor that has been reported to affect the properties of tantalum doped TiO\(_2\) is the annealing temperature. On the one hand, an increase of the annealing temperature can reduce the activity of the nanorods due to thermal or mechanical stress at the rod/FTO interface or an increased sheet resistance of FTO\(^{10}\), while on the other hand, a study on the desorption of chloride ions on hydrothermally grown rutile nanorods showed that a minimum annealing temperature is needed to remove the adsorbed chloride ions that block oxygen vacancies\(^{17}\), which have been widely reported to be the main active sites for the dissociation of water and are therefore a significant reason for a hampered water splitting activity\(^{18}\).

Since the concentration of the dopants and the annealing temperature strongly influence the effectiveness of the resulting material, differently doped nanorods were annealed at temperatures between 450 and 650 °C and investigated by PEC water splitting experiments conducted under simulated sunlight. As shown in Figure 3c, increasing the annealing temperature decreases the PEC water splitting activity significantly, while the XRD shows no change to crystal structure due to the increased temperature (Figure 2d).

The maximum photocurrent for each doping ratio could be increased significantly by annealing at a temperature of 450 °C. This always resulted in the best performing nanorods, as can be seen in Figure S1c, with a more than 100% increase in water splitting activity compared to the undoped sample annealed at the same temperature and are close to the best reported values of doped rutile nanorods\(^{7}\).

![Figure 3](image-url)

Figure 3 a) ToF-SIMS sputter depth profile of tantalum doped nanorods. b) ToF-SIMS of tantalum doped rutile nanorods with starting precursor concentration of V(Ta)/V(Ti) = 0.016 c) PEC water splitting curves for tantalum doped rutile nanorods with a tantalum to titanium precursor volume ratio of 0.028, annealed at different temperatures nanorods d) Log-log graph of transport time constants calculated from IMPS measurements for doped and undoped nanowires annealed at 450°C vs $\Phi^{1/2}$.

To investigate the reasons for this improvement, photocurrent measurements, impedance spectroscopy, Mott-Schottky measurements and UV impedance spectroscopy were used to provide information on the spectral behavior as well as on the electronic properties of the samples as described in the supporting information. As can be seen in Figure S2a no red shift of the IPCE is caused by the increase of the electron diffusion length in tantalum doped rutile. From UV impedance spectra, the electron transport time constants $\tau_e$ were calculated. In Figure 3d a log-log graph of the transport time constant over $\Phi^{1/2}$ is shown for undoped and doped samples. The linear dependence of the transport time constant on the inverse square root of the photon flux in the logarithmic scale is in agreement with a mechanism driven by diffusion with $\tau_e$ reducing as light intensity increases. When comparing the doped and undoped sample, a 5 to 10 times higher transport time constant for the undoped sample is observed, which could explain the improved performance of the doped samples. From Mott-Schottky type measurements, the $N_0$ (the apparent donor density per cubic centimeters) was calculated as 9.11 X 10\(^{19}\), 5.59 X 10\(^{20}\) and 3.44 X 10\(^{21}\) for the undoped, best and highly doped samples respectively as described in the supporting information (Figure S3).

In summary, the presented work shows that tantalum doped nanowires can be grown on rutile nanorods pre-seeded FTO substrates by a new seeding approach, which doubles the water splitting activity of the afterwards grown tantalum doped rutile nanorods. The efficiency of hydrothermally grown rutile nanorods decreases when annealed at temperature above 450 °C and depends strongly on dopant concentration. For optimized tantalum doped rods a maximum photocurrent of ~1.8 mA/cm\(^2\) could be achieved, which is higher than for any previously reported tantalum doped rutile nanorods and up to 4 times higher than for undoped nanorod reference samples. This enhancement by tantalum doping is due to the improved electron transfer time constant and increased ICPE in the UV region of the light due to a larger carrier diffusion length. It is reasonable to predict that the maximum photocurrent and photo conversion efficiency can still be increased by post synthetic treatments like ammonium and hydrogen annealing. Therefore hydrothermally grown tantalum doped rutile nanowires have a high potential in any photovoltaic or chemical TiO\(_2\) application.

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