Heterostructured TiO$_2$ Nanoparticles/Nanotube Arrays: In Situ Formation from Amorphous TiO$_2$ Nanotube Arrays in Water and Enhanced Photocatalytic Activity

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Heterostructured TiO$_2$ nanoparticles/nanotube arrays (NPs/NTAs) are produced from as-anodized amorphous TiO$_2$ nanotube arrays in water at a temperature as low as 90°C. The phase and morphology transformation of the as-anodized amorphous TiO$_2$ nanotube in water can be attributed to a water-induced dissolution and recrystallization mechanism in which the as-anodized amorphous TiO$_2$ NTAs are gradually self-sacrificed, and then spontaneously morphing into the composite NPs/NTAs structure consisting of anatase NPs and thinner amorphous NTs. The composite can be further crystallized into anatase TiO$_2$ NPs/NTAs consisting of anatase NT and anatase NPs by annealing in air at 450°C for 3 hours. The composite anatase TiO$_2$ NPs/NTAs have a surface area that is 1.4 times larger than that of the anatase TiO$_2$ NTAs and possess enhanced photocatalytic activity in the photodecomposition of organic pollutants and water splitting. The photodecomposition rate of the organic pollutant rhodamine B by the anatase TiO$_2$ NPs/NTAs photocatalyst is two times higher than that by the annealed anatase TiO$_2$ NTAs. The enhanced photocatalytic activity of the hererostructured TiO$_2$ NPs/NTAs arises from the large surface area of the TiO$_2$ NPs and superior electron transport in anatase TiO$_2$ NT. The in situ hydrothermal conversion of the microstructure from amorphous TiO$_2$ NTAs into hererostructured TiO$_2$ NPs/NTAs in water is very simple thereby enabling the design and fabrication of highly photoactive one-dimensional TiO$_2$-based functional materials applicable to photocatalysis and solar energy conversion.

Introduction

Semiconductor photocatalysts have recently received considerable attention owing to their wide applications to environmental purification, solar energy conversion, and water splitting.[1, 2] TiO$_2$ nanoparticles (NPs) such as Degussa P25 have been extensively investigated as a promising photocatalyst to remove environmental pollutants.[3] However, recovery of the suspended TiO$_2$ NPs from the slurry after the photocatalytic reaction is very difficult and energy consuming. TiO$_2$ nanotube arrays (TiO$_2$ NTAs) can overcome such drawbacks and allow easy recovery for recycling purposes. Anodization is a relatively simple and efficient method to fabricate highly ordered TiO$_2$ NTAs on Ti foils or any three-dimensional (3D) nonplanar surfaces.[2, 4] The anodized TiO$_2$ NTAs grow directly and adhere strongly to the underlying Ti substrate, thus allowing easy recovery of the photocatalyst. In addition, the TiO$_2$ NTAs film possesses improved charge transport properties because the nanotube wall provides a direct path for electron transport resulting in enhanced photoelectrochemical properties.[5] Hence, highly ordered TiO$_2$ NTAs prepared by electrochemical anodization have attracted increasing attention and are gaining popularity in environmental purification, photoelectrochemical decomposition of water, solar cells, and biological coatings.[6]

