Spaced Titania Nanotube Arrays Allow the Construction of an Efficient N-Doped Hierarchical Structure for Visible-Light Harvesting

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Regularly spaced \( \text{TiO}_2 \) nanotubes were prepared by anodizing a titanium substrate in triethylene glycol electrolyte at elevated temperature. In comparison to conventional \( \text{TiO}_2 \) nanotubes, spaced nanotubes possess an adjustable spacing between the individual nanotubes; this allows for controlled buildup of a hierarchical nanoparticle-on-nanotube structure. Here, we use this principle for layer-by-layer decoration of the tubes with \( \text{TiO}_2 \) nanoparticles. The hierarchical structure after \( N \) doping and \( \text{NH}_3 \) treatment at \( 450 \) °C shows a significant enhancement of visible-light absorption, although it only carries a low doping concentration of nitrogen. For optimized \( N \)-doped and particle-decorated spaced \( \text{TiO}_2 \) nanotubes, a considerable improvement in photocatalytic activity is obtained in comparison with conventional \( N \)-doped \( \text{TiO}_2 \) nanotubes or comparable \( N \)-doped nanoparticle films. This is attributed to an enhanced visible-light absorption through the \( N \)-doped nanoparticle shell and a fast charge separation between the shell and the one-dimensional nanotubular core.

Ever since the groundbreaking work of Fujishima and Honda[1] on the photoelectrochemical splitting of water on \( \text{TiO}_2 \) electrodes, \( \text{TiO}_2 \) has become the most investigated semiconductor material for photoelectrolysis of water to hydrogen and oxygen and for the photodegradation of organic compounds in a liquid or gas environment.[1–12] However, owing to its wide band gap (ca. 3.2 eV for anatase), photocatalysis in \( \text{TiO}_2 \) can only be activated under UV-light irradiation, which contributes only around 5% to the total energy of solar spectrum.[13] Therefore, introducing modifications that allow the use of \( \text{TiO}_2 \) in both UV and visible light to enhance the photocatalytic efficiency is of great significance. Many efforts have been dedicated to establishing the absorption of \( \text{TiO}_2 \) for visible light, including sensitizing \( \text{TiO}_2 \) with dyes[5,14] and doping \( \text{TiO}_2 \) with metal (V, Fe, Mn) or non-metal (N, C, S, B) elements that form \( p \)-states near the valence band of \( \text{TiO}_2 \).[15–23] Alternatively, cation doping results in localized \( d \)-states deep in the band gap of \( \text{TiO}_2 \), but also leads to a lower activity through the formation of recombination centers.[16]

The most widely and successfully used approach for visible-light absorption is to dope \( \text{TiO}_2 \) with nitrogen, which results in photocatalytic activity under visible-light irradiation.[18,24] Asahi et al. proposed that the \( \text{TiO}_2 \) band gap becomes narrower because the delocalized \( N_2p \) state of the dopant mixes with the \( O2p \) valence band of \( \text{TiO}_2 \).[24] Others proposed that \( N \) doping induces a higher energy valence band caused by the high density of localized \( N_2p \) states in the band structure of \( \text{TiO}_2 \).[25,26] In either case, low-energy photons in the visible region can excite electrons from these occupied high-energy states to the conduction band of \( \text{TiO}_2 \). For photocatalytic reactions, after excitation, generated electrons and holes migrate to the surface and are then transferred to redox couples in the electrolyte. In spite of the advantages of \( N \) doping, the process induces recombination states for electron–hole pairs that can significantly reduce carrier lifetime, that is, \( N \)-doped \( \text{TiO}_2 \) typically provides only short carrier diffusion lengths.[27]

To overcome this drawback, herein we introduce a hierarchical structure based on the formation of a spaced \( \text{TiO}_2 \) nanotube (NT) core as a current conductor decorated with suitable \( \text{TiO}_2 \) nanoparticle (NP) layers. Spaced NT layers can be formed with a large and adjustable spacing between them that allows for a defined layer-by-layer coating of \( \text{TiO}_2 \) NPs on the wall of the NTs (Figure 1a). These decorated NTS then can be annealed in \( \text{NH}_3 \) atmosphere to induce \( N \) doping of the \( \text{TiO}_2 \) NPs on the \( \text{TiO}_2 \) core, that is, a hierarchical structure that shows an enhanced photocatalytic performance. The key here is that spaced NTS allow for a controlled NP decoration; thus, the structure provides both an enhanced surface area and facilitated electron-transport properties when optimally designed.

