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Hydrothermal growth of highly oriented single crystalline Ta$_2$O$_5$ nanorod arrays and their conversion to Ta$_3$N$_5$ for efficient solar driven water splitting

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We grow vertically aligned single crystalline Ta$_2$O$_5$ nanorod arrays that can be converted to a Ta$_3$N$_5$ nanorod array by nitridation. Combined with cobalt phosphate (Co-Pi) as a co-catalyst, such Ta$_3$N$_5$ nanorod photoanodes can yield photocurrent densities of ~3.6 mA cm$^{-2}$ at 1.23 V$_{RHE}$, and ~8.2 mA cm$^{-2}$ at 1.59 V$_{RHE}$ under AM 1.5G (100 mW cm$^{-2}$).

To grow the Ta$_2$O$_5$ nanorod arrays as shown in the scanning electron microscopy (SEM) images of Fig. 1a and b, we immersed Ta foils in a 250 ml Teflon-lined autoclave into 100 ml 0.1 M HF and 0.59 M H$_2$O$_2$ solution, which was then heated to 240 °C and kept for 24 h. After synthesis, a densely packed nanorod array is obtained that uniformly covers the entire surface of the Ta foil substrate. The nanorods grow perpendicularly from the Ta substrate on a base oxide layer with a thickness of about 0.7 μm. The average length and diameter of the nanorods are about 0.6 μm and 100 nm, respectively.

Figure 1c displays the XRD pattern of Ta$_2$O$_5$ nanorod arrays grown on the Ta surface. All the diffraction peaks can be assigned to the Ta substrate and the orthorhombic phase of Ta$_2$O$_5$ (JCPDS No. 01-089-2843, a=0.620 nm, b=0.366 nm, c=0.389 nm). It is impressive that only crystal planes parallel to the (001) plane show diffraction peaks, and other diffraction peaks which usually appear in a powder diffraction of an orthorhombic phase of Ta$_2$O$_5$, such as (110), (200), and (111) peaks are absent. This indicates that the Ta$_2$O$_5$ nanorod arrays grown are single crystalline and highly oriented, with a growth axis in the [001] direction perpendicular to the Ta substrate.

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Figure 1. Top view (a) and cross-sectional view (b) SEM images, and (c) corresponding XRD pattern of vertically aligned TaO5 nanorod arrays grown hydrothermally in 0.1 M HF and 0.59 M H2O2 at 240 °C for 24 h with a solution filling factor of 40%. HRTEM images in (d) and (e) show the microstructures of a single nanorod and the base oxide layer of the hydrothermally grown TaO5 films. The insets in (d) and (e) are corresponding SAED patterns.

High resolution transmission electron microscopy (HRTEM) images and a corresponding selected area electron diffraction (SAED) pattern of a typical single nanorod of TaO5 are shown in Figure 1d. The fringes with an interspace of 0.39 nm match well with the (001) crystal planes of orthorhombic TaO5, confirming that the nanorods were grown in the (001) direction. The SAED pattern with disperse diffraction spots periodically arranged in two dimensions confirms that the nanorod is single crystalline but contains some stacking faults. Typical HRTEM image of the base oxide layer underneath the nanorod arrays in Figure 1e shows that the oxide layer composes of many nanocrystallites which show only an amorphous characteristic diffuse ring in the SAED pattern due to the very small size of the nanocrystals. Many micropores with a size of about 1.5 nm are revealed by low magnification TEM image in Figure S1.

The main chemical reactions in the autoclave can be written as:

1. $2\text{Ta} + 14\text{HF} = 2\text{H}_2\text{TaF}_7 + 5\text{H}_2$
2. $2\text{H}_2\text{TaF}_7 + 5\text{H}_2\text{O} = \text{Ta}_2\text{O}_5 + 14\text{HF}$

At low $\text{H}_2\text{TaF}_7$ concentration, the formed TaO5 can be readily dissolved back to $\text{H}_2\text{TaF}_7$ by excess HF solution according to the back reaction of equation (2). In this work, no oxide layer was observed on the Ta substrate after 6 h reaction. After this initial incubation period, microporous nanocrystalline TaO5 films are able to grow on the Ta substrate as an appropriate $\text{H}_2\text{TaF}_7$ concentration is established. Single crystal TaO5 nanorods grow probably from nanocrystalline TaO5 nuclei. To minimize the surface energy, TaO5 nanorods tend to grow slowly along the [001] direction via a thermodynamically controlled process, consistent with previous reported hydrothermal growth of dispersed branched TaO5 nanorods. Since the growth and dissolution of the oxide compete with each other according to the forward and back reaction of equation (2), clear stripes can be observed on the wall of all the nanorods as pointed by arrows in Figure 1a. This explains how single crystalline TaO5 nanorod arrays grow in diameter and length after 12 h and 24 h of reaction. The morphology of the 12 h grown TaO5 films is shown in Figure 2a and c. As the reaction continues, the growth rate of TaO5 increased accordingly with further increasing concentration of $\text{H}_2\text{TaF}_7$, which finally facilitates the fast growth of base oxide layer consisting of TaO5 nanocrystallites and suppresses the single crystal nanorod growth. The dissolution of the single crystal nanorods by the solution may cause thinning of the nanorods and induce disorder of the nanorod alignment. Figure 2b and d show that the 48 h grown samples have much thicker base oxide layer, but with smaller, shorter and less ordered nanorod arrays compared to the 24 h grown sample in Figure 1. The influence of various experimental parameters such as pre-oxidation of the Ta, Ta foil size, and solution amount in the autoclave on the morphologies of TaO5 film were studied as outlined in the supplementary information. These experiments further support the above suggestion that hydrothermal growth of TaO5 films on Ta foils is greatly determined by the $\text{H}_2\text{TaF}_7$ concentration.