The photocatalytic activity and photoelectrochemical properties of TiO$_2$ are related to its morphology, surface area, phase structure, as well as photogenerated charge separation and transport performance.[7] The as-anodized TiO$_2$ NTAs are usually in the amorphous state, and so a high-temperature treatment is generally required to form the more photocatalytically active anatase structure. Although the anatase TiO$_2$ NTAs exhibit high charge transport and collection efficiency, the surface area is smaller than that of nanoparticles or the mesosponge structure, thereby leading to lower dye absorption and light harvesting.[2] In contrast, anatase TiO$_2$ NPs provide a high surface area for light harvesting, but the random zigzag electron transport paths stifle electron transport in films composed of TiO$_2$ NPs.[8] In view of these factors, the heterostructured TiO$_2$ NPs/NTAs composite structure composed of anatase TiO$_2$ NTAs and anatase NPs should exhibit improved photoelectrochemical properties because they combine the merits of the large surface area of NPs and superior electron transport properties of the NTs. Recently, efforts have been devoted to the fabrication of TiO$_2$ NPs/NTAs composite nanostructures includ-
The as-anodized amorphous TiO$_2$ NTAs on Ti are not stable under hydrothermal treatment in water at a temperature as low as 90 °C. This hydrothermal process does not require any other additive or Ti precursor except water. Formation of the composite TiO$_2$ NPs/NTAs from amorphous TiO$_2$ NTAs is attributed to a water-induced dissolution and recrystallization mechanism, in which the as-anodized amorphous TiO$_2$ NTAs are gradually self-sacrificed, and then spontaneously morphing into the composite NPs/NTAs structure consisting of anatase NPs and thinner amorphous NTs and finally into TiO$_2$ nanorod arrays (NRAs) composed of connecting anatase NPs. The spontaneously formed composite TiO$_2$ NPs/NTAs have a surface area 1.4 times larger than that of the annealed anatase TiO$_2$ NTAs, thus leading to enhanced photocatalytic activity in the photo-decomposition of organic pollutants and water splitting in comparison with the pristine TiO$_2$ NTAs. Moreover, the photocatalytic activity of the hydrothermally formed TiO$_2$ NPs/NTAs can be further improved by subsequent annealing to form the anatase TiO$_2$ NPs/NTAs structure. The photodecomposition rate of the organic pollutant rhodamine B (RhB) on the anatase TiO$_2$ NPs/NTAs photocatalyst is two times larger than that on the annealed anatase TiO$_2$ NTAs. The in situ hydrothermal conversion of the microstructure from amorphous TiO$_2$ NTAs to NPs/NTAs in water is very simple and environmentally friendly. Furthermore, if a metal (M) ion is present in water, the hetero-structured MTiO$_3$ NPs/TiO$_2$ NTAs can be easily obtained by a similar hydrothermal treatment of amorphous TiO$_2$ NTAs. The results presented herein are applicable to the design and fabrication of highly photoactive 1D TiO$_2$-based functional materials, which have potential use in photocatalysis and solar energy conversion.

**Results and Discussion**

Figure 1a depicts the typical top-view image of the field-emission scanning electron microscopy (FE-SEM) image of the NTAs fabricated by anodization in an ethylene glycol electrolyte containing 0.5 wt% NH$_4$F and 5 vol% distilled (DI) water at 60 V for 1 hour, showing that uniform NTAs with an inner diameter of 110 nm and wall thickness of 15 nm are formed. The side view FE-SEM image in Figure 1b reveals that the NT has a smooth outside surface and the length of NTAs is about 6 μm. Although the outer diameter remains the same, the wall thickness of the NT increases with depth from 15 nm at the top to 50 nm on the bottom. The transmission electron microscopy (TEM) image in Figure 1c also shows the gradually thickened wall with depth. The diffuse ring of selected-area electron diffraction (SAED) pattern in the inset of Figure 1c of the single NT indicates the amorphous nature of the as-anodized NTAs. The glancing angle XRD pattern (GAXRD, glancing angle of 1°) of the as-anodized NTAs shows no diffraction peaks of any TiO$_2$ phases, thus further indicating the amorphous nature of the as-anodized NTAs (curve 1 in Figure 1d). However, the anatase TiO$_2$ peaks can be clearly observed when the as-anodized NTAs are annealed at 450 °C for 3 hours in air (curve 2 in Figure 1d). The high-resolution X-ray photoelectron spectroscopy (XPS) Ti(2p) spectra of the as-anodized NTAs after Ar sputtering for 10 nm are located at 455.3/461.5 eV, 457/463.1 eV, and 464.8/459.3 eV (curve 1 in Figure 1e) corresponding to Ti$^{4+}$/TiO, Ti$^{3+}$/Ti$_2$O$_3$, and Ti$^{4+}$ in TiO$_2$, respectively, thus suggesting that the as-anodized NTAs contain a large amount of suboxide species. However, when the NTAs are annealed at 450 °C for 3 hours in air, only the Ti(2p) peaks corresponding to Ti$^{4+}$ in TiO$_2$ exist (Figure 1e, Curve 2). The results evidently suggest that the anodized titania NTAs are amorphous and composed of not only TiO$_2$ but also an abundant amount of titanium suboxide species such as TiO and Ti$_2$O$_3$.

