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Photoelectrochemical properties of N-doped self-organized titania nanotube layers with different thicknesses

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The present work reports nitrogen doping of self-organized TiO_2 nanotubular layers. Different thicknesses of the nanotubular layer architecture were formed by electrochemical anodization of Ti in different fluoride-containing electrolytes; tube lengths were 500 nm, 2.5 μm, and 6.1 μm. As-formed nanotube layers were annealed to an anatase structure and treated in ammonia environment at 550 °C to achieve nitrogen doping. The crystal structure, morphology, composition and photoresponse of the N-doped were characterized by scanning electron microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, and photoelectrochemical measurements. Results clearly show that successful N-doping of the TiO_2 nanotubular layers can be achieved upon ammonia treatment. The magnitude of the photoresponse in ultraviolet and visible light is strongly dependent on the thicknesses of the layers. This effect is ascribed to recombination effects along the tube length.

I. INTRODUCTION

For several decades, titanium dioxide (TiO_2) has been known as an excellent photocatalyst.[1,2] TiO_2 is an *n*-type semiconductor with band gap energy $E_g \sim 3.2$ eV for anatase and 3.0 eV for the rutile phase. Due to these relatively high band gap energies, a significant photoresponse can only be excited by ultraviolet (UV) light ($\lambda < 380$ nm). To make TiO_2 more responsive in the visible light range (vis) and thus to the natural solar spectrum, several modifications have been investigated. There have been essentially two extensively investigated approaches, on the one hand, dye-sensitization[3,4] and on the other hand, doping with suitable impurities. For the latter approach, transition metals[5,6] or other elements, including C,[7] P,[8] and N[9] were more or less successfully used. At present, in appears N-doping of TiO_2 is the most promising path toward narrowing the band gap energy.[9–11] Under optimal conditions, oxygen atoms in the TiO_2 lattice are substituted with nitrogen ions, and thus the corresponding N ($2p$) states are located above the valence band edge. In other words, mixing of N ($2p$) states with O ($2p$) states can result, and the narrowing of the band gap occurs. This leads to higher photocurrents achieved under vis irradiation. To form N-doped TiO_2 photocatalyst the common approaches include sputtering of TiO_2 in a gas mixture of N_2 with Ar,[9] annealing in pure ammonia gas,[10] or direct current (dc) magnetron sputtering of TiO_2 electrodes in an $Ar/O_2/N_2$ mixture.[11]

In view of an efficient solar cell, except for the light absorption in the visible light region, the surface area of TiO_2 (e.g., provided by the TiO_2 nanoparticle size) and crystallinity are also very important factors. Therefore the recently developed technique for fabricating self-organized TiO_2 nanotube layers[12–14] opens new perspectives for "high surface area" applications. Recently, we have shown that the tubes can be grown to a length of several micrometers, giving an aspect ratio of a few hundreds.[15–19] This can be achieved by tailored anodization in neutral solutions containing NH_4F[15–17] or NaF[18] or in glycerol/NH_4F mixtures.[19] We have already used the nanotubular structures to dye-sensitize them in the visible light[4] or as a catalyst support for methanol electrochemical oxidation,[20] and we have shown how to use ion implantation[21,22] and thermal treatment to N-dope the tubes.[23]

In the present work, we investigated length effect on photoresponse. Therefore, we used highly ordered tubular layers with three different thicknesses of 0.5, 2.5, and 6.1 μm and investigated the influence of their thicknesses on the photoresponse in both UV and vis light regions.

II. EXPERIMENTAL

Prior to experiments, titanium samples—foils with a thickness of 0.1 mm (99.6% purity, Goodfellow, England)—were degreased by sonication in acetone, isopropanol, and methanol, rinsed in de-ionized (DI)

