Silver Nanoparticles-Decorated Titanium Oxynitride Nanotube Arrays for Enhanced Solar Fuel Generation

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We demonstrate, for the first time, the synthesis of highly ordered titanium oxynitride nanotube arrays sensitized with Ag nanoparticles (Ag/TiON) as an attractive class of materials for visible-light-driven water splitting. The nanostructure topology of TiO2, TiON and Ag/TiON was investigated using FESEM and TEM. The X-ray photoelectron spectroscopy (XPS) and the energy dispersive X-ray spectroscopy (EDS) analyses confirm the formation of the oxynitride structure. Upon their use to split water photoelectrochemically under AM 1.5 G illumination (100 mW/cm2, 0.1 M KOH), the titanium oxynitride nanotube array films showed significant increase in the photocurrent (6 mA/cm2) compared to the TiO2 nanotubes counterpart (0.15 mA/cm2). Moreover, decorating the TiON nanotubes with Ag nanoparticles (13 ± 2 nm in size) resulted in exceptionally high photocurrent reaching 14 mA/cm2 at 1.0 V SCE. This enhancement in the photocurrent is related to the synergistic effects of Ag decoration, nitrogen doping, and the unique structural properties of the fabricated nanotube arrays.

Over the past few decades, metal oxides have been extensively explored as photoelectrodes for solar-driven production of fuel due to their exceptional stability, semiconducting properties, abundance, and low cost1–8. However, most metal oxides have absorption activity that is limited to the ultraviolet spectral region because of their wide band gap (>3.0 eV). This is inconvenience because the ultraviolet spectral region contains only 3–5% of all incident solar energy. Besides, metal oxides with narrow band gaps (<3.0 eV), such as Fe2O3 and WO3, have stability concerns or improper band alignment for water splitting and require a large external bias2.

An alternative class of solar energy conversion materials is transition metal oxynitrides. Since metal-nitrogen bond has higher potential energy than metal-oxygen bond, oxynitrides9–16 have narrower band gap energies compared to their metal oxides counterparts. Additionally, oxynitrides are stable in alkaline media making them ideal water splitting photoelectrodes9–12. Particularly, titanium oxynitride (TiON) is a promising material for visible light absorption and appropriate band-edge positions for water splitting13–16. Vitiello et al.14 used NH3 nitridation to fabricate TiON nanotube arrays from anodized Ti foil. Their TiON showed enhanced photoelectrochemical properties and significant visible light response. Efficient nanostructured mesoporous TiON thin films were reported by Ferrero et al.15. The films resulted in a shift of the titania absorption edge, due to the introduction of N atoms. Alternatively, Kim et al.16 used Ti-N substrates to fabricate TiO-N nanotubes via anodization, resulting in a significant visible light response. Asahi et al.17 reported that N-doped TiO2 has an influence on the photocatalytic activity for the decomposition of acetaldehyde and methylene blue at wavelengths up to 550 nm. Recently, Gebauer et al.18 have investigated the oxygen reduction reaction (ORR) on N-doped titanium dioxide. It was found that N-doped titanium oxide significantly improve the ORR performance compared to non-doped TiO2.18 Decorating TiON materials with nanoparticles and/or sensitizers19–24 has also been recently proposed as an effective method to enhance the surface catalytic activity of a plethora of materials23–24. Hiroaki et al.22 have

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examined the effect of Ag nanoparticles (NPs)-decorated TiO$_2$ nanotube arrays. This hybrid device resulted in higher photocatalytic activity and solar energy conversion efficiency (~3.5 $\mu$A) compared to bare TiO$_2$ electrode (~0.5$\mu$A). This enhanced catalytic effect was related to the formation of hydroxyl radicals, which were made possible through better charge-transfer processes.

However, most of the reported TiON materials are in the form of either powders or thin films, which are not practical for a scalable photolysis process. With thin films, the light absorption and carrier collection are in competition, i.e., although thick films are needed to harvest a reasonable amount of the solar spectrum, thicker films than the carrier diffusion length (usually tens of nanometers) will result in poor carrier collection efficiency.