The as-anodized amorphous TiO$_2$ NTAs on Ti are not stable in water under hydrothermal conditions. They are first converted into the composite TiO$_2$ NPs/NTAs structure and finally mesoporous anatase TiO$_2$ NRAs. Figure 2a–c depicts the SEM images of the as-anodized amorphous TiO$_2$ NTAs after hydrothermal treatment in water at 90 °C for different periods of time (3–4 h). Image a in Figure 2 depicts the FE-SEM image of the pristine as-anodized TiO$_2$ NTs hydrothermally treated in...
water for over 3 hours at 90 °C, and indicates that many small particles with a size of 10 nm are formed and uniformly attached on the surface of NT to form the composite NPs/NTs structure. When the hydrothermal treatment time is increased to 3.5 hours, more and bigger particles with a size of 20–30 nm are formed. At the same time, the nanotube wall becomes thinner although the tubular structure is retained. After increasing the hydrothermal treatment time to over 4 hours, the original morphology of NTs is not visible, but instead NRs are formed (Figure 2 c). The XRD patterns obtained at different hydrothermal treatment time are depicted in Figure 2 d. The anatase TiO₂ diffraction peaks can be clearly observed from the samples after 3 hours of hydrothermal reaction and the relative intensity of the anatase TiO₂ peaks increases when the NTs are fully converted into NRs.

Figure 3 displays the representative TEM micrographs and energy-dispersive X-ray spectroscopy spectrum of the composite TiO₂ NPs/NTs corresponding to the sample shown in Figure 2 b. Figure 3 a indicates that NPs with a size 20–30 nm are attached onto the inner wall of the NT forming the composite NPs/NT structure. The EDS spectrum of the composite (Figure 3 b) reveals well-resolved and strong signals of Ti and O, thus suggesting that the NPs/NT composites are composed of mainly Ti and O. In comparison with the pristine as-anodized NT with a tube wall thickness of 15 nm, the thickness of the tube wall in the composite NPs/NT is thinner and about 9 nm as shown in Figure 3 c. Because there is no extraneous Ti source, the NPs should be from the NT wall, which is formed by partial self-sacrifice and recrystallization. The high-resolution TEM (HR-TEM) images in Figure 3 d,e suggests that the NPs comprise crystallized anatase phase, but the NT wall still remains in the amorphous state. The distance of 0.35 nm between two neighboring fringes of the NP can be clearly identified in Figure 3 e. It corresponds to the d-spacing of [101] planes of anatase TiO₂. The results evidently demonstrate that

the heterostructured nanostructures composed of anatase NPs and amorphous NTs can be spontaneously and controllably synthesized in situ by using a mild hydrothermal reaction at 90 °C without any foreign reactants except water. This heterostructure composed of anatase TiO₂ NPs and amorphous NT can be further converted into anatase TiO₂ NPs/NTs consisting of anatase NPs and anatase NT by annealing at 450 °C for 3 hours in air.

