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To cite this article: Menglin Li *et al* 2013 *Nanotechnology* **24** 305706

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Biocompatible and freestanding anatase TiO₂ nanomembrane with enhanced photocatalytic performance

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Received 5 February 2013, in final form 16 May 2013

Published 10 July 2013

Online at stacks.iop.org/Nano/24/305706

Abstract

Biocompatible and freestanding TiO₂ nanotube membranes with improved photocatalytic activity were fabricated through a water-vapour-assisted annealing treatment at relatively low temperatures. Photoluminescence results and structure characterization prove that the obtained TiO₂ nanotube membranes not only possess an enhanced anatase crystallinity from water molecule-intermediated dissolution–precipitation reactions, but are also covered with abundant hydroxyl groups which are hardly influenced by external disturbances. The anatase crystallinity, the superficial hydroxyl groups and the nanotubular morphology of the membrane treated with water vapour thus lead to enhancement in photocatalytic activity. This new approach is simple and time-saving, opening up new opportunities in various areas, including tissue-engineering, watersplitting, dye-sensitized solar cells and photocatalysis.

 Online supplementary data available from stacks.iop.org/Nano/24/305706/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the first report on photosplitting of water on a single-crystal titanium dioxide (TiO₂) electrode by Fujishima and Honda [1], TiO₂ has been discussed intensively for decades due to its strong oxidizing power, long-term photostability and lower cost [2]. It has been viewed as a leading candidate for semiconductor materials in the construction of electronic devices [3], in the manufacturing of pigments and coatings [4], in solar cells [5–8], sensors [9], cosmetics, as a catalyst support in several processes [10–13], as a photocatalyst in the degradation of organic compounds in environmental protection processes [14] and in biomedical applications such as biological substrates [15]. In particular, arrays of one-dimensional (1D) TiO₂ nanostructures such as TiO₂ nanotubes (TiNTs) have drawn ever-increasing attention because they not only have a high surface area but also offer the advantage of directed carrier transport, which can facilitate

the collection of photogenerated charge carriers and therefore are expected to provide perfect carrier transport channels in many photoconversion applications, for example, in the process of organic waste degradation [16–19].

Upon exposure to light, holes and electrons in TiNTs will be separated (under the field of the Schottky junction with the environment), reach the semiconductor–environment interface and react with appropriate redox species in the environment [20]. Several highly reactive species are generated, for example, from the surrounding water by charge exchanges at the valence band ($\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{OH}^\cdot$) and at the conduction band ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\cdot-}$) [21]. For TiNTs, the key point to increase the photocatalytic efficiency is to optimize the transportation channels for carriers and to prepare a sufficient amount of surface reactive species that are ready to accept the carriers [22–24]. Previous research has used calcinations at various temperatures and in different atmospheres to promote a phase transition, since

the anatase phase usually implies better carrier transportation channels [25–28]. However, problems exist as the process consumes a lot of energy and the final product is normally a mixture of anatase and rutile TiO₂. Wang *et al* [29] has recently come up with an energy-saving route by immersing the membrane into water at room temperature to achieve the amorphous–anatase phase transition. Nevertheless, the tubular morphology can barely survive and the process takes a long time, making it difficult to apply in mass production.

Here, we represent a facile and quick method to transform amorphous TiNTs to the anatase phase while the nanotubular geometry is mainly retained. In order to decorate the surface structure and improve the anatase crystallinity of the TiNT membrane, water vapour was introduced into the annealing system at a relatively low temperature. Experimental results show the treated TiNT nanomembranes can provide a biocompatible environment for stem cells and possess promoted photocatalytic ability as well, suggesting the great potential of such TiNT membranes in various applications, including photocatalytic degradation, cell cultivation and solar energy conversion.

2. Experimental methods

2.1. Fabrication of annealed TiNT membranes

TiNT membranes were fabricated by anodization of Ti foils in a two-electrode electrochemical cell. Prior to anodization, Ti foil was first washed, sequentially, by ethanol, acetone and de-ionized water under ultrasonication treatment for several minutes. In order to effectively reduce impurities and defects on the surface, a pre-anodization step was engaged. The pre-anodization was performed by using the Ti foil as anode and a Mo plate as cathode at room temperature for 1 h. The voltage was set to 60 V and an ethylene glycol electrolyte containing 0.3 wt% NH₄F and 1.8 wt% H₂O was adopted. TiNT formed in this step was then removed in dilute HNO₃ solution. The residual Ti substrate was anodized again with the same parameters for 1 h. At the end of the anodization, the voltage was increased abruptly to 140 V to peel off the membrane (see figure S2, available at stacks.iop.org/Nano/24/305706/mmedia). The as-prepared samples were annealed at 200 and 300 °C in different atmospheres (N₂ or N₂/H₂O mixture) for 30 min. The heating procedure started at room temperature with a ramping rate of 5 °C min^{−1}. Water vapour was introduced into the annealing system by passing high-purity N₂ (the gaseous flow rates of N₂ and vapour is 0.4 and 0.415 l min^{−1} respectively) through a saturator filled with boiling water (for details see figure S1, available at stacks.iop.org/Nano/24/305706/mmedia). Samples annealed in pure N₂ have also been prepared at the same temperature as references.

