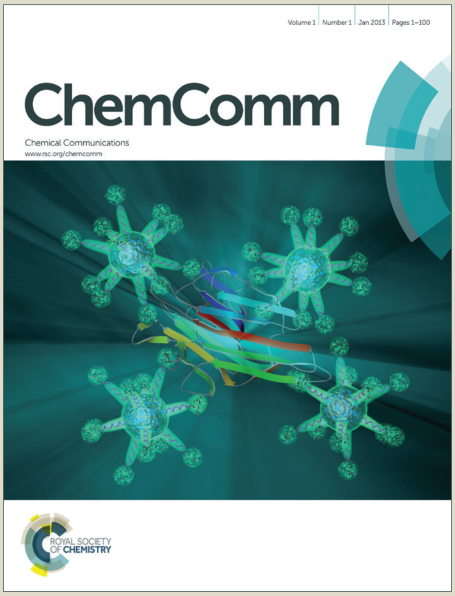

Journal Name

COMMUNICATION

Surface Engineering for Enhanced Photoelectrochemical Response of TiO_2 Nanotube Arrays by Simple Surface Air Plasma Treatment

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A simple method to improve the photoelectrochemical performance of TiO_2 nanotube arrays (NTs) by simple air plasma post-treatment is reported. The air plasma treated sample shows higher photocurrent density and incident photo current efficiency with high stability, about 3-4 times than that of the pristine TiO_2 NTs even after six months.

With the increasing demand of sustainable and eco-friendly energy sources, developing and exploiting solar energy is one of the promising routes against energy issue. Ever since 1972, the photoelectrochemical (PEC) water splitting to produce clean hydrogen energy with solar light and water has attracted more and more attentions.[1, 2] As a well-known semiconductor material, TiO_2 has been extensively investigated for PEC water splitting,[3, 4] owing to its abundance, low cost, low toxicity, superior photo-chemical stability, and high intrinsic catalytic activity. However, the low light to hydrogen conversion efficiency and low photocurrent density under solar light (~0.5 mA/cm^2) still limit its practical applications.

To improve the TiO_2-based PEC water splitting efficiency, many strategies were investigated according to the PEC water splitting principle in previous reports,[5] such as adjusting the band gap by doping or compositing other elements,[6, 7] designing ordered structure or phases heterojunctions to accelerate the separation and migration of photoexcited electrons and holes,[8, 9] screening suitable cocatalysts to suppress the recombination of electron-hole pairs and speed up the surface redox reactions,[10, 11] and so on. Moreover, PEC water splitting refers to a complex solid-liquid-gas three-phase system, and the surface and interface states among electrode, electrolyte, and the new-formed gas play critical roles in photocatalytic hydrogen production.[12, 13] Especially, the surface composition, microstructure and wettability of the photoanode could directly influence the PEC water splitting efficiency. For example, the impurities on the surface of TiO_2 NTs photoanode may inhibit the wetting of nanotubes or serve as the trap sites for the recombination of electrons and holes, which has negative effects on PEC performance. By contrary, the PEC water splitting efficiency be improved by applying appropriate chemical modification and surface post-treatment, such as wet chemistry based surface passivation or surface fluorination, which facilitated the charge transfer and improve the PEC performance.[14,15] Besides, a thin film coating on the surface of photoanode could also contribute to depress the combination of photoexcited charges at the interface site of photoanode and electrolyte.[16] These issues are critically important but easy to overlook. Although many strategies have been used to improve the PEC water splitting performance, the facile, low-cost, and efficient method to further enhance the hydrogen production efficiency, still remains a challenge.

Plasma treatment is a simple and powerful surface treatment technology, which is commonly used in industry for cleaning, etching, activating and functionalizing a variety of surfaces prior to coating, printing or adhesion. In the field of photocatalysis, H_2, N_2, and He plasma treatments have been used to enhance the photocatalytic properties by doping to adjust the band gap of TiO_2 materials.[17-19] Huang et al. prepared hydrogenated TiO_2 nanoparticles in a thermal plasma furnace by hydrogen plasma at 500 °C for 8 h.[17] Sharma et al. gained helium plasma treated TiO_2 nanotubes at 12 kV increasing the photocurrent density by 25%.[19] However, the harsh treatment conditions usually limit the practical applications. Therefore, a simple, low cost and highly effective plasma treatment method to improve the activities of photoanodes is an urgent necessity.