The microstructure and morphology of the NRs are also investigated. Figure 4 a shows the typical FE-SEM images of the NRs and the NRs have similar geometrical dimensions (130 nm in diameter and 6 µm in length) in comparison with the pristine amorphous NTs. The representative TEM image of a single NR suggests that the NR is composed of accumulated NPs as shown in Figure 4 b. The NPs have a diameter of 30–50 nm and are linked together to form a NR. The HR-TEM picture in Figure 4 c reveals single-crystalline anatase TiO₂ and it is consistent with the XRD data in Figure 2 d.
The hydrothermal temperature affects the transformation rates of amorphous TiO$_2$ NTAs to NPs/NTAs and finally anatase TiO$_2$ NRAs in water. At a higher temperature such as 200°C, amorphous TiO$_2$ NTAs can only retain its pristine morphology within 35 minutes (Figure S1a in the Supporting Information). After 40 minutes, the smooth surface of NTAs becomes rough and particles emerge on the surface (Figure S1b). When the hydrothermal reaction time is increased to 45 minutes, the pristine morphology of NTAs disappears completely and NRAs are formed (Figure S1d). However, at a lower temperature of 80°C, the amorphous TiO$_2$ NTAs can retain the original tubular morphology after undergoing the hydrothermal reaction over 8 hours (Figure S2c).

To explore the role of water in the spontaneous phase and morphological transformation from amorphous TiO$_2$ NTAs to NPs/NTAs and NRAs, the as-anodized amorphous TiO$_2$ NTAs are also hydrothermally treated in pure ethanol and a mixture of ethanol and water under the same experimental conditions. In 40 mL of pure ethanol (Figure 5a), the amorphous TiO$_2$ NTAs retain the original ordered tubular structure at 200°C for 6 hours. However, by adding 1 mL water to 40 mL of ethanol (Figure 5b), some NPs appear and composite NPs/NTAs are produced. When the amount of water is increased to 2 mL, the quantity of NPs increase and the size becomes bigger as shown in Figure 5c. After adding 4 mL of water, the nanotubular structure vanishes completely and TiO$_2$ NRAs are formed instead (Figure 5d). The corresponding XRD patterns of the sample obtained with different water amounts are depicted in Figure 5e. No diffraction peaks related to anatase phase can be observed from the sample hydrothermally treated in pure ethanol. However, the strong anatase peaks can be observed clearly from samples hydrothermally treated in the ethanol and water mixture. In addition, the relative intensity of the anatase peaks is enhanced with larger water contents.

Our results indicate that the morphology and phase evolution from amorphous titania to NPs/NTAs and finally NRAs under hydrothermal conditions are governed by water-assisted dissolution and precipitation. As schematically shown in Figure 6, when the amorphous titania NTAs are hydrothermally treated in water, the unstable TiO$_6^{2-}$ octahedrons of amorphous TiO$_2$ and titanium suboxide species first absorb water molecules through the surface hydroxy groups to form insoluble species of Ti(OH)$_6^{2-}$, which can be further dehydrated and precipitated by bridging together and sharing faces to form anatase TiO$_2$. The overall reaction is described as follows by Equations (1) and (2):

\[
\text{TiO}_x + 4\text{H}_2\text{O} + (1-x/2)\text{O}_2 \rightarrow \text{Ti(OH)}_6^{2-} + 2\text{H}^+ \quad (1 < x \leq 2) \quad (1)
\]

\[
\text{Ti(OH)}_6^{2-} + 2\text{H}^+ \rightarrow \text{TiO}_2 + \text{H}_2\text{O} \quad (2)
\]