2.2. Structural characterizations

Scanning electron microscopy (SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, Philips CM200 FEG) were both used to characterize the morphological and structural properties of the samples. The x-ray diffraction

(XRD) patterns of the membranes were obtained with a Bruker D8 x-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Photoluminescence (PL) spectra of the samples were measured with a Renishaw inVia laser Raman spectrometer using the 514.5 nm line of an Ar⁺ laser as the excitation source.

2.3. Cell adhesion ability assay and morphological observation

Six-week-old male Fisher 344 rats were obtained from the Ninth People's Hospital Animal Centre (Shanghai, China). The animal process protocols were approved by the Animal Research Committee of the Ninth People's Hospital affiliated to Shanghai Jiao Tong University, School of Medicine. Rat bone marrow stromal cells (BMSCs) were isolated and cultured according to Jiang *et al* [30]. Primary cells were cultured at 37 °C in an atmosphere of 5% CO₂ in Dulbecco's modified Eagle's medium supplemented with 10% foetal bovine serum, 100 units ml^{−1} penicillin and 100 mg ml^{−1} streptomycin, and the fourth passage cells were used in the following experiments. In cell adhesion assays, BMSCs were seeded on biomaterial discs in six-well plates at a density of 3×10^4 cells cm^{−2} in triplicate, and alamarBlue reagent [31] (Life Tech.) was used to evaluate the cell adhesion abilities on different TiNT membranes according to the manufacturer's instructions after 4 and 24 h, respectively. The results were recorded spectrophotometrically for absorbance with a microplate reader (Thermo Scientific Multiskan MK3) at wavelengths of 570 and 600 nm, respectively. For cell morphological examination, cell seedings were performed according to the cell adhesion assay. After the cultivation assays of 4 and 24 h, cells were fixed in 4% paraformaldehyde for 10 min at room temperature and treated with 0.1 Triton X-100 for 2–3 min to permeabilize cellular membrane, then the actin cytoskeletons were stained with FITC-phalloidin (Sigma Aldrich) for 30 min at room temperature in the dark and the nuclei were stained with DAPI (Life Tech.) for another 5 min. Cell spreading on different TiNTs was observed using an Olympus fluorescence microscope GX71.

2.4. Measurement of photocatalytic performance of TiNT membranes

The photocatalytic performances of the samples were evaluated by measuring the catalytical degradation rates of azo-dye solutions on a Shimadzu UV-2550 spectrometer. Photocatalytic degradations of methyl orange (MO) and Rhodamine B (RhB) were carried out in a quartz reaction vessel with a quartz cover to prevent water evaporation. TiNT membranes with an area of 4.5 cm² were placed into 6 ml MO (RhB) solution with an initial concentration of 10 mg l^{−1} and a 200-W xenon lamp (Lanpu, China) positioned 50 cm away from the MO (RhB) solution as a light source to trigger the photocatalytic reaction. The solution was then kept for 30 min in the dark to reach the adsorption equilibrium. To quantitatively evaluate the degradation rate of the dye solution, the absorbance of the degraded solution was measured every 10 min with a

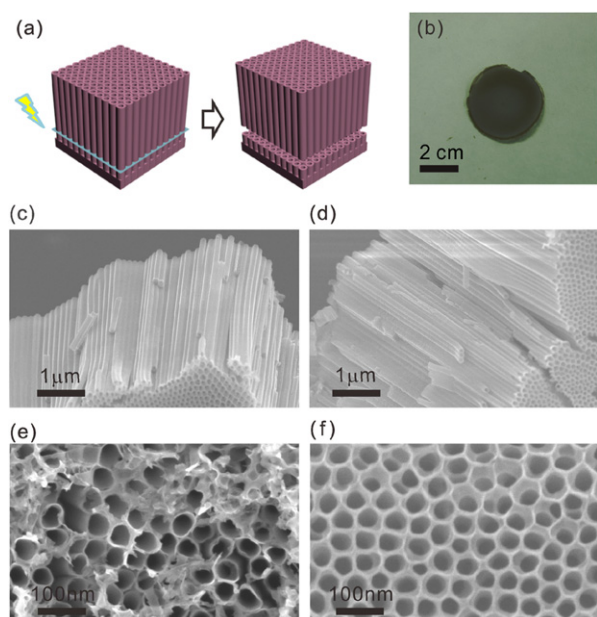


Figure 1. (a) Schematic representation of the fabrication process of the freestanding TiNT membrane. (b) Typical photograph of a freestanding TiNT membrane. (c) SEM image of a TiNT membrane annealed at 300 °C in N₂. (d) SEM image of a TiNT membrane annealed at 300 °C in N₂/H₂O. (e) SEM image of a TiNT membrane fabricated without the pre-anodization treatment. Impurities are noticeable for the sample without pre-anodization. (f) SEM image of a TiNT membrane fabricated with the pre-anodization treatment.

Shimadzu UV-2550 spectrometer. Figure S5 (available at stacks.iop.org/Nano/24/305706/mmedia) shows the evolution of the MO absorption spectra measured in our experiment. The changes of absorption intensities at 464 and 554 nm, which are reported as the maximum absorption wavelengths of MO and RhB respectively, were extracted to calculate the degradation rate [32]. For the dye solution with a low concentration, its photocatalytic decolourization is a pseudo first-order reaction and its kinetics can be expressed as $\ln(C_0/C) = kt$, where t is the time duration, k is the apparent rate constant and C_0 and C are the initial and reaction concentrations, respectively [33]. We thus can calculate the pseudo first-order rate constant k in the degradation process to evaluate the photocatalytic efficiency of the sample.