It was then interesting to combine both advantages of light absorption and low overpotential catalytic activity. Herein, we report for the first time, the fabrication of silver NPs-decorated titanium oxynitride (Ag/TiON) nanotube arrays to investigate their performance as photoanodes in photoelectrochemical water splitting cells.

**Materials and Methods**

Titanium foil (0.25 mm thick, purity 99.8%) was polished into portions and cleaned in acetone, ethanol and deionized water, respectively. Two-electrode electrochemical cell was used for anodization in which the Ti metal foil (positive electrode) and a platinum foil (negative electrode) were connected to a DC power supply at 30 V. Ethylene glycol-based solutions containing 0.5 M NH$_4$F and 3 ml H$_2$O. All samples were anodized for 120 minutes at room temperature. The resulting titanium oxide nanotubes were then annealed in ammonia flow (200 sccm) at 600 $^\circ$C for two hours. The heating and cooling rates were as low as 2 $^\circ$C/min to preserve the nanotubular architecture and avoid their detachment. As a reference, titanium oxide nanotubes sample was annealed in air (450 $^\circ$C and 2 $^\circ$C/min for 2 hours). The Ag nanoparticles were prepared by the borohydride reduction method. A 100 ml of 1 mM AgNO$_3$ (Sigma-Aldrich, 99.999%) was added to a mixture of 30 ml of 2 mM NaBH$_4$ (Sigma-Aldrich, 98%) under vigorous stirring. For the preparation of Ag decorated TiON nanotube arrays, 50 $\mu$l of Ag colloidal solution (the loading density is 3.42 $\times$ 10$^{11}$ Ag NPs per 1 cm$^2$ foil) was drop-casted onto the TiON foil and left to dry overnight.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) measurements were carried out using an FEI electron scanning microscope. The powder X-ray diffraction (XRD) measurements were carried out at room temperature using Rigaku Miniflex II diffractometer with Cu K$_\alpha$ radiation at 30 kV and 20 mA between 20 angles of 20 and 80° with scanning rate of 0.025° per step per second. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Kratos Axis Ultra XPS with a monochromatic Al K$_\alpha$ radiation source (1486.6 eV) in a UHV environment (ca. 5 $\times$ 10$^{-9}$ Torr). Transmission electron microscopy (TEM) images were acquired by an FEI Philips Technai 20 transmission electron microscope with an accelerated voltage of 200 kV. The optical absorption of the samples was measured using a Cary 5000 UV-Vis-NIR spectrophotometer. The J-V measurements were carried in a three-electrode electrochemical cell with a saturated calomel electrode (SCE), a platinum wire and the tested sample were used as reference, counter, and working electrodes, respectively. The area of the working electrode was 0.88 cm$^2$ and that of the counter electrode was 3.145 cm$^2$. The electrode (SCE), a platinum wire and the tested sample were used as reference, counter, and working electrodes, respectively. The area of the working electrode was 0.88 cm$^2$ and that of the counter electrode was 3.145 cm$^2$. The working electrode was immersed in 0.1 M KOH (Carl-Roth, Germany 99.98%). The KOH solution was prepared from ultrapure water (18.2 MΩ cm at 25 $^\circ$C, TOC < 1 ppb) and was purged with nitrogen gas during the measurement. A scanning potentiostat (Gamry 3000) was used to measure dark and illuminated currents at a scan rate of 10 mV/s. A 100 W ozone-free xenon lamp (Abet Technologies, USA) was used as the light source, with an AM 1.5 G filter to simulate sunlight at 100 mW/cm$^2$.

**Results and Discussion**

Figure 1a shows an FESEM top-view image of the fabricated titanium oxide nanotubes. The well-aligned, densely packed nanotube arrays that are several microns long were formed and distributed uniformly with full coverage even after annealing in air (Fig. 1a) or ammonia ambient for 2 h (Fig. 1b). Note that the nanotubular structure has not been affected by annealing, where the diameter is slightly increased into 54 nm and the wall thickness is 14 ± 2 nm. Figure 1c shows the Ag nanoparticles-decorated nanotubes. Also, Fig. 1d shows HRTEM image of the silver nanoparticles. To prepare such electrodes, 50 $\mu$l of Ag colloidal solution was drop casted onto the TiON foil and left to dry overnight. Then, the Ag/TiON surface was washed with ultrapure water. Note that the Ag nanoparticles are well-dispersed on the TEM grid with uniform size (13 ± 2 nm) and spherical shape.