The freshly formed TiO$_2$ NPs attach onto the surface of the remaining amorphous TiO$_2$ NT wall and consequently, heterostructured TiO$_2$ NPs/NTAs composed of anatase NPs and amorphous NT are produced as schematically shown in Figure 6. In this process, the NPs are only from the self-sacrificed amorphous NT wall because there is no foreign Ti source. As a result, the nanotube thickness of the NPs/NTAs becomes thinner compared to the pristine amorphous NTAs as shown in Figure 1c and Figure 3c. Because the space between the adjacent TiO$_2$ NTs of a few nanometers is far smaller than the interior of the NTs of about 100–110 nm, water molecules can easily access the inner surface and dissolution/precipitation of TiO$_2$ onto the inner shell of the tube walls is more kinetically favorable. Therefore, anatase TiO$_2$ NPs are formed and attach onto the inner surface of the remaining TiO$_2$ NT, thus resulting...
in the formation of composite NPs/NTAs composed of anatase TiO2 NPs and amorphous TiO2 NT, as schematically illustrated in Figure 6. The remaining amorphous nanotube wall of the composite NPs/NTAs can be further etched by water molecules until the tube wall disappears under hydrothermal conditions, and thus the mesoporous anatase TiO2 NRAs are finally formed as schematically shown in Figure 6. Owing to the presence of titanium suboxide species in the NT wall, oxygen molecules dissolved in water participate in the in situ hydrothermal conversion of the microstructure from amorphous TiO2 NTAs to heterostructured TiO2 NPs/NTAs as suggested by Equation (1). If the dissolved oxygen in water is eliminated by purging with high purity N2 for 1 hour and the Teflon-lined autoclave was sealed while the hydrothermal reaction was carried out under similar experimental conditions, then the NTs still retain the tubular morphology after hydrothermal treatment as shown by Figure S3.

The hydrothermally and spontaneously formed composite NPs/NTAs could crystallize into anatase TiO2 NPs/NTAs by thermal annealing at 450 °C for 3 hours in air. The anatase TiO2 NPs/NTAs have good hydrothermal stability and could retain the NPs/NTAs composite structure under hydrothermal conditions (Figure S4). The surface areas of the TiO2 NTAs, TiO2 NPs/NTAs composite, and mesoporous anatase TiO2 NRAs are measured to be 36.2, 49.0, and 52.4 m²g⁻¹ according to Brunauer–Emmett–Teller (BET) analysis through N₂ adsorption (Figure S5). The results provide evidence that anatase NPs/NTAs composite and mesoporous anatase TiO2 NRAs with a larger surface area can be easily and controllably fabricated from as-anodized amorphous TiO2 NTAs by a water-induced dissolution and recrystallization process.

The photocatalytic activity of the TiO2 NTAs, composite TiO2 NPs/NTAs (hydrothermal reaction (HR) for 3 h), and mesoporous TiO2 NRAs is evaluated by means of photodegradation of rhodamine B (RhB) in an aqueous solution under illumination with UV light and compared to that of the thermally annealed counterparts treated at 450 °C in air for 3 hours. The results are depicted in Figure 7a. The as-anodized amorphous TiO2 NTAs exhibit weak photocatalytic activity owing to the amorphous nature, but on the other hand, the hydrothermally formed TiO2 NPs/NTAs composite and mesoporous anatase TiO2 NRAs show obviously enhanced photocatalytic activity. When the three samples are annealed at 450 °C for 3 hours in air, the mesoporous TiO2 NRAs show no discernible change in the photocatalytic activity because the hydrothermally obtained mesoporous NRAs already have an anatase structure and heat treatment cannot alter the phase and crystalline structure. However, the annealed TiO2 NTAs and TiO2 NPs/NTAs exhibit clearly improved photocatalytic activity relative to their counterparts without calcination because thermal calcination in air at 450 °C enables the amorphous nanotube walls to crystallize into the more photocatalytically active anatase structure. In comparison with anatase TiO2 NTAs, the as-obtained mesoporous TiO2 NRAs show improved photocatalytic activity owing to the improved surface area and the annealed anatase TiO2 NPs/NTAs has the highest photocatalytic activity among the samples. The excellent photocatalytic property of heterostructured anatase TiO2 NPs/NTAs can be attributed to the combined merits of the large surface area of the TiO2 NPs and superior electron transport properties of anatase TiO2 NT. The photodegradation behavior of RhB in the presence of these photocatalysts obey the first-order reaction kinetics expressed as \( \ln(C/C_0) = -kt \), where \( k \) is the rate constant, \( t \) is the irradiation time, and \( C_0 \) and \( C \) are the initial and reaction concentrations of the RhB aqueous solution, respectively. As shown in Figure 7b. The \( k \) value of anatase mesoporous NRAs is 0.4 h⁻¹ and 1.5 times larger than that of anatase TiO2 NTAs. The enhancement in photocatalytic activity of the mesoporous TiO2 NRAs can be ascribed to the larger surface area according to the BET analysis shown in Figure S5. The annealed TiO2 NPs/NTAs possess the highest photocatalytic activity among the samples and the \( k \) value of the annealed TiO2 NPs/NTAs is 0.56 h⁻¹, which is two times larger than that of the annealed TiO2 NTAs. However, the photocatalytic activity cannot be fully accounted for by the improved surface area, because the surface area of the anatase TiO2 NPs/NTAs is merely 1.4 times larger than that of the thermally annealed TiO2 NTAs. In addition, the mesoporous TiO2 NRAs have a larger surface area than the anatase TiO2 NPs/NTAs, but inversely, the annealed TiO2 NPs/NTAs have higher photocatalytic activity than the mesoporous TiO2 NRs.