3. Results and discussion

Figure 1(a) is a schematic representation illustrating the fabrication process of the freestanding TiNT membranes. The abruptly increased voltage/current in our work would introduce a large compressive stress at the metal/oxide interface, which could finally induce the separation at the oxide/metal interface [34]. A typical photograph of a freestanding TiNT membrane after this separation step is shown in figure 1(b). One can see that the TiNT membrane obtained is completely freestanding, without a Ti substrate attached, which is important in applications such as flow-through photocatalytic applications [17]. Morphology characterization demonstrated that, after 1 h growth,

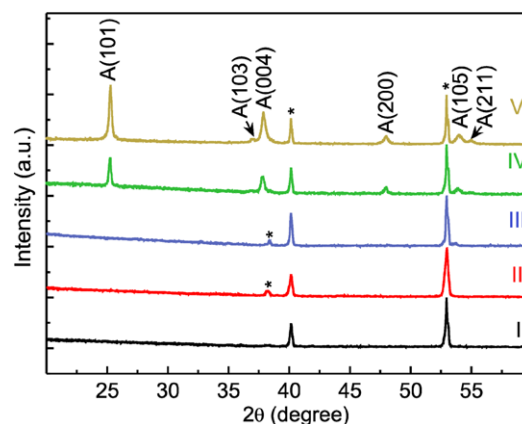


Figure 2. XRD patterns of TiNT membranes (I) without annealing, and annealed at (II) 200 °C in N₂, (III) 200 °C in N₂/H₂O, (IV) 300 °C in N₂ and (V) 300 °C in N₂/H₂O. All the peaks can be indexed to the anatase TiO₂ except for the peaks from the Ti substrate (marked by stars).

nanotubes with diameters of 80–100 nm can be as long as 3 μ m. Figures 1(c) and (d) show SEM images of membranes annealed at 300 °C with and without introduced water vapour, and ordered TiNT arrays due to the effect of pre-anodization can be observed to survive the annealing process [35, 36]. The SEM images also indicate that annealing with vapour hardly leads to any distinguishable morphological evolution, except for a few cracks (figure 1(d)). The formation of these cracks can be attributed to a phase transformation in the membrane, as will be discussed later.

In addition, we noticed that the pre-anodization process is critically necessary for nanomembrane fabrication with a high quality, since Ti substrate needs to be polished before the formal anodization. Any defects and impurities on the initial Ti foil have a strong influence on the growth and the subsequent morphology of the final TiNT membranes. Figures 1(e) and (f) show the SEM images of TiNT membranes prepared without and with the pre-anodization treatment respectively. We found that the pre-anodization treatment left a net-like layer on the top of the Ti foil, which could help develop highly ordered TiNTs in the following anodization. It has been reported that the net-like trace left by pre-anodization not only reduces the defects and impurities, improving the ordering, but also benefits optical applications of TiNT membranes [35].

Figure 2 shows the XRD patterns of as-anodized and annealed TiNT membranes. The results indicate that the as-anodized TiNT membrane is amorphous, while the samples annealed at 200 °C in atmospheres with and without vapour show similar degrees of crystallization. A slight difference can only be identified at $2\theta = 53.94^\circ$ (corresponding to (105) plane of anatase TiO₂). The sample annealed at 200 °C with water vapour shows a stronger peak, demonstrating that the membrane has better crystallinity if water is mixed into the annealing atmosphere. The effect of water becomes more evident when the annealing temperature is elevated to 300 °C, as two distinct peaks at 36.99° and 55.11° can only be detected from the sample annealed with water

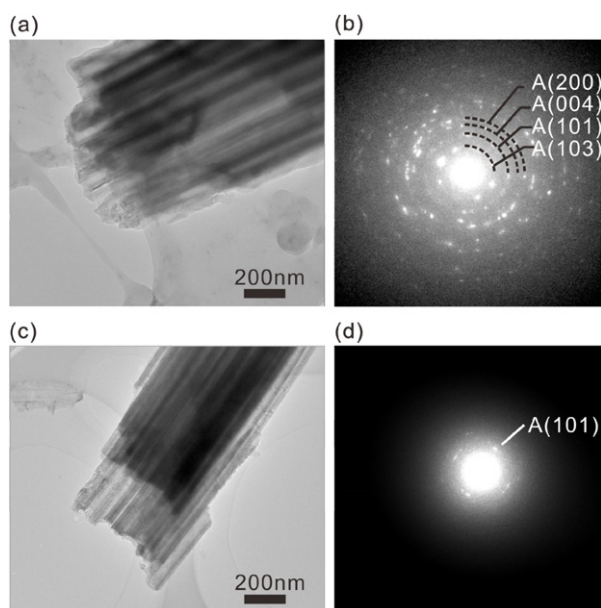


Figure 3. (a) TEM image of a TiNT membrane annealed at 300 °C in N_2/H_2O . (b) ED pattern corresponding to (a). (c) TEM image of a TiNT membrane annealed at 300 °C in pure N_2 . (d) ED pattern corresponding to (c).