To investigate the structure and composition of the fabricated nanotube arrays, EDX (Fig. 2a), XRD (Fig. 2b) and XPS (Fig. 3) analyses were performed. Figure 2a shows the EDX spectra for (i) air-annealed, (ii) ammonia-annealed, and (iii) Ag-decorated ammonia-annealed titanium dioxide nanotube arrays. The peak at 2.77 eV is related to carbon species, whereas the peak at 0.252 eV is related to oxygen species. Note that the intensity of the peak at 0.252 eV decreased after annealing in ammonia and another peak emerged at 0.392 eV, which is assigned to nitrogen atoms. The sharp peak at 2.984 eV is a good indication for Ag decoration on TiON nanotube arrays. The common peak around 4.508 eV belongs to titanium species. Figure 2b shows the XRD patterns of the nanotubes annealed in air and those annealed in ammonia, revealing crystalline structures of titanium oxide. The appearance of the characteristic diffraction peaks at 25°, 38.1°, 47.8°, 52.8°, and 53.9°, corresponding to the (101), (004), (200), (105), and (211) facets, respectively elucidate the crystalline structures of titanium oxide. Note that the peak at 20 = 43° appeared in the XRD spectra of NH$_3$-annealed sample corresponds to the cubic phase of titanium oxynitride as reported by Zukalova et al. Furthermore, the signature of the underlying Ti metal is apparent as indicated from the sharp peak at 40°. Upon annealing in ammonia, the peaks are still located at the same angle, however the intensity of the peaks decreased (Fig. 2b,ii). Note that both oxides and oxynitrides are usually having virtually overlapping XRD patterns.
As XRD could not distinctively confirm the formation of TiON nor the presence of the Ag nanoparticles, XPS being a surface sensitive technique, is believed to resolve the differences between the oxides and oxynitrides\(^\text{10}\). Figure 3 shows the XPS high-resolution scans of the four elements; Ti, O, N and Ag for air-annealed, ammonia-annealed, and Ag-decorated ammonia-annealed nanotube samples and the data are listed in Table 1. Figure 3a shows the Ti 2p XPS lines. The Ti 2p spectrum of the air-annealed TiO\(_2\) sample (Fig. 3a,i) exhibits two peaks at 458.5 and 464.3 eV characteristic of Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\), with a spin orbit splitting of 5.8 eV, indicating Ti\(^{4+}\) oxidation state\(^\text{15}\). Upon annealing in ammonia (Fig. 3a,ii) and Ag decoration (Fig. 3a,iii), both peaks are shifted to low energy side. This can be related to the introduction of a less electronegative atom into the crystal lattice of TiO\(_2\). This finding suggests the introduction of N into the titania lattice because it has a smaller electronegativity (3.04 on Pauling scale) compared to O (3.44 on Pauling scale)\(^\text{28}\). Figure 3b shows O1s XPS spectra.
acquired for air-annealed, ammonia-annealed, and Ag-decorated nanotube samples. The spectrum shown in Fig. 3ai exhibits small shoulder at 532.2 eV and a singlet peak at 531.4 eV. The peak at 531.4 eV is attributed to O-H groups, and the small shoulder at 532.2 eV can be attributed to physisorbed water29. The position of the shoulder shifted a little to lower binding energies after annealing in ammonia (ii, iii). Such shift caused by the increase of titanium in low valence states29. Note that the Ti 2p3/2 photoemission line at 458.5 eV is diagnostic for oxynitride (Ti-O-N)29. Figure 3c shows the N1s XPS spectra acquired for air-annealed, ammonia-annealed, and Ag-decorated ammonia-annealed samples. The N 1s peak observed at 402.3 eV can be attributed either to incorporation of nitrogen into the nanotubes30,31, or to chemisorbed nitrogen30–32. Clearly one can see a small shoulder at 400 ± 0.2 eV (Fig. 3c,ii,iii), which can be ascribed to γ-N state, which is molecularly chemisorbed N2.
385 nm (3.2 eV) to 410 nm (3.03 eV). However, annealing in ammonia resulted in a significant red-shift in the nanotube (Ag/TiON) samples. Annealing in air resulted in a small red-shift in the absorption wavelength from photogenerated electron-hole pairs, thereby enhancing the IPCE. Upon the use of 0.2 V and 0.4 V (Fig. 4d), Ag/TiON showed similar IPCE behavior except for a small hump at 480 nm. The applied bias assists the separation of the films in the visible light, in accordance with the absorption spectra shown in Fig. 4a. Note that the Ag/TiON films results on N-doped TiO$_2$ nanotubes, indicating the high quality of the nanotubes. Interestingly, the oxynitride nanotubes showed exceptional photocatalytic activity compared to the TiO$_2$ and TiON nanotube photoanodes counterparts, indicating more favorable photoelectrochemical activity.