Figure 8a,b displays the photocurrent density as a function of applied potential (vs. Ag/AgCl) and transient photocurrent responses in a 0.5 M Na₂SO₄ solution under UV irradiation of
Conclusion

Heterostructured TiO$_2$ nanoparticles/nanotube arrays (NP/NTAs) are produced spontaneously from as-anodized amorphous TiO$_2$ nanotube arrays in water at a temperature as low as 90 °C. The phase and morphological transformation of the as-anodized amorphous TiO$_2$ nanotubes in water are characterized and a mechanism encompassing water induced dissolution and recrystallization is proposed. The amorphous TiO$_2$ nanotube wall can be gradually etched by water molecules and converted into anatase nanoparticles, which are attached onto the remaining thinner amorphous nanotube wall, thus resulting in the formation of the composite NPs/NTAs structure. The TiO$_2$ NPs/NTAs have an improved surface area that is about 1.4 times larger than that of the pristine TiO$_2$ NPs. The photocatalytic activity can be further improved by annealing to form the anatase TiO$_2$ NPs/NTAs structure composed of anatase NPs and NT by annealing in air at 450 °C for 3 hours. The photosensitization rate of the organic pollutant RhB on the anatase TiO$_2$ NPs/NTAs photocatalyst is two times larger than that on the annealed anatase TiO$_2$ NPs. The enhanced photocatalytic activity achieved from the heterostructured TiO$_2$ NPs/NTAs is ascribed to the large surface area of TiO$_2$ NPs and superior electron transport in the anatase TiO$_2$ NT. The results suggest a facile and practical route to improve the photocatalytic activity of composite NPs/NTAs by simple hydrothermal modification and also pave the way for the design of various TiO$_2$-related functional materials by doping, deposition, and sensitization applicable to photocatalysis and solar energy conversion.

Experimental Section

Fabrication of amorphous titanium oxide nanotube arrays and in situ hydrothermal transformation into composite anatase TiO$_2$ nanoparticles/nanotube arrays

The amorphous titanium oxide nanotube arrays were fabricated by electrochemical anodization. In brief, Ti foils (99.7 % pure, Aldrich, 10 × 20 × 1 mm$^3$) were first polished by SiC sandpaper and then ultrasonically cleaned with acetone, ethanol, and deionized water sequentially. Electrochemical anodization was carried out in a two electrode configuration with a graphite plate cathode and Ti foil anode. After anodization in an ethylene glycol solution with 0.5 wt% NH$_4$F and 5 vol% H$_2$O at 60 V for 1 hour, the samples were rinsed in distilled (DI) water and dried in air. Then the samples were annealed at 200 °C in air to strengthen adhesion between the Ti substrate and as-anodized NTAs film. Afterwards, the samples were placed vertically and immersed in 40 mL of H$_2$O solution in a 60 mL Teflon-lined autoclave on a holder. The autoclave was sealed and heated in an oven for different time periods. After the hydrothermal reaction, the specimens were removed from the vessel and ultrasonically washed with DI water for 5 minutes and then dried in air to obtain the sample of composite anatase TiO$_2$ nanoparticles/nanotube arrays (TiO$_2$ NPs/NTAs).