vapour. The crystal sizes normal to the (101) direction calculated by using Scherrer equation are ~ 38 and ~ 31 nm respectively for samples annealed at 300 °C with and without vapour. The integral intensity of the (101) peak increases by $\sim 20\%$ in the sample annealed with vapour, suggesting a remarkable increase in the number of nanocrystals, since the crystal only slightly enlarged. The detailed mechanism can be explained as follows. When water molecules were introduced, dissolution–precipitation reactions occurred at the surface of TiO_2 [37]. Water molecules were attracted during annealing by the original hydroxyl groups attached to the TiO_2 structure. The surface hydroxyl groups on two different TiO_6^{2-} octahedra, sharing one common vertex, reacted with one water molecule at the same time and the octahedra coalesced with each other, forming covalent bonds of Ti–OH [29]. After that, a third octahedron driven by water is linked with the above two by sharing edges. The TiO_6^{2-} octahedra are all collected by this means with the assistance of water molecules and finally convert into an anatase cluster due to its lower Gibbs free energy [38]. In contrast, without the participation of water, crystallization becomes difficult because the breakage and rebuilding of the covalent bonds must rely in the application of external heat energy. It is worth noting that a similar crystallization process of TiNT in liquid water has previously been reported by Yu *et al* [33]. In their work, TiNT membranes were soaked into water and then heated to 180 °C for hours in pursuit of the anatase phase. Nevertheless, TiNT membrane can be easily broken up when immersed into water for a long duration [34], so the approach described in this work is most likely to provide a more feasible and reliable controllability, as well as being time-saving. Moreover, we should stress that water molecules suffer less limitation when travelling through the nanochannels in the vapour state and thus the reaction

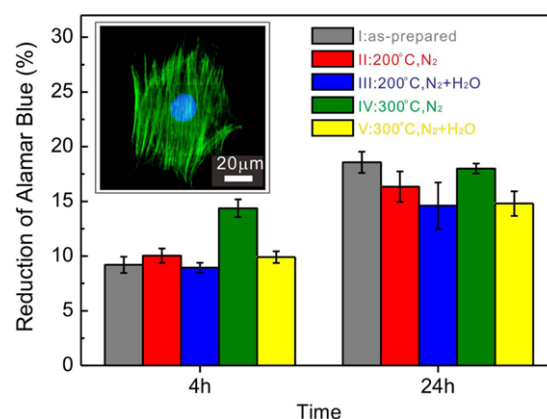


Figure 4. Cell adhesion assay. After rat bone marrow stem cells (rat BMSCs) were seeded on different TiNT membranes for 4 h and 24 h, respectively, the cell adhesion ability was evaluated by alamarBlue assay (purchased from Life Technol.). TiNT membranes (I) without annealing, and annealed at (II) 200 °C in N_2 , (III) 200 °C in N_2/H_2O , (IV) 300 °C in N_2 and (V) 300 °C in N_2/H_2O . The insets show the typical fluorescent image of a stem cell cultivated for 4 h on the surface of TiNT membranes annealed at 300 °C in N_2/H_2O . The nucleus was stained blue and the cytoskeleton was stained green (see section 2 for details).

could take place in the interior region of the TiNT membrane due to the longer diffusion length of water molecules in the gaseous state [39].

Here, to obtain more details about the enhanced crystallinity, we carried out TEM characterization on samples annealed at 300 °C. The results are shown in figure 3. Figures 3(a) and (c) correspond to TiNT samples annealed with and without water vapour respectively. Except for similar tubular morphologies, a significant difference can be noticed from the corresponding electron diffraction (ED) patterns (figures 3(b) and (d)). For the TiNT membrane annealed at 300 °C in N_2 , only a few weak diffraction spots are shown (figure 3(d)), indicating a poor crystallinity. The anatase crystallinity is greatly enhanced when water vapour is introduced, and thus the quasi-polycrystalline nature can be proved by the stronger lattice diffraction in figure 3(b). The increased crystallinity is further identified by the high-resolution TEM results shown in figure S3 (available at stacks.iop.org/Nano/24/305706/mmedia). Clear lattice fringes of anatase TiO_2 can be detected from TiNT annealed at 300 °C with water vapour, while such fringes are hardly observed in a sample annealed in pure N_2 (figure S3(b) available at stacks.iop.org/Nano/24/305706/mmedia).

Among the numerous materials proposed for implants, Ti [40–43] and Ti-based materials [44, 45] have attracted attention because of their good biocompatibility, corrosion resistance and the possession of physical properties close to those of bone [46]. Thus the biological performance of TiO_2 material is also of interest to researchers. Herein, to check the bioactivity of TiNT membranes annealed with water vapour for potential biological applications in the future, rat bone marrow stem cells were cultured on surfaces of the membranes in biomaterial discs. The inset in figure 4 shows the typical morphologies of stem cells cultivated for 4 h on

the surface of a TiNT membrane annealed with water vapour at 300 °C. The morphology of the cells varied as a function of replicative age from the initial spindle shape to a more flattened square or star shape, as shown in the inset. The green FITC-phalloidin interacted with the F-actin of the cells and implied changes of the cytoskeleton, demonstrating the biocompatibility of the TiNT substrate. The living states of the cells can be further quantified by measuring the reduction rate of the alamarBlue dye (see section 2 for details). The results summarized in figure 4 indicate that the numbers of surviving stem cells on samples annealed with or without water vapour were almost the same, indicating that all the TiNT membranes are biocompatible, although those annealed with water vapour even show a slight disadvantage. The reason for this will be discussed in the following paragraphs.