Figures 1b and 1c show SEM images of spaced \( \text{TiO}_2 \) NTS after anodization in a hot triethylene-glycol-based electrolyte containing \( \text{NH}_3\text{F} \) and \( \text{H}_2\text{O} \) (see the Experimental Section in the Supporting Information). The individual NTS have a length of \( 3 \) μm and a diameter of \( 170 \) nm. It is apparent that each NT is...
The decorated spaced NTs were then annealed in the NH$_3$ environment at 450 °C for 3 h to induce N doping of the TiO$_2$. In the XRD patterns, the intense peak at 2θ = 25.3° (Figure 2a) remains present, corresponding to the anatase phase after the previous thermal treatment in air at 450 °C. That is, after NH$_3$ treatment, the crystallography of the samples remains unchanged although the intensity of anatase peaks slightly decreases. Successful N doping is confirmed by the appearance of N1s peak at 396.5 eV in the XPS spectra (Figures 2b and 2c). Furthermore, the concentration of nitrogen is approximately 2.4 at% and it remains unchanged even at a depth of 100 nm (Figure 2d). This indicates that N doping occurs not only on the surface, but also within the TiO$_2$ structure.

The N-doped samples were then investigated with photocurrent spectra (Figures 3a and 3b). The N-doped samples show significant enhancement of incident photon-to-current conversion efficiency.
efficiency (IPCE) in the visible-light range. The results in Figure 3a also reveal that NP decoration can enhance the IPCE (at 450 nm) almost fivefold, in comparison with plain spaced NTs (1 and 5%, respectively). We found that the maximum IPCE for spaced NTs is obtained after eight layers of decoration and 3 h of NH\textsubscript{3} treatment, whereas lower or higher loadings of TiO\textsubscript{2} particles led to a decrease of photocurrent under visible-light irradiation (Figures S2 and S3). Figure S4 shows the IPCE of different lengths of spaced TiO\textsubscript{2} NTs decorated with eight layers of NPs. We found that the longer the spaced NTs, the higher the IPCE in the visible range. A maximized IPCE was obtained for 10 μm long tubes (Figure S5). The results of photoelectrochemical measurements under visible light show that the N-doped hierarchical structures can be used to more efficiently harvest photocurrent than corresponding non-doped layer (Figure S6).

Figure 3b shows the IPCE results of different samples that illustrate the main difference of the hierarchical NTs, compared with classic close-packed TiO\textsubscript{2} NTs (denoted NTs-NH\textsubscript{3}, Figure S7) and TiO\textsubscript{2} NP layers on FTO substrate (prepared through the doctor blading method, denoted NP layers-NH\textsubscript{3}). In general, NP layers-NH\textsubscript{3} deliver a much lower photocurrent compared to NT samples, owing to the high recombination of electrons and holes in the NP layers.\[37\] Furthermore, under visible light (at 450 nm), the IPCE value of spaced NTs is 5.19%—that is over seven times higher than that measured for classic TiO\textsubscript{2} NTs (0.66%). This is ascribed to the much higher particle loading of the spaced NTs and the higher surface area resulting from several layers of TiO\textsubscript{2} NP decoration.\[29,30,38\]

Additionally, TiO\textsubscript{2} NP decoration obtained from TiCl\textsubscript{4} treatments on TiO\textsubscript{2} NTs has been reported to be able to passivate surface states of NTs, thereby strongly reducing the recombination centers.\[39\] This benefit is also examined in the present work by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated voltage spectroscopy (IMVS). Herein, IMPS and IMVS measurements were carried out under visible light (530 nm) (Figures 3c and 3d). It is found that the spaced NTs decorated with TiO\textsubscript{2} NPs show a significantly faster electron transport time in comparison with conventional NTs, and the transport rate is a hundred times faster than NP layers on FTO. Furthermore, Figure 3d shows that the electron lifetime constants for the spaced NTs with NPs are one and two orders of magnitude longer than for classic NTs and NP layers, respectively. This indicates that the TiCl\textsubscript{4} treatment associated with NP decoration can passivate the defects on TiO\textsubscript{2} NTs, thereby clearly improving the electronic properties.\[40\]

To evaluate the efficiency of the hierarchical structure not only on the photoelectrochemical properties—as described above—but also on photocatalytic effects, we investigated classic target models for photocatalysis in gas form (acetaldehyde) and in liquid form (methylene blue). To test for an activated visible-light response in the gas phase, we examined the above hierarchical structures for the photodegradation of acetaldehyde under solar simulator AM 1.5 conditions with a 420 nm cut-off filter. Figure 4a shows the amount of photocatalytic CO\textsubscript{2} generated for spaced NTs, compared to NTs and TiO\textsubscript{2} particle layers, after an 8 h irradiation. The results clearly indicate that, as expected, no visible-light photocatalytic activity was detected for non-doped samples. However, all the investigated N-doped materials show visible-light activity, and clearly the N-doped hierarchical spaced NTs show by far the largest amount of generated CO\textsubscript{2} in comparison with N-doped NTs or NP layers on FTO (8 μmol cm\textsuperscript{-2} compared to 2 and
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Conflict of Interest

The authors declare no conflict of interest.

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