The incident photon conversion efficiency (IPCE) experiments were performed in a two-electrode arrangement with the TiO$_2$, TiON, or Ag/TiON nanotube array films as the working photoelectrodes and platinum foil as a counter electrode in 0.1 M KOH solution. Figure 4c shows the obtained IPCE for the nanotube array films as a function of the irradiation wavelength under no bias. The IPCE was calculated using Eq. 1, where $\lambda$ is the wavelength of incident light, $i_{ph}$ is the photocurrent density under illumination at $\lambda$ and $I_o$ is the incident light intensity at $\lambda$. 

$$\text{IPCE}\% = \left(\frac{1240 \text{ eV. nm}}{\lambda \text{ nm}}\right) \times \left(\frac{i_{ph} \text{ mA. cm}^{-2}}{I_o \text{ mW. cm}^{-2}}\right) \times 100$$

The obtained IPCE values, Fig. 4c, in the wavelength range from 400 to 550 nm indicate the activity of TiO$_2$ nanotubes in the visible light, in accordance with the absorption spectra shown in Fig. 4a. Note that the Ag/TiON films showed similar IPCE behavior except for a small hump at 480 nm. The applied bias assists the separation of the photogenerated electron-hole pairs, thereby enhancing the IPCE. Upon the use of 0.2 V and 0.4 V (Fig. 4d), Ag/TiON films showed an enhancement in the IPCE: between 350–400 nm, the IPCE increases up to 25%, then it further increases to 41% in the wavelength range 450–510 nm, after which it declines indicating that the photocurrent occurs as a result of the band gap transition. Note that the maximum IPCE peak was observed around 480 nm, which is the commonly reported plasmonic peak or Ag nanoparticles, suggesting that the enhancement in the photoelectrochemical activity is partially supported by the plasmonic effect of Ag NPs. The obtained IPCE

Table 2. Traditional and Kröger-Vink notations of defects in TiO$_2$ and N-doped TiO$_2$ systems.

| Traditional Notation | Description | Kröger-Vink Notation |
|----------------------|-------------|----------------------|
| Ti$_{i}^{3+}$ | Ti$^{3+}$ ion in titanium lattice site | Ti$_{i}^{3+}$ |
| Ti$_{i}^{+}$ | Ti$^{+}$ ion in titanium lattice site | Ti$_{i}^{+}$ |
| V$_{Ti}$ | Titanium vacancy | $V_{Ti}^{*}$ |
| Ti$_{i}^{3+}$ | Ti$^{3+}$ in an interstitial site | Ti$_{i}^{3+}$ |
| Ti$_{i}^{+}$ | Ti$^{+}$ in an interstitial site | Ti$_{i}^{+}$ |
| O$_{i}^{2-}$ | O$^{-}$ ion in an oxygen lattice site | O$_{i}^{2-}$ |
| V$_{O}$ | Oxygen vacancy | $V_{O}^{*}$ |
| O$_{i}$ | O$^{-}$ ion in an oxygen lattice site | O$_{i}^{*}$ |
| N$_{i}^{-3}$ | N$^{-}$ ion in an oxygen lattice site | N$_{i}^{*-3}$ |
| N$_{i}$ | N$^{-}$ ion in an interstitial site | N$_{i}^{*-3}$ |

Additionally, the peak at 396 ± 0.2 eV belongs to β-N state, which is essentially atomic N in the form of mixed titanium oxide-nitride (TiO$_2$-xN$_x$). This indicates that the heat treatment in ammonia atmosphere indeed leads to the substitution of some oxygen sites by nitrogen, see Table 2. This finding is in good agreement with previous results on N-doped TiO$_2$ samples. Figure 3d is Ag 3d core level XPS scan over a small energy window at higher resolution. The Ag 3d$_{5/2}$ peak appears at 368.3 eV and the Ag 3d$_{3/2}$ peak is found at 374.3 eV, with a splitting of the 3d doublet of 6.0 eV, indicating that Ag mainly exists in metallic state on the sample of Ag-decorated nanotubes.

