Herein, highly ordered TiO$_2$ nanotube (NT) arrays on a Ti substrate is synthesized in a fluoride-containing electrolyte, using the electrochemical anodization method, which yields amorphous oxide tubes. The effects of different thermal annealing profiles for the crystallization of the amorphous TiO$_2$ NTs are studied. It is found that the temperature ramping rate has a significant impact on the magnitude of the resulting photocurrents (incident photon-to-current conversion efficiency [IPCE]) from the tubes. No appreciable changes are observed in the crystal structure and morphology of the TiO$_2$ NTs for different annealing profiles (to a constant temperature of 450 °C). The electrochemical properties of the annealed TiO$_2$ NTs are investigated using intensity-modulated photocurrent spectroscopy (IMPS), open-circuit potential decay, and Mott–Schottky analysis. The results clearly show that the annealing ramping rate of 1 °C s$^{-1}$ leads to the highest IPCE performance. This beneficial effect can be ascribed to a most effective charge separation and electron transport (indicating the least amount of trapping states in the tubes). Therefore, the results suggest that controlling the annealing ramping rate is not only a key factor affecting the defect structure but also a powerful tool to tailor the physical properties, and photocurrent activity of TiO$_2$ NTs.

1. Introduction

Titanium dioxide (TiO$_2$) is a crucial and widely studied material due to its nontoxic nature, low cost, high chemical stability, good biocompatibility, and remarkable physical, chemical, electronic and optical properties.$^{[1,2]}$ TiO$_2$ has attracted extensive attention because of its wide range of applications in gas sensors, lithium-ion batteries, dye-sensitized solar cells, environmental purpose, hydrogen production, organic light-emitting diodes, and photovoltaic energy production.$^{[13–10]}$ 1D structures, especially nanotubes (NTs), have been in the focus of significant scientific, academic, and industrial interest since the introduction of carbon nanotubes (CNTs) by Iijima and coworkers.$^{[11,12]}$ Although anodic TiO$_2$ NTs do not have a layered structure like CNTs, but exhibit exclusive properties such as a high surface area, a high electron mobility with directional charge transport as compared with the bulk form. Moreover, 1D TiO$_2$ NTs exhibit remarkable optical, chemical, and electronic properties as well as have a defined geometry with good control of their nanotopography.$^{[13]}$ These outstanding properties lead to an upsurge in its application in different fields such as physics, chemistry, material science, and biomedicine.$^{[14,15]}$

TiO$_2$ is an n-type semiconductor that mainly exists in three different crystalline forms—anatase, rutile, and brookite.$^{[16–18]}$ Anatase and rutile crystallize in tetragonal structures whereas brookite crystallizes in orthorhombic structure. Rutile is the most stable form among all polymorphs, but anatase and brookite can convert into rutile phase upon heating, as shown in Figure 1a.$^{[16,19]}$ The Fermi level of anatase is 0.1 eV higher than rutile, and possesses a 3.2 eV bandgap. The suitable band edges position for water decomposition make anatase the desired form for photoelectrochemical and photocatalytic water splitting applications.$^{[20–23]}$ Many physical properties of TiO$_2$ NTs predominantly depend on the crystal structure. However, the crystalline structure can be influenced by intrinsic point/structural defects$^{[24]}$ that play a crucial role in controlling the physical properties, especially while dealing with nanometer-sized tubes.$^{[25]}$ In addition to the nanometer dimension, an ideal geometry is also an important factor for high surface area, long-term stability, and generation of charge carriers with directional charge transport. Therefore, various methods have been reported for the synthesis of 1D TiO$_2$ nanotubular geometry.