water, and dried in a nitrogen stream. As-prepared samples were anodized in 1 M H_2SO_4/HF (0.15 wt%), 1 M Na_2SO_4/NaF (0.5 wt%), and 1,2,3-propanetriol/NH_4F (0.5 wt%) electrolytes to form nanotubular layers 500 nm (short tubes), 2.5 μm (medium tubes), and 6.1 μm (long tubes) thick. A conventional three-electrode configuration with a platinum gauze as a counter electrode and a Haber–Luggin capillary (Germany) with Ag/AgCl (1 M KCl) reference electrode at room temperature connected to a high-voltage potentiostat Jaissle IMP 88 (Germany) was used. The anodization treatment consisted of a potential ramp (50 mV/s) from the open-circuit potential (OCP) to 20 V, followed by holding 20 V constant for 2 h (short tubes), 3 h (medium tubes), and 13 h (long tubes), respectively. Afterwards, the anodized samples were rinsed with DI water and dried in a nitrogen stream. All electrolytes were prepared from reagent-grade chemicals. To produce defined anatase structure, all samples were annealed at 450 °C during 3 h in air with heating and cooling rate of 30 °C/min by using a Jetfirst Rapid Thermoannealer (RTA, Jipelec, France). The samples were N-doped by decomposing pure ammonia gas (NH_3 99.8 %, Linde Gas, Germany), flowing through a quartz glass tube (flow rate approximately 100 cm^3/h) placed in a pipe furnace (Heraeus, Germany). The structure of the samples was identified using an x-ray diffractometer (Phillips X'pert-MPD PW3040, The Netherlands) with Cu K_α radiation (wavelength 1.54056 Å). The morphology of the samples was investigated using a scanning electron microscope (SEM; Hitachi FE-SEM 4800, Japan). Direct SEM cross-sectional observations were carried out on mechanically bent and cracked samples.

Photocurrent spectra were recorded at 500 mV (versus Ag/AgCl electrode) in 0.1 M Na_2SO_4 electrolyte with 5-nm steps in the range of 700–250 nm using Oriel 6356 150 W Xe-arc lamp (Oriel Instruments, Stantford, CT), an Oriel Cornerstone 7400 1/8 m monochromator, a lock-in amplifier/chopper (f_{chop} = 30 Hz), and an electrochemical cell with a quartz window. The chemical composition of the N-doped samples was carried out by x-ray photoelectron spectroscopy (XPS; PHI 5600 XPS, Germany) using Al 2 mm K_α monochromatic radiation (1486.6 eV; 300 W) as the exciting source and using the Ti peak at 459 eV, the O peak at 529 eV, the C peak at 285 eV, and the N peak at 396 and 400 eV, with a resolution of 0.1 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows SEM images of the self-organized TiO_2 nanotubular layers grown to a thickness of 500 nm [Fig. 1(a), short tubes], 2.5 μm [Fig. 1(b), medium tubes], and 6.1 μm [Fig. 1(c), long tubes] based on previously published recipes in F^--containing electrolytes of
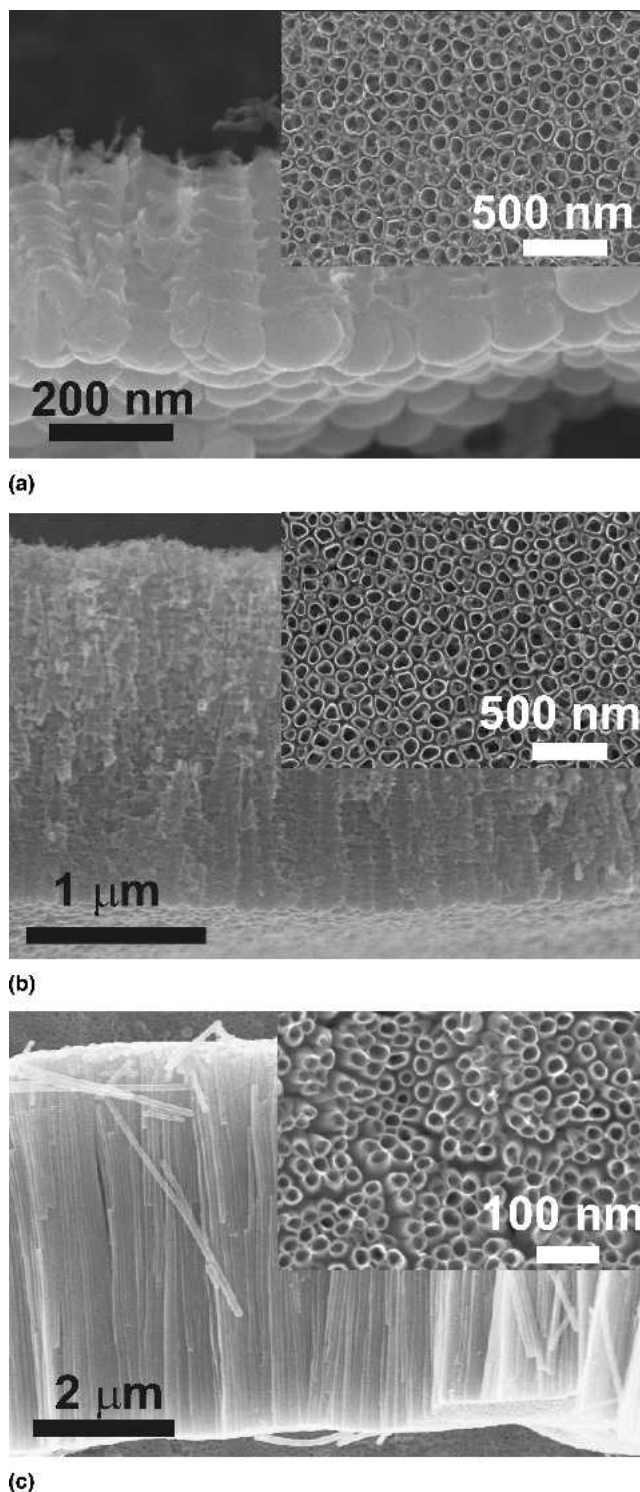