Table 2. Traditional and Kröger-Vink notations of defects in TiO$_2$ and N-doped TiO$_2$ systems.

$\lambda$ and $\lambda_{ph}$ are the wavelength of incident light and photocurrent, respectively.
for TiON and Ag/TiON nanotube films are much higher than that obtained for the pristine TiO₂ nanotube film, in good agreement with the UV-vis DRS results shown in Fig. 4a. We note that our obtained IPCE is higher than that reported for N-doped titanium dioxide nanotube arrays39.

Considering the correlation between the structure of the fabricated photoanodes and the observed enhanced photoresponse, the thin wall thickness of the synthesized TiON nanotube arrays is expected to play a vital role. The nanotubular architecture, with a wall thickness of 14 ± 2 nm, ensures that the photogenerated holes are never generated far from the semiconductor-electrolyte interface40. Furthermore, since half the wall thickness is significantly less than the minority carrier diffusion length (~20 nm in TiO₂)41, charge-carrier separation takes place efficiently. The potential drop (Δ∅₀) within the tube wall was shown to follow the relation36:

\[ Δ∅₀ = \frac{kT r₀^2}{6eL_D} \]  

where \( r₀ \) is half the width of the wall, \( T \) is the temperature, and \( L_D \) is the Debye length, given by42:

\[ L_D = \left[ \frac{\varepsilon_{\infty} kT}{2e^2N_D} \right]^{1/2} \]  

where \( N_D \) is the number of ionized donors per cubic centimeter42. It is important to note that this potential drop across the wall thickness may not be enough to separate the photogenerated electrons and holes. However, because of the nanoscale dimensions of the walls, the holes can easily diffuse into the surface, which was shown to take place on a scale of picoseconds43. It was also reported that minority carriers generated within a distance from the surface equal to the sum of the depletion layer width and the diffusion length (retrieval length) escape recombination and reach the electrolyte44. Note that the relevant dimensional features of our TiON nanotube arrays (half the wall thickness) are all smaller than 10 nm, which is the range reported for crystalline TiO₂.
retrieval length. Therefore, bulk recombination is expected to be reduced and the photoconversion efficiency to be enhanced.

Conclusions
In summary, we report the first demonstration of a facile method for the fabrication of highly ordered titanium oxyxinitride nanotubes with large surface area and high crystallinity. The as-anodized TiO\textsubscript{2} array films retain their morphology upon annealing in ammonia ambient, realizing the opportunity to convert TiO\textsubscript{2} into TiON at temperatures as low as 600 °C. Interestingly, titanium oxyxinitride nanotubes showed significant increase in the photocurrent (6 mA/cm\textsuperscript{2}) compared to the as-anodized TiO\textsubscript{2} nanotubes counterpart (0.15 mA/cm\textsuperscript{2}). In addition, decorating the TiON nanotubes with Ag nanoparticles resulted in exceptionally high photocurrent reaching 14 mA/cm\textsuperscript{2} at 1.0 V\textsubscript{SC}. Finally, this proposed platform of titanium oxyxinitride nanotubes array films holds promise for a variety of applications of the future design of optoelectronic devices.

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Author Contributions
N.K.A., A.S.A. and S.Y.A. supervised and coordinated all aspects of the project. K.A.S. synthesized the nanotubes and performed most of the electrochemical measurements, A.F.Z. synthesized the silver nanoparticles and acquired the XRD and TEM data, A.K. performed the UV-Vis and IPCE measurements, H.A.E. performed the nitridation and optimized the process to obtain the desired oxynitride. All authors contributed to the writing of the manuscript. N.K.A. took care of the submission and revision of the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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