The biocompatibility can be significantly influenced by the surface condition. It is therefore natural to deduce that the surface changes after the annealing treatment. In this work, we tried to probe this change optically by measuring the PL spectra of the treated samples and found that the samples annealed with water vapour emit visible light, while the unannealed samples or those annealed in N₂ show negligible emission, as displayed in figure 5(a). The obviously asymmetrical feature of the PL bands from samples annealed with water vapour at 200 and 300 °C suggests that more than one PL centre should contribute to the observed broad band [47]. To clarify its origin, each PL peak is divided into two Gaussian subbands (see dashed lines in figure 5(a)), which are located at ~593 and ~680 nm, respectively. Previously, electron traps were demonstrated to dominate the emission spectrum of anatase TiO₂ nanocrystals, which show a PL peak at ~650 nm [48]. Detailed investigations ascribed this red PL to the radiative recombination of trapped electrons, about 0.7–1.6 eV below the conduction band edge, with valence band holes [49]. Considering the similar emission wavelength and nanocrystal nature of our samples, as proved by the aforementioned XRD and TEM results, we believe the subband at longer wavelengths might be connected to the electron traps in nanocrystal TiO₂. In our case, TiNT membranes are oxygen-deficient [47] and those annealed with water vapour turned dark brown instead of the original yellow appearance, illustrating that a large amount of undercoordinated Ti⁴⁺ formed [50–53], which can be cited as likely sites for electrons to be trapped, finally causing the red emission [48, 49].

The subband at ~593 nm should have another origin. Qian *et al* [54] reported an emission at ~588 nm from TiNTs fabricated by a soft chemical process and considered the emission to be connected with an optical transition in the Ti–OH complex. Similar results have also been mentioned in the study of water-annealed silica nanotubes, in which the strong emission is attributed to OH groups on the inner and outer surfaces [55]. As the water molecules travel into the annealing system, the nucleation of anatase is accelerated by the existence of water, which forces the TiO₆ octahedral units to rearrange to the more compact anatase structure [56], leading to an increase of superficial hydroxyl groups. On the other hand, the vapour-surrounded

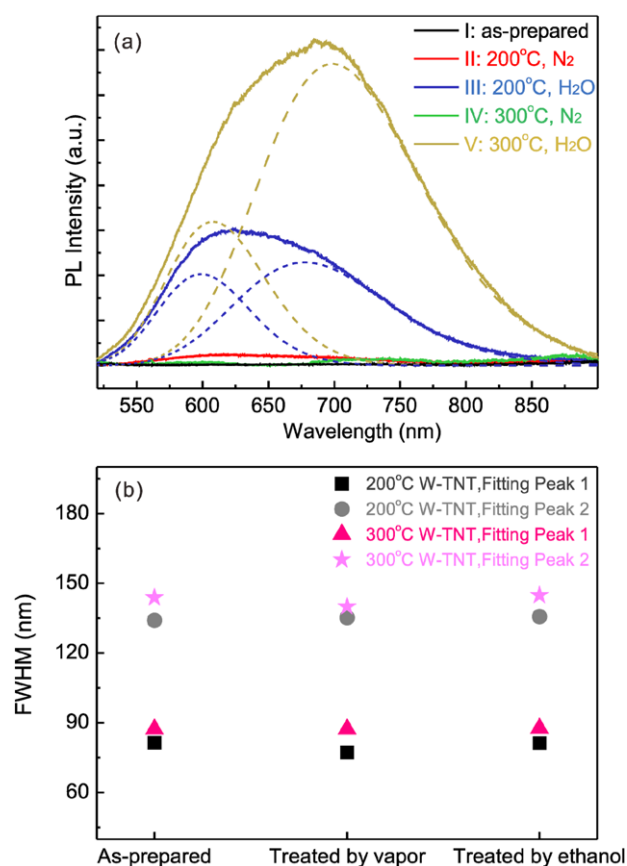


Figure 5. (a) PL spectra of TiNT samples (I) without annealing, and annealed at (II) 200 °C in N₂, (III) 200 °C in N₂/H₂O, (IV) 300 °C in N₂ and (V) 300 °C in N₂/H₂O. Fitting results (two Gaussian subbands) of PL spectra from samples (III) and (V) are shown by dashed lines. (b) FWHM of the two subbands after post-treatment.

environment can effectively prevent the formed hydroxyl groups being destroyed by the dehydration reaction at high temperature ($\text{Ti-OH} + \text{Ti-OH} \rightarrow \text{Ti-O-Ti} + \text{H}_2\text{O}$) [33]. To go deeper into the light emission mechanism, we carried out more control experiments: the samples were first sealed into a container filled with water vapour at room temperature for 40 h, then soaked in ethanol for 20 min. The PL spectra from these post-treated samples were measured (figure S4 available at stacks.iop.org/Nano/24/305706/mmedia) and we noticed that there was no obvious variation in the lineshapes of either subband. The full width at half maximum (FWHM) of the two subbands from these post-treated samples was measured and is shown in figure 5(b). One can see that the FWHM of both subbands is unchanged, indicating the nature of both PL centres is unaffected. However, the relative intensity between the two subbands varies after water vapour immersion at room temperature (figure S4 available at stacks.iop.org/Nano/24/305706/mmedia). The increase of the emission band at longer wavelengths is believed to be due to the improved crystallinity and the correspondingly increased undercoordinated Ti⁴⁺ sites from the aforementioned water-intermediated dissolution–precipitation reactions [33]. On the other hand, the emission from superficial hydroxyl groups hardly increases, since the

surface is already saturated. From figures S4(e) and (f) (available at stacks.iop.org/Nano/24/305706/mmedia), one may also deduce a good stability of these superficial hydroxyl groups because they are hardly impacted by the exterior conditions and even the strong dehydrogenating agent, i.e. ethanol, cannot remove them.