(a)

(b)

(c)

FIG. 1. SEM cross-section images of self-organized TiO_2 nanotube layers grown to a thickness of (a) 500 nm, (b) 2.5 μm, and (c) 6.1 μm. The insets show the top-views of the corresponding samples.

sulfuric acid,[14] sodium sulfate,[18] and glycerol,[19] respectively by anodization at 20 V. The insets show SEM top views of the respective structures. It can be seen that the first two types of tubes have diameters of approximately

100 nm and tube-wall thicknesses of about 15 nm [Figs. 1(a) and 1(b)], and the longest tubes [Fig. 1(c)] have 50 nm and 12 nm, respectively. All images show samples after the doping treatment in ammonia gas at 550 °C for 3 h. Clearly, no structural damage can be observed after the N-doping. Untreated samples (TiO_2) have a gray tone, and the color of samples after the N-doping changed from dark yellow, through dark blue, to a black tone with increasing thickness.

We have shown in previous work[24] that the as-anodized samples have an amorphous structure, which can be transformed to anatase structure with a high photo-response gain. Figure 2 shows XRD spectra of tubes shown in Fig. 1 after annealing in air at 450 °C during 3 h. Clearly an anatase TiO_2 structure can be identified in all cases; some traces of rutile are detected in the short tubes.

Figure 3 shows the photocurrent action spectra recorded for samples (a) before and (b) after doping in ammonia flow for 3 h at 550 °C. Figure 3(c) shows a $(I_{ph}h\upsilon)^{1/2}$ versus $h\upsilon$ plot for all doped samples of Fig. 3(b) to evaluate the influence of NH_3 treatment on the TiO_2 band gap.[25] It can be clearly seen that the sample after the NH_3 treatment (N-doping) generates significantly higher photocurrent in the visible range than the undoped samples do. It is evident that the highest I_{ph} in the UV light range is achieved for short tubes whereas in the vis light region it is the lowest. In other words, increasing the length of the doped tubes from 500 nm to 6.1 μm drastically decreases the UV response but significantly increases the visible response. This drop in the UV region can be ascribed to recombination effects, in particular because an increase in the tube length for the non-doped samples [Fig. 3(a)] also leads to a clear decrease in the photoresponse. The fact that this effect is much less pronounced the longer the wavelength can be
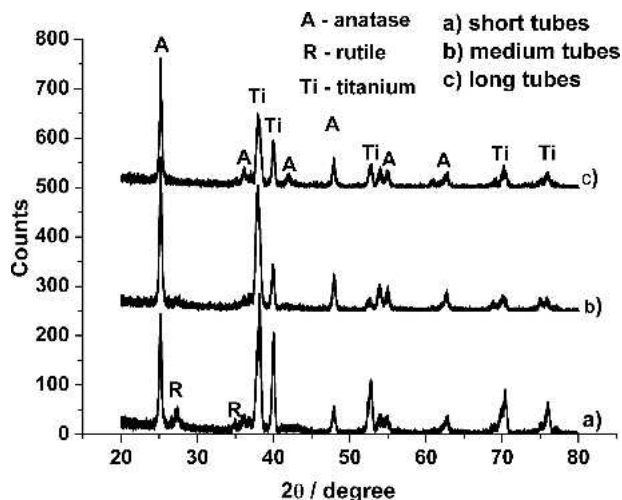