Herein, a simple room temperature air plasma method introduced to improve the PEC water oxidation performance of TiO_2 photoanode material, which is promising for industry applications. Compared with the pristine TiO_2 NTs, the photocurrent density and incident photo current efficiency (IPCE) of the air plasma treated sample enhanced by 3-4 times, owing to the formation of massive hydroxyl group and oxygen vacancies to improve the wettability and increase the separation efficiency of electron-hole pairs.

Fig. 1a shows the schematic of illustration of preparation of TiO_2 NTs and the air plasma treatment processes. The strategy is that TiO_2 NTs is firstly prepared via anodization and then exposed to air plasma at 98 W for 20 min. The TiO_2 NTs was fabricated by a modified anodization method as previous reports.[20] The experimental detail is described in the supporting information. After heat treatment at 450 °C for 2 h, the anatase TiO_2 NTs were obtained. F

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

1b and 1c show the morphologies of the as-prepared TiO_2 NTs with an average diameter of 90 nm and the length of 13 µm, respectively. After the air plasma treatment for 20 min, the morphology of the sample has no obvious change (Fig. 1d). Besides, the anatase phase and the optical color of the TiO_2 NTs photoanode also have no changes as shown in Fig. S1.

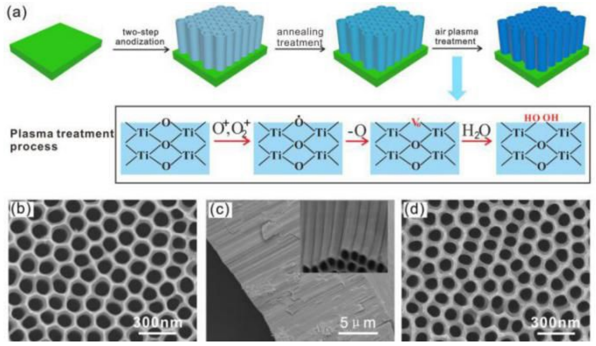

Fig. 1 (a) Schematic of the fabrication of air plasma treated TiO_2 NTs. FESEM images of TiO_2 NTs before (b,c) and after (d) air plasma treatment.

To evaluate the PEC performance of TiO_2 NTs photoanodes before and after air plasma treatment, the measurements details have be elaborated in supporting information.[21] Fig. 2a shows the current-potential curves of pristine and air plasma treated TiO_2 NTs electrodes with different treatment time. The results indicate that the photocurrent density of TiO_2 NTs electordes increases with the extension of air plasma exposure time from 1 min to 20 min. Significantly, the sample treated for 10 min shows very high photocurrent density of approximately 2.4 mA/cm^2 at the potential of 1.23 V vs RHE, about 4 times than that of the pristine TiO_2 NTs (0.6 mA/cm^2) under simulated sunlight illumination. Further increasing the air plasma treatment time to 20 min, the sample shows almost the equal photocurrent density as that treated for 10 min. Except plasma treatment time, the air flow rate used in the plasma treatment process also plays an important role in the PEC performance of the TiO_2 NTs photoanodes. Fig. S2 shows the photocurrent-time curves of the samples under different air flow rates, indicating that the best air flow rate is 6 mL/min. Besides, there is slight change in onset potential toward more positive values for air plasma treated samples (Fig. S3), indicating the difference in band bending between the Fermi level of the semiconductor and the redox potential of electrolyte. The sample without air plasma treatment has higher photocurrent density under 0.25-0.4 V vs. RHE, owing to its quicker separation efficiency of electrons and holes which is the rate-controlled step for the water oxidation reaction.The lower charge separation efficiency of the plasma treated samples under low bias mainly attributes to the decrease of the grains size and crystallinity of TiO_2 NTs resulting in more grain boundary barrier and trap/defect. When the surface reaction kinetics become the rate-controlled step (> 0.4 V vs. RHE), the air plasma treated samples have higher photocurrent, owing to their surface hydroxyl groups to accelerate the surface oxidation reaction. Fig. S4 shows the transient photocurrent (i-t) of TiO_2 NTs photoanodes with repeated on/off cycles at the potential of 1.23 V vs RHE. The sharply increase/decrease of photocurrent density with the switch on/off indicates the quick photoresponse.[22]