Characterization methods

The samples were characterized by glancing angle X-ray diffraction with Cu$_{K\alpha}$ radiation (λ = 1.5418 Å; XRD, Philips X’Pert Pro), field-

Figure 8. Photocurrent density as a function of applied potential (vs. Ag/AgCl; a) and transient photocurrent responses (b) in a 0.5 M Na$_2$SO$_4$ solution under UV irradiation for the samples of annealed TiO$_2$ NTAs, TiO$_2$ NPs/NTAs, and TiO$_2$ NRAs electrodes.
emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano), energy dispersive X-ray spectroscopy (EDS, Oxford INCA 200), transmission electron microscopy (TEM; Philips CM20), high-resolution TEM (HR-TEM; JEM-2100F), as well as X-ray photoelectron spectroscopy (XPS, ESCALAB MK-II). The \( N_2 \) adsorption/desorption measurements were carried out at \(-196 \)°C after drying in vacuum at \(100 \)°C for 6 hours on a CHEMBET-3000, and the BET (Brunauer–Emmett–Teller) surface areas of the samples were calculated using the BET equation.

**Photocatalysis and photoelectrochemical measurement**

The photocatalytic activity was assessed by photodegradation of RhB in an aqueous solution. The sample with a size of \( 1 \times 1 \) cm\(^2 \) was immersed in an aqueous solution of RhB (20 mL) with an initial concentration of 2.5 mg L\(^{-1} \). The solution was stirred in darkness for 2 hours to saturate the photocatalyst with RhB. The photodegradation experiments were performed at the natural pH of the RhB dye. The solution was aspirated continuously with air during the photocatalytic reaction. A high pressure mercury lamp (500 W, primary wavelength of 365 nm) was used as the UV irradiation source and the average UV intensity impacting the samples surface was measured to be 5.0 \( \text{mW cm}^{-2} \).

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Heterostructured TiO₂ Nanoparticles/Nanotube Arrays: In Situ Formation from Amorphous TiO₂ Nanotube Arrays in Water and Enhanced Photocatalytic Activity

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Figure S1 FE-SEM images of as-anodized TiO$_2$ NTAs after hydrothermal treatment at 200 °C for (a) 35 min, (b) 40 min, (c) 42 min, and (d) 45 min. The scale bar is 500 nm.
Figure S2 FE-SEM images of as-anodized TiO$_2$ NTAs after hydrothermal treatment in water at 100 °C for (a) 1 h and (b) 1.5 h as well as (c) at 80 °C for 8 h. The bar scale is 500 nm.
**Figure S3** FE-SEM images of as-anodized TiO$_2$ NTAs after hydrothermal treatment in water in nitrogen circumstance. (a) and (b) at 90 °C for 5 h and (c) and (d) at 200 °C for 1 h. The bar scale is 500 nm. Nitrogen is bubbled into the water for 1 h and the autoclave is kept under nitrogen before sealing.
Figure S4. (a) XRD patterns of as-anodized TiO$_2$ NTAs sintered at 200 - 450 °C for 3 h in air together with the corresponding FE-SEM images of the pre-thermally treated specimens after undergoing hydrothermal treatment in water at 200 °C for 50 min (b) and (c), 20h (d) and (e). The scale bar is 500 nm.
Figure S5 N$_2$ absorption/desorption isotherms of the thermally annealed TiO$_2$ NTs, TiO$_2$ NPs/NTAs and TiO$_2$ NRAs.