FIG. 2. XRD patterns of different tubes after annealing at 450 °C during 3 h with heating and cooling rate of 30 °C/min.
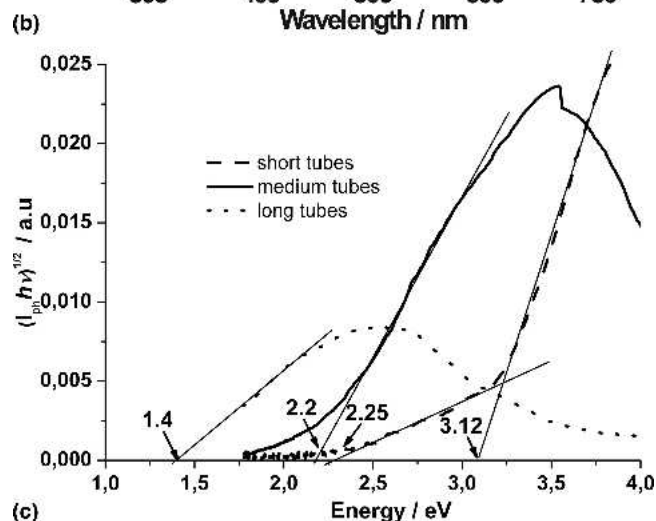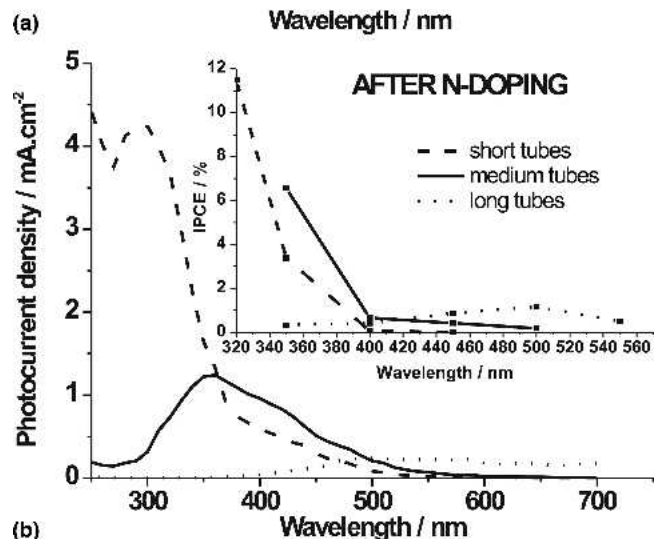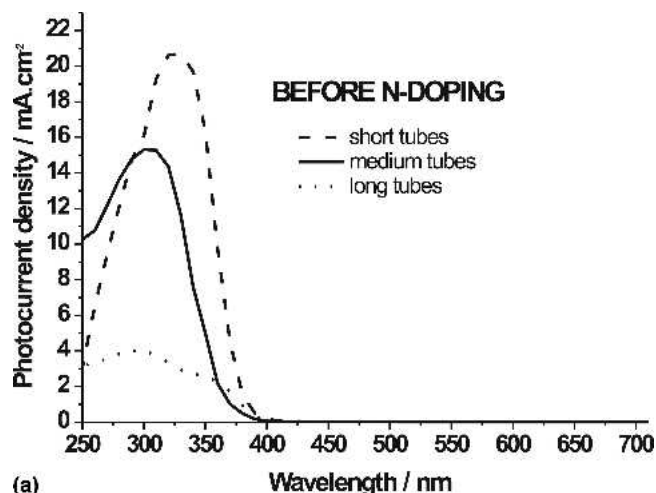

FIG. 3. Photocurrent (I_{ph}) action spectra for (a) undoped and (b,c) doped samples show the evaluation of the band gap energy (E_g) of the N-doped samples.

ascribed to the different penetration depth for the UV and visible light.

The absorption coefficient (α) of a semiconductor as a function of the wavelength (λ) of the incident light can be described by following equation:[26]

$$\alpha \propto \frac{(h\upsilon - E_g)^n}{h\upsilon} \quad \text{with } h\upsilon = hc/\lambda \quad , \qquad (1)$$

where h is Planck constant, υ is the frequency, c is the velocity of light, E_g is the band gap energy of the semiconductor, and n is 2 for indirect electron transitions. From Eq. (1), it is evident that the absorption coefficient drastically increases, the shorter the wavelength. According to literature,[27] the experimentally determined absorption coefficient for TiO$_2$ ranges from 10^2 cm^{-1} at 410 nm to 10^4 cm^{-1} at 340 nm. This results in 50% absorption depth of approximately 50 μm at 410 nm and 500 nm at 340 nm. This means for shorter wavelength, a much longer portion of the incident light is absorbed in the outer part of the tubular structure. This portion of the generated charge carriers has to travel a longer diffusion/migration path through the tube walls to reach the substrate than charge carriers created at longer wavelength (in this latter case, the entire nanotubular structure is entirely penetrated by light, and a high amount of charge carriers is generated close to the electron collecting tube bottom). This effect is very apparent for the longest tubes, where for the doped samples, the UV response is almost completely lost and only a part of the visible response—to an even longer wavelength—can be detected. When the magnitude of the photocurrent conversion efficiency in Figs. 3(a) and 3(b) is compared, it is evident that the doped tubes for the same length show a lower UV efficiency. This can be ascribed to an increase of the rutile content in the material[28] and possible specific N-effects after doping.