The PL characterizations thus give us a clue as to the reason for the aforementioned change in biocompatibility (see figure 4). We have already noticed that the samples annealed with water vapour are covered with more superficial hydroxyl groups. These hydroxyl groups and the corresponding highly reactive hydroxyl radicals generated when TiNT membranes were immersed in the aqueous medium are, unfortunately, found to be somewhat harmful to the cell walls [57]. This degrades the cell adhesion and, in turn, is likely to be disturbing to the living state of the cell, leading to slightly decreased biocompatibility for TiNT membranes annealed with water vapour.

Finally, the photocatalytic activity of the samples was examined by using the decolourization of MO and RhB as probes. Figure 6(a) shows the degradation of MO solutions as a function of irradiation time by calculating the absorbance of MO molecules at the peak feature at 464 nm [58]. Details of the photocatalytic measurement can be discovered in figure S5 (available at stacks.iop.org/Nano/24/305706/mmedia). The sample annealed at 300 °C with water vapour demonstrates the highest degradation efficiency. Within a short period of 60 min, the TiNT membrane is able to degrade over 46% of the original MO, as depicted in figure 6(a), corresponding to a pseudo first-order rate constant of 0.0076 min^{-1} (figure 6(b)), while the rate for the sample annealed at 300 °C in N_2 is only 0.002 min^{-1} . The enhancement is noticed also in the samples annealed at 200 °C. As exhibited in figure 6(b), the degradation rate of MO in 1 h by the sample annealed at 200 °C with water vapour was 25.10%, which is roughly four times greater than that by the sample annealed in N_2 (6.27%). To validate the universality of the enhanced photocatalytic performance, the degradation rates of RhB were also recorded and are summarized in figure 6(b). The results obtained justify the conclusion that TiNT membranes annealed with water vapour exhibit obviously promoted performance in the degradation processes. We also compared the photocatalytic efficiencies of our samples to those reported in the literature [59–61] and found that the current samples show a better performance, even if the others were treated longer at higher temperatures. Previous work suggests that the superficial hydroxyl groups may contribute to the enhancement of the photocatalytic property, because they can subsequently react with the photogenerated holes to form oxidative hydroxyl radicals ($\text{OH}^\cdot$), via the reaction: $\text{OH}^- + \text{h}^+ \rightarrow \text{OH}^\cdot$ [33, 62]. Our above PL results have already shown the existence of abundant hydroxyl groups on the surface of TiNT membranes annealed with water vapour. During photocatalysis, these hydroxyl groups are transformed to hydroxyl radicals, which are the principal oxidants for degradation of the dye molecules [63], and consequently enhance the photocatalytic performance by accelerating the degradation reactions. Moreover, we believe that the improved

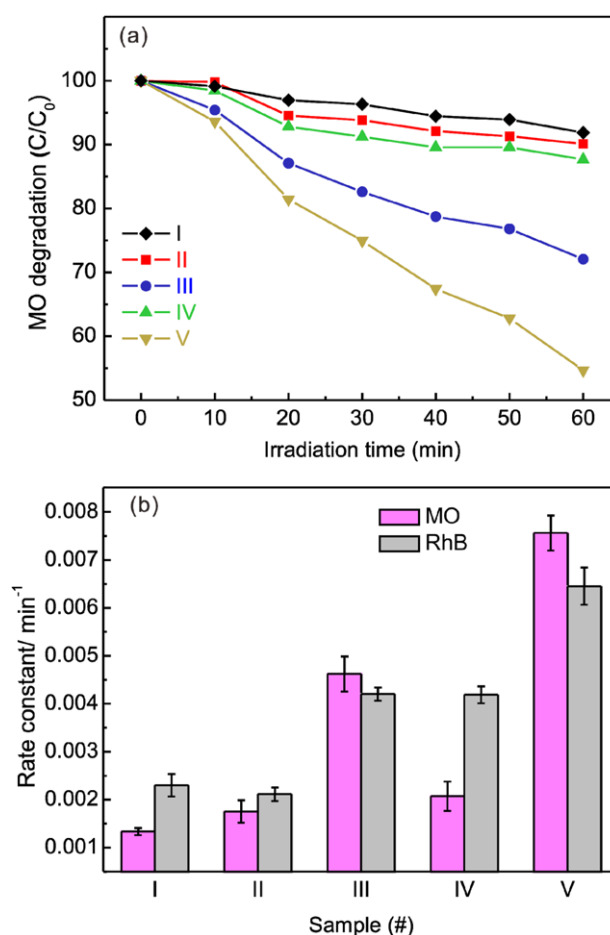


Figure 6. (a) Photocatalytic ability of TiNT membranes annealed at different atmospheres and temperatures in terms of the MO degradation rate: (I) without annealing, (II) TiNT membrane annealed at 200 °C in N_2 , (III) TiNT membrane annealed at 200 °C in $\text{N}_2/\text{H}_2\text{O}$, (IV) TiNT membrane annealed at 300 °C in N_2 and (V) TiNT membrane annealed at 300 °C in $\text{N}_2/\text{H}_2\text{O}$. (b) Comparison of MO and RhB degradation rates. The above five samples were used as photocatalysts.

anatase crystallinity (increased anatase nanocrystals) may also contribute to the enhancement of photocatalytic ability, because anatase is reported to be more advantageous in photocatalytic degradation than amorphous structure since it consists of more ordered TiO_6^{2-} octahedra and thus smooth photoexcited carrier transport channels as well [58, 64]. We should stress that compared with the previous approaches of hydroxyl group introduction [29, 54], the water-assisted annealing process presented here not only produces a large amount of superficial hydroxyl groups but also maintains the unique one-dimensional geometry of the nanotubes, which in turn promotes the photocatalytic ability by providing a directed travelling path for photogenerated electrons [33, 65].