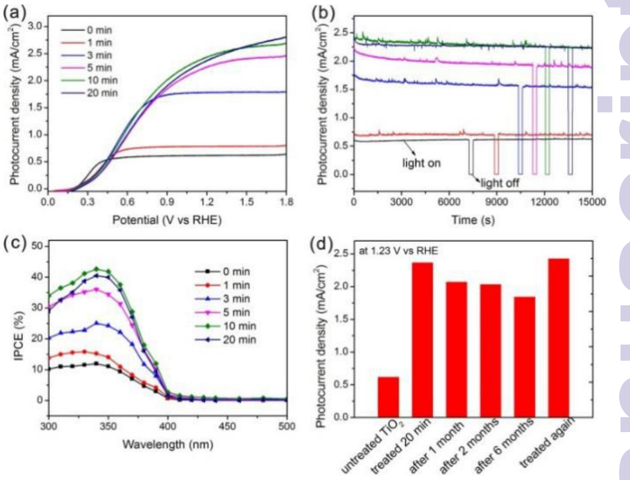

Fig. 2 (a) Linear-sweep voltammograms (b) Time courses for the photocurrent density at 1.23 V versus RHE and (c) Wavelength dependence of IPCE at 1.23 V versus RHE TiO_2 NTs photoanodes before and after air plasma treatment for different time from 1 min to 20 min under 300 W xenon lamp irradiation with an AM 1.5 filter. (d) Photocurrent density at 1.23 V versus RHE of TiO_2 NTs photoanodes by exposing to air plasma for 20 min after different time, and treated again by air plasma after 6 months.

The air plasma treated TiO_2 NTs photoanode has relative PEC stability as shown in Fig. 2b. There is nearly no decrease of the photocurrent density of the air plasma treated TiO_2 NTs photoanodes for several hours. Especially, the sample treated for 20 min has the similar PEC performance after storing in air for one month, and the photocurrent density only reduces by 25% after six month (Fig. 2d). Importantly, the photocurrent density can recover the high value by air plasma treatment for 20 min again, indicating potential practical applications. The air plasma treatment time can also influence the time durability of TiO_2 NTs photoanodes. Extending air plasma treatment time (<20 min) can result in longer high-performance maintaining time as shown in Fig. S5, but note that not the longer the better. The photocurrent density of the sample treated for 1 min nearly decreased by 100% after 2 days, while that of the sample treated for 3 min decreased by 100% after 7 days. The photocurrent density of sample treated for 5 min and 10 min decreased by above 60% after 1 month and 2 months, respectively. While the photocurrent density of sample treated for 20 min decreased by only 25% after 6 months. Further increasing the air plasma treatment time, we found the photocurrent density decrease (Fig. S5f, slight decrease for the sample treated for 30 min), and the long-term stability turn bad (the photocurrent density decreases more 50 % after 1 week), which is because the decreasing of grains size and crystallinity of TiO_2 NTs lead by the air plasma etching effect. The air plasma treated TiO_2 NTs photoanode shows high IPCE value which is measured at 1.23 V vs RHE under the illumination of a 150 W xenon lamp of SM-25 Hyper Monolight. Compared with pristine TiO_2 (10 % at 340 nm), the air plasma treated TiO_2 NTs electrodes (10 min and 20 min) have significant increase to about 40 % around 340-350 nm, depending upon the better charge carrier transport property. Therefore, there should be an optimized plasma treatment time, because there is a balance between the increase in charge transport/transfer and the decrease in light absorption of the plasma treated TiO_2 NT material.

To analyze the mechanism, the surface composition and chemical states of the TiO_2 NTs photoanodes were characterized by XPS before and after air plasma treatment (Fig. S6 and Fig. 3a). As shown in Fig. S6a of the survey spectra, there is no new peak appearance indicating no other element was doped or composited into TiO_2 NTs by air plasma treatment. Fig. S5b shows the multi-element spectra of Ti 2p with slight shift of about 0.1 eV, which is dominantly derived from the change of electron cloud by formation of oxygen deficiency after plasma treatment.[23] From multi-element spectra of O 1s (Fig. 3a and 3b), the peaks at 531.8 eV have obvious increase with increasing the air plasma treatment time, which can be contributed to the formation of hydroxyl group on the surface of TiO_2.[24] Fig. 3a shows the spectra of O 1s of TiO_2 NTs before and after plasma treatment for 20 min, which were fitted to Ti-O-Ti and Ti-O-H peaks attributable to different chemical states. From the fitted results, it is seen that the content of the hydroxyl groups is very low (only 8.61%) in the pristine TiO_2 NTs, while the value increased to 37.44 % after air plasma treatment for 20 min. More detailed fitted results of O 1s after plasma treatment are shown in table 1 in supporting information.