From Fig. 3(c), one can extract for the doped samples a primary band gap of $E_g \approx 3.2$ eV (corresponding to the value for undoped anatase[1–4]) and a sub-band gap (E_g') of 2.2 eV for the doped short and medium length tubes. These results for E_g' are well in line with previous values reported for the N-doped TiO$_2$.[9] However, for the 6.1-μm-long tubes, a result for a sub-band gap response of 1.4 eV can be extracted from Fig. 3(c). This is significantly lower than the results typically observed for N-doping.

To obtain additional information, XPS characterization of the tubes was carried out. Figure 4 shows the XPS spectrum acquired for the thickest N-doped nanotubular layers formed as in Fig. 1. The inset shows the N1s peak for the 6.1- and 2.5-μm layers. Clearly, strong peaks can be observed at 396 ± 0.2 eV, which corresponds to the so-called β–N state, which represents atomic N in form of mixed titanium oxide-nitride (TiO$_{2-x}$N$_x$). This indicates that heat treatment indeed leads to the substitution of some oxygen sites by nitrogen.[29] In previous works,[22,23] we also detected a peak at 400 ± 0.2 eV ascribed to the γ–N state, which was molecularly chemisorbed N$_2$. Clearly, the N in both N-doped samples is present in the β state. In other words, different binding of
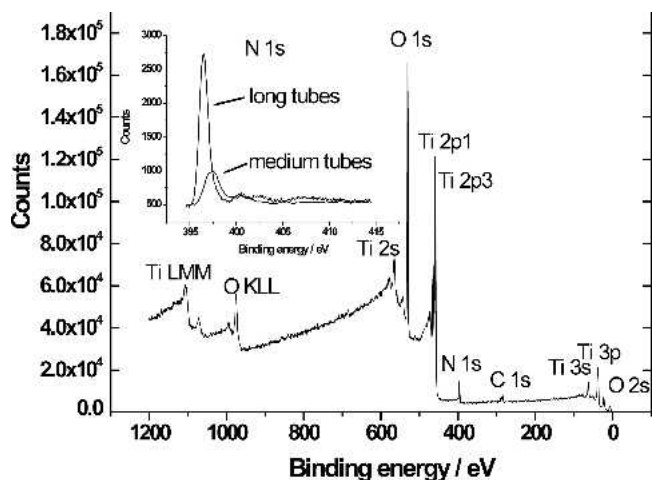

FIG. 4. XPS spectra of the N-doped TiO$_2$ nanotubular layer of sample formed as in Fig. 1(c). The peak at 396 ± 0.2 eV exhibits the β–N state (nitride). The inset shows comparison of the N-peak for 2.5-μm (medium) and 6.1-μm (long) thick nanotube layers.

the nitrogen cannot be the origin of the different spectral response of 6.1-μm-long tubes. Another possible reason for this unusual behavior could be an unintentional carbon-doping[7] of the longest tubes (as these samples were produced in glycerol electrolytes, remnant C-traces could be incorporated during annealing). However, the carbon peak in the XPS spectrum is comparably small, and therefore this seems an unlikely explanation for this behavior. When the morphology of the tubes is compared [Figs. 1(a)–1(c)], however, it is clear that the surface of the 6.1-μm-long tubes is much smoother (and has a more uniform thickness) than the short tubes. Therefore, it may be speculated that the "deep" visible response is associated with surface recombination effects present in the rippled "rough" tubes but are to a large extent eliminated in the case of the smooth tubes.

IV. CONCLUSIONS

The photoresponse of N-doped TiO$_2$ nanotube layers with a different tube length was investigated. The results clearly show that the tube length has a pronounced influence on the magnitude and spectral distribution of the photoresponse. An increased tube length from 500 nm to 6.1 μm shows a drastic decrease of the UV response, while a significant increase of the visible response is obtained. This behavior is ascribed to carrier recombination along the tubes combined with wavelength/dependent light absorption characteristics (visible light penetrates the tubes deeper than UV light). An unusual long tail to 1.4 eV of the photoresponse was observed for 6.1-μm-long N-doped TiO$_2$ nanotubes. The results are of crucial significance for the use of doped TiO$_2$ nanotube layers for photonic applications.

ACKNOWLEDGMENTS

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