4. Conclusions

To sum up, freestanding TiNT membranes with improved anatase crystallinity were fabricated by introducing water vapour into the annealing atmosphere. A stem cell culture experiment was carried out to check the biocompatibility

of the TiNT membranes with hydroxyl group covering and the results disclose the influence from the hydroxyl groups. The samples annealed with water vapour show visible emission due to body defects and stable hydroxyl groups on their surface, and both are produced by the water-assisted annealing. A promoted photocatalytic activity is also disclosed and attributed to the anatase crystallinity, the superficial hydroxyl groups and the tubular morphology. The fabrication method presented here is simple and time-saving, and can be scaled up easily to produce TiO₂-related materials used in photocatalysis, optics and biomedical applications.

Acknowledgments

This work is supported by the Natural Science Foundation of China (Nos 51102049 and 61008029), Specialized Research Fund for the Doctoral Program of Higher Education of China (20110071120009), Program for New Century Excellent Talents in University (No. NCET-10-0345), Shanghai Pujiang Program (No. 12PJ1400500) and 'Shu Guang' project by Shanghai Municipal Education Commission and Shanghai Education Development Foundation. Gaoshan Huang and Yongfeng Mei would like to thank the Scientific Research Foundation for Returned Overseas Chinese Scholars, State Education Ministry, for financial support.