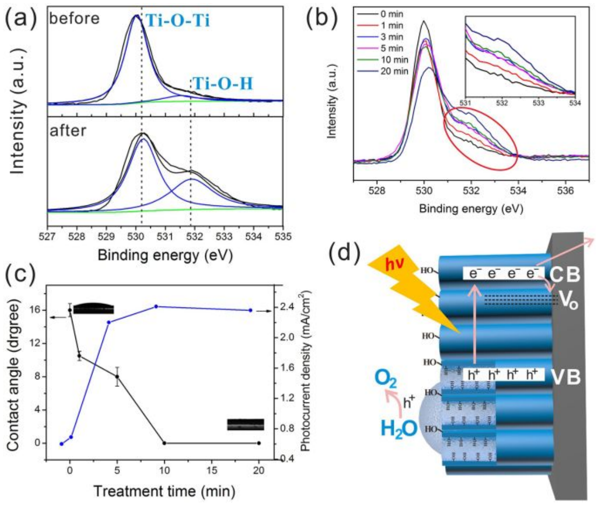

Fig. 3 (a) XPS analysis of the O 1s region of TiO_2 NTs phtoanodes before and after air plasma treatment for 20 min. (b) High-resolution XPS spectra of O 1s for TiO_2 NTs under treatment different time, the inset shows a magnified view in the binding energy region of 531-534 eV. (c) Relationship between the air plasma treatment time and water contact angle (CA) and photocurrent density of TiO_2 NTs photoanodes. The Inset shows photographs of a spherical water droplet with CA. (d) Schematic illustration for enhanced PEC process of TiO_2 NTs photoanode under irradiation.

The surface plasma treatment also improves the wettability of TiO_2 NTs photoanode by forming hydroxyl groups. Fig. 3c shows the variation of water contact angle with air plasma treatment time. The contact angle of pristine TiO_2 NTs is approximately 16°. After air plasma treatment, the contact angle decrease, and the surface of TiO_2 NTs becomes superhydrophilic with the contact angle of about 0° after plasma treatment for 10 min. The better electrode/electrolyte interfacial contact can further decrease the interface reaction resistance and accelerate the surface redox reaction rate, which contributes to improving their PEC performance by increasing the photocurrent density from 0.6 mA/cm^2 to 2.4 mA/cm^2.

Therefore, after air plasma treatment for 20 min with a gas flow rate of 6 mL/min, TiO_2 NTs photoanode has the best PEC performance. The enhancement should be ascribed to the following factors. Firstly, the air plasma treatment can remove the organic impurities absorbed on the surface of TiO_2 NTs.[19] These contaminants block the interface electrochemical reactions and serve as an electron/hole trap center to decrease the efficiency of PEC water splitting. The PEC performance is significantly dependent upon the surface interface properties of TiO_2 NTs photoanode, which is attributed to the kinetics of water oxidation and the charge recombination loss at electrode surface. Secondly, the formation of hydroxyl group on the surface of TiO_2 NTs by plasma treatment can improve the wettability of the photoanode and contributes to the enhancement of PEC performance, which is the most important factor. Last, plasma treatment can produce oxygen vacancies which serve as the trap centers for photo-generated electrons to suppress the recombination of electrons and hole. So, the electrons-holes pairs could more effectively separate and transport. The more holes participate in water oxidation on the TiO_2 NTs photoanode (Fig. 3d).

In summary, we developed a simple and effective method to improve the PEC water splitting performance of TiO_2 NTs photoanodes by simple air plasma treatment at room temperature. By exposing the as-prepared anatase TiO_2 NTs to air plasma for 20 min with the air flow rate of 6 mL/min, the photocurrent density and IPCE of the TiO_2 NTs photoanode increase about 4 times. The enhancement is mainly due to the synergistic effect of the increased surface hydroxyl group and the formation of oxygen vacancies of the samples. Moreover, the air plasma treated TiO_2 NTs photoanode shows good stability for more than 6 months with high performance, indicating promising practical applications, as well as in solar cells, sensors, and photocatalysis.

Thanks for the financial support of the NSFC (21303227, 21303233) and the “Hundred Talents Program” of Chinese Academy of Sciences.

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