Figure 2. Top view (a,b), and cross-sectional view (c,d) SEM images of TaO5 nanorod arrays grown hydrothermally in 0.1 M HF and 0.59 M H2O2 at 240 °C for 12 h (a,c) and 48 h (b,d).

For nitridation, typical TaO5 nanorod arrays grown by 24 h hydrothermal reaction (as shown in Fig. 1a) were placed into a quartz tube, which were then heated to 1000 °C for 2 h with a NH3 flow of about 200 sccm. XRD analysis of the products revealed that the TaO5 films had been converted to tantalum nitrides completely, the structure in line with hexagonal TaN (JCPDS No. 01-089-5197) and the major phase, orthorhombic Ta5N3 (JCPDS No. 01-079-1533) as shown in Figure 3. The
densities of TaN, Ta$_3$N$_5$ and Ta$_2$O$_3$ are ~15 g cm$^{-3}$, 14 9.8 g cm$^{-3}$ and 8.2 g cm$^{-3}$, corresponding to a Ta atomic density of ~0.0769 mol cm$^{-3}$, 0.0482 mol cm$^{-3}$ and 0.0371 mol cm$^{-3}$ respectively. This is the origin of the observed significant volume contraction during nitridation of Ta$_2$O$_3$. As can be seen from the FE-SEM images in Figure 3, the diameter and length of Ta$_3$N$_5$ nanorods are much smaller than for the original Ta$_2$O$_3$ nanorods shown in Figure 1. The base oxide layer underneath the nanorods arrays changed to a mesoporous nanoparticle layer with a lower thickness, as well. The average size of the nanoparticles is about 30 nm, while the average pore size is about 10 nm. The HRTEM image shown in Figure 3c reveals a mesoporous nature of the Ta$_3$N$_5$ nanorods. Both the mesoporous 1D nanorod arrays and the mesoporous nanoparticle layers of Ta$_3$N$_5$ can act as efficient photocatalysts for the PEC water splitting due to their high specific surface areas and good charge transport properties.

Figure 3. Top-view (a) and cross-sectional view (b) SEM images of Ta$_3$N$_5$ nanorods arrays obtained by 2 h nitridation at 1000 °C of Ta$_2$O$_3$ nanorods grown hydrothermally in 0.1 M HF and 0.59 M H$_2$O$_2$ at 240 °C for 24 h with a filling factor of 40%. The inset of (b) is an enlarged image of the nanoparticle layer. (c) Typical HRTEM image of a single nanorod. (d) XRD pattern of the nanorod arrays.

In the PEC water splitting process, when using Ta$_3$N$_5$ as the photoanode, photo-generated holes with strong oxidative ability tend to oxidize the photoanode if they cannot be effectively transferred away from the anode/electrolyte interface, which significantly impairs the stability of the photoanode. Surface modification with co-catalysts such as IrO$_2$, Co$_3$O$_4$, Co(NO$_3$)$_2$, Co-Pi, and Co(OH)$_x$ are reported to stabilize the Ta$_3$N$_5$ photoanode and improve the water splitting efficiency significantly.

To deposit a layer of Co(OH)$_x$ nanoparticles on Ta$_3$N$_5$ nanorods as a co-catalyst, the Ta$_3$N$_5$ nanorod array films were simply immersed in a mixed solution of CoSO$_4$ and NaOH for 25 min, then rinsed by deionized water and finally dried in N$_2$. In comparison, the Co-Pi co-catalyst was loaded on the nanorod surface by electrodeposition in a solution of 0.5 mM Co(NO$_3$)$_2$ in 0.1 M potassium phosphate buffer at pH=7 at 1 V versus Ag/AgCl for 8 min. As shown in Figure 4, the Co(OH)$_x$ treated Ta$_3$N$_5$ nanorod photoanode yields a photocurrent density of ~1.5 mA cm$^{-2}$ at 1.23 V RHE, which increases to ~10.4 mA cm$^{-2}$ at 1.59 V RHE. For the Co-Pi/Ta$_3$N$_5$ photoanode, typical photocurrent densities of ~3.6 mA cm$^{-2}$ at 1.23 V RHE and ~8.2 mA cm$^{-2}$ at 1.59 V RHE were obtained. Some fluctuation in the initial spike height is just due to the use of a comparably slow sampling rate (data acquisition). In both cases the appearance of spike-like initial transients depends on the applied potential, indicating that at lower potentials, photogenerated electrons and holes show considerable recombination.