References

- [1] Fujishima A and Honda K 1972 *Nature* **238** 37
- [2] Hoffmann M R, Martin S T, Choi W Y and Bahnemann D W 1995 *Chem. Rev.* **95** 69
- [3] Sakai N, Ebina Y, Takada K and Sasaki T 2004 *J. Am. Chem. Soc.* **126** 5851
- [4] Drew C, Liu X, Ziegler D, Wang X Y, Bruno F F, Whitten J, Samuelson L A and Kumar J 2003 *Nano Lett.* **3** 143
- [5] Ushiroda S, Ruzyski N, Lu Y, Spitler M T and Parkinson B A 2005 *J. Am. Chem. Soc.* **127** 5158
- [6] Cherepy N J, Smestad G P, Gratzel M and Zhang J Z 1997 *J. Phys. Chem. B* **101** 9342
- [7] Lopez-Luke T, Wolcott A, Xu L P, Chen S, Wen Z, Li J, De La Rosa E and Zhang J Z 2008 *J. Phys. Chem. C* **112** 1282
- [8] Wolcott A, Smith W A, Kuykendall T R, Zhao Y and Zhang J Z 2009 *Small* **5** 104
- [9] Feng L A, Liu Y J and Hu J M 2004 *Langmuir* **20** 1786
- [10] Dzwigaj S et al 2003 *Appl. Catal. B* **41** 181
- [11] Breyse M, Portefaix J L and Vrinat M 1991 *Catal. Today* **10** 489
- [12] Ramirez J, Cedeno L and Busca G 1999 *J. Catal.* **184** 59
- [13] Inoue S, Muto A, Kudou H and Ono T 2004 *Appl. Catal. A* **269** 7
- [14] Wang H, Wu Y and Xu B Q 2005 *Appl. Catal. B* **59** 139
- [15] Pan C, Cheng S A, Wei H M, Han G Z, Zhang J Z, Fujishima A and Gu Z Z 2007 *Mater. Res. Bull.* **42** 1395
- [16] Mor G K, Shankar K, Paulose M, Varghese O K and Grimes C A 2005 *Nano Lett.* **5** 191
- [17] Albu S P, Ghicov A, Macak J M, Hahn R and Schmuki P 2007 *Nano Lett.* **7** 1286
- [18] Richter C and Schmittenmaier C A 2010 *Nature Nanotechnol.* **5** 769
- [19] Varghese O K, Paulose M and Grimes C A 2009 *Nature Nanotechnol.* **4** 592
- [20] Roy P, Berger S and Schmuki P 2011 *Angew. Chem. Int. Edn* **50** 2904
- [21] Song Y Y, Roy P and Paramasivam I 2010 *Angew. Chem. Int. Edn* **49** 351
- [22] Bingham S and Daoud W A 2011 *J. Mater. Chem.* **21** 2041
- [23] Boronat M and Corma A 2011 *Catal. Today* **169** 52
- [24] Salmi M, Tkachenko N, Lamminmaki R J, Karvinen S, Vehmanen V and Lemmetyinen H 2005 *J. Photochem. Photobiol. A* **175** 8
- [25] Zhu K, Neale N R, Halverson A F, Kim J Y and Frank A J 2010 *J. Phys. Chem. C* **114** 13433
- [26] Ma Q, Qin T P, Liu S J, Weng L Q and Dong W Y 2011 *Appl. Phys. A* **104** 365
- [27] Allam N K and Grimes C A 2009 *J. Phys. Chem. C* **113** 7996
- [28] Fabrega C, Andreu T, Gueell F, Daniel Prades J, Estrade S, Manuel Rebled J, Peiro F and Ramon Morante J 2011 *Nanotechnology* **22** 235403
- [29] Wang D, Liu L, Zhang F, Tao K, Pippel E and Domen K 2011 *Nano Lett.* **11** 3649
- [30] Jiang X, Zhao J, Wang S, Sun X, Zhang X, Chen J, Kaplan D L and Zhang Z 2009 *Biomaterials* **30** 4522
- [31] Lancaster M V and Fields R D 1996 *US Patent*
- [32] Guo C, Xu J, He Y, Zhang Y and Wang Y 2011 *Appl. Surf. Sci.* **257** 3798
- [33] Yu J, Dai G and Cheng B 2010 *J. Phys. Chem. C* **114** 19378
- [34] Wang D and Liu L 2010 *Chem. Mater.* **22** 6656
- [35] Wang F, Liu Y, Dong W, Shen M and Kang Z 2011 *J. Phys. Chem. C* **115** 14635
- [36] Li S, Zhang G, Guo D, Yu L and Zhang W 2009 *J. Phys. Chem. C* **113** 12759
- [37] Vittadini A, Selloni A, Rotzinger F P and Gratzel M 1998 *Phys. Rev. Lett.* **81** 2954
- [38] Finnegan M P, Zhang H and Banfield J F 2007 *J. Phys. Chem. C* **111** 1962
- [39] Lewis W K and Whitman W G 1924 *Indust. Eng. Chem.* **16** 1215
- [40] Cacciafesta P, Hallam K R, Watkinson A C, Allen G C, Miles M J and Jandt K D 2001 *Surf. Sci.* **491** 405
- [41] Pouilleau J, Devilliers D, Garrido F and Durand-Vidal S 1997 *Mater. Sci. Eng. B* **47** 235
- [42] Liu D P, Majewski P, O'Neill B K, Ngothai Y and Colby C B 2006 *J. Biomed. Mater. Res.* **77A** 763
- [43] Liu Q, Ding J, Mante F K, Wunder S L and Baran G R 2002 *Biomaterials* **23** 3103
- [44] Kasemo B 2002 *Surf. Sci.* **500** 656
- [45] Gawalt E S, Avaltroni M J, Danahy M P, Silverman B M, Hanson E L, Midwood K S, Schwarzbauer J E and Schwartz J 2003 *Langmuir* **19** 200
- [46] Lin C J, Han H J, Zhang F and Li A M 2008 *J. Mater. Sci.-Mater. Med.* **19** 2569
- [47] Huang G S, Wu X L, Mei Y F, Shao X F and Siu G G 2003 *J. Appl. Phys.* **93** 582
- [48] Mercado C C, Knorr F J and McHale J L 2012 *ACS Nano* **6** 7270
- [49] Mercado C C, Knorr F J, McHale J L, Usmani S M, Ichimura A S and Saraf L V 2012 *J. Phys. Chem. C* **116** 10796
- [50] Liu L Z, Xu W, Wu X L, Zhang Y Y, Chen H T and Chu P K 2012 *Appl. Phys. Lett.* **100** 121904
- [51] Cao F, Oskam G, Searson P C, Stipkala J M, Heimer T A, Farzad F and Meyer G J 1995 *J. Phys. Chem.* **99** 11974
- [52] Chen X, Liu L, Yu P Y and Mao S S 2011 *Science* **331** 746
- [53] Wang G M, Wang H Y, Ling Y C, Tang Y C, Yang X Y, Fitzmorris R C, Wang C C, Zhang J Z and Li Y 2011 *Nano Lett.* **11** 3026
- [54] Qian L, Jin Z S, Yang S Y, Du Z L and Xu X R 2005 *Chem. Mater.* **17** 5334
- [55] Zhang M, Ciocan E, Bando Y, Wada K, Cheng L L and Pirouz P 2002 *Appl. Phys. Lett.* **80** 491
- [56] Yanagisawa K, Yamamoto Y, Feng Q and Yamasaki N 1998 *J. Mater. Res.* **13** 825

- [57] Kuhn K P, Chaberny I F, Massholder K, Stickler M, Benz V W, Sonntag H G and Erdinger L 2003 *Chemosphere* **53** 71
- [58] Sohn Y S, Smith Y R, Misra M and Subramanian V 2008 *Appl. Catal. B* **84** 372
- [59] Diamanti M V, Ormellese M, Marin E, Lanzutti A, Mele A and Pedferri M P 2011 *J. Hazard. Mater.* **186** 2103
- [60] Wang S, Lian J S, Zheng W T and Jiang Q 2012 *Appl. Surf. Sci.* **263** 260
- [61] Yu J G, Yu H G, Cheng B, Zhao X J, Yu J C and Ho W K 2003 *J. Phys. Chem. B* **107** 13871
- [62] Wang J, Liu X, Li R, Qiao P, Xiao L and Fan J 2012 *Catal. Commun.* **19** 96
- [63] Yu Y, Yu J C, Yu J G, Kwok Y C, Che Y K, Zhao J C, Ding L, Ge W K and Wong P K 2005 *Appl. Catal. A* **289** 186
- [64] Ramires P A, Romito A, Cosentino F and Milella E 2001 *Biomaterials* **22** 1467
- [65] Roy P, Kim D, Lee K, Spiecker E and Schmuki P 2010 *Nanoscale* **2** 45