Figure 4. Current-potential curves of PEC water splitting cell with a photoanode of Ta$_3$N$_5$ nanorods arrays obtained from 2 h nitridation at 1000 °C of 24 h grown Ta$_2$O$_3$ nanorods modified by (a) Co(OH)$_x$ and (b) Co-Pi. All curves were measured in aqueous KOH solution (pH=13.7) under chopped AM 1.5G simulated sunlight, with a scan rate of 10 mV s$^{-1}$ from negative to positive.

The PEC water splitting performance of Ta$_3$N$_5$ nanorods after different hydrothermal time is shown in Figure S2. It was found that an increase in the time of hydrothermal growth of Ta$_2$O$_3$ to 48 h or a decrease to 12 h in both cases, the performance of the corresponding Ta$_3$N$_5$ nanorods decreases considerably. The 12 h grown nanorods and sub-spongy layer seem too short to achieve an efficient visible light absorption (400 nm<λ<700 nm), especially when the volume contraction during nitridation is taken into consideration. The oxide layer for the 48 h grown sample is too thick for an efficient charge transport. On the other hand, the TEM and SAED pattern taken in the sponge layer (Fig. S3) identify the presence of TaN in the Ta$_3$N$_5$ photoanode.

Compared with the Co(OH)$_x$ decoration, the electrode with the Co-Pi treatment exhibits not only an onset potential that is negatively shifted but also an improved photocurrent. The Co(OH)$_x$/Ta$_3$N$_5$ electrode shows relatively stronger spike-like transients, but compared to literature reported on Ta$_3$N$_5$ nanorod with Co(OH)$_x$ decoration, our electrode shows a higher saturation photocurrent (~10.4 mA cm$^{-2}$ at 1.59 V RHE).

Among all the currently available Ta$_3$N$_5$ photoanodes reported, thermal Ta$_3$N$_5$ films after removal of the surface passivation layer as reported by Zou et al. and templated aligned Ta$_3$N$_5$ nanorod arrays doped by barium as reported by Domen et al. currently represent, to the best of our
knowledge, the highest solar photocurrent densities. In the first case, the photoanode has a photocurrent density of ~5.5 mA cm⁻² at 1.23 V_RHE and a saturated photocurrent density of ~8 mA cm⁻² at 1.60 V_RHE. The barium doped Ta_N₅ nanorod photoanodes have a high photocurrent density at low bias region after optimized loading of Co-Pi by photo-assisted electrodeposition, e.g., ~4.75 mA cm⁻² at 0.9 V_RHE and ~6.7 mA cm⁻² at 1.23 V_RHE.

For our structure, while the onset conversion efficiency in previous work is slightly lower than in the best reported case, the saturation solar photocurrent density of our Ta_N₅ nanorod photoanode is higher than the highest value reported for Ta_N₅ based photoanodes. This illustrates the high potential of the present approach, namely if optimization of the co-catalyst loading is achieved, to improve the performances in lower applied voltage region.

In summary, highly oriented single crystalline Ta₂O₅ nanorod arrays were successfully grown on Ta foils by a facile hydrothermal method without any template. Upon nitridation in NH₃ atmosphere at 1000 °C for 2 h, the grown nanorods were converted to Ta_N₅ nanorod arrays that represent highly efficient anodes for PEC water splitting. By deposition of a layer of Co(OH)₃ nanoparticles on Ta_N₅ nanorod arrays as co-catalyst, we obtained solar photocurrents of 1.5 mA cm⁻² at 1.23 V_RHE and 10.4 mA cm⁻² at 1.59 V_RHE; the latter is the highest values reported for Ta_N₅ photoanodes to the best of our knowledge. Ta₂O₅ nanorods modified by electrodeposition of Co-Pi yield typical solar photocurrents of 3.6 mA cm⁻² at 1.23 V_RHE and 8.2 mA cm⁻² at 1.59 V_RHE. In future studies, optimization of the experimental conditions is required to control the growth of Ta₂O₅ and the subsequent Ta_N₅ nanorod arrays to strengthen the advantage of the 1D nanorod structure, and more importantly, co-catalyst treatments will need to be optimized to lower the onset potential of photocurrent and the efficiency under low bias conditions.

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**Notes and references**

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