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Among the various methods, electrochemical anodization is the most straightforward approach to produce highly ordered arrays of closely packed, vertically oriented, size-controlled, and back contacted NTs on metal substrate (Ti).[26] The synthesis of TiO$_2$ NTs is based on a simple electrochemical anodization of metallic titanium in fluoride-containing electrolytes in the presence of self-organizing conditions.[27,28] The size of the tubes can be altered in dimension (i.e., length and diameter) by changing the anodization conditions. However, such electrochemical anodization provides only an amorphous form of TiO$_2$ NTs. For many applications, the tubes need to be converted to an anatase/rutile or anatase–rutile mixture with suitable heat/annealing protocols.[29] In general, annealing of TiO$_2$ NTs in the presence of air at $T > 300$ °C results in an anatase phase, whereas heating at $T > 500$–600 °C alters them to rutile phase or anatase/rutile mixture.[30] It has been reported that the introduction of point/structural defects in TiO$_2$ NTs will enhance the activity for various applications.[31–33] Such point defects can also be introduced in TiO$_2$ NTs under different annealing conditions[34,35] that also leads to a modification of the composition and electron transport properties, and accordingly to changes in physical properties of TiO$_2$ NTs. Numerous studies show for photoelectrochemical applications, that a most effective conversion of amorphous tubes to anatase by an annealing treatment at 450–500 °C for 1–3 h. However, annealing temperature and time are generally well investigated.[36] Some other crucial factors such as the thermal ramping/annealing rate, is much less explored. Generally, annealing treatments are performed in a furnace, but this can also be carried out in rapid thermal annealers (RTAs) if annealing with specific ramping/annealing rates is desired.

While some early reports address some effects of the temperature ramping rate,[37] we provide herein a systematic investigation of the photoreponse from a most typical anodic NTs morphology of anatase using different annealing ramping/annealing rate. The causes for the observed significant effect of the ramping rate were examined.

2. Experimental Section
2.1. Reagents and Chemicals

Titanium foil (125 μm) with 99.6% purity was purchased from Advant Research Materials England, ethylene glycol was obtained from Sigma-Aldrich, ammonium fluoride (NH$_4$F) was purchased from MERCK, Germany. We used deionized water (DI) in all experiments.

2.2. Growth of TiO$_2$ NTs

For the growth of TiO$_2$ NTs, we used titanium foil of 125 μm thickness. For all experiments, the obtained titanium foil was cut into 1.5 × 1.5 cm$^2$ pieces and cleaned with acetone, ethanol, and DI water using sonication for 30 min followed by drying in an N$_2$ stream. Fresh electrolyte was prepared using ethylene glycol (EG) with the addition of 0.15 M NH$_4$F containing 3.0 wt% DI water. The highly ordered TiO$_2$ NTs were synthesized using a two-electrode potentiostatic electrochemical cell configuration with a platinum electrode as a cathode and titanium foil (1.5 × 1.5 cm$^2$) as an anode, which was mounted at the bottom of the cell. Anodization was carried out by applying a constant voltage (60 V) from the open-circuit potential (OCP) for 30 min using VOLTRAFT VLP2403 Pro DC power supply. After completion of the anodization experiment, the samples were washed with ethanol and DI water followed by drying in an N$_2$ stream. All experiments were carried out at room temperature. The obtained TiO$_2$ NTs were amorphous and annealed at 450 °C for 1 h in air using RTA (Jipelec Jetfirst 100) for obtaining anatase TiO$_2$ NTs, as shown in Figure 1b. To see the effect of annealing temperature and time, we annealed all samples at different ramping/annealing rates. The samples were annealed at 50, 10, 1, and 0.1 °C ramping rates with different heating times such as 9, 43, 430, and 4300 s, respectively, and named as T-50, T-10, T-1, and T-0.1, respectively.

Figure 1. a) Change in the crystal phase of TiO$_2$ as a function of temperature. b) Schematic illustration for the synthesis of annealed TiO$_2$ NTs using electrochemical anodization method.
2.3. Characterization

The X-ray diffractogram (XRD) of the prepared TiO$_2$ NTs were measured with a Panalytical Xcelerator detector using graphite-monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å). The crystallite size was calculated using Scherrer Equation (1).

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $D$ is the crystallite size, $K$ is the Scherrer constant, $\lambda$ is the wavelength of the used X-ray radiation, $\beta$ is the full width at half-maximum (FWHM) in X-ray diffraction reflections of the anatase peak (101) of TiO$_2$, and $\theta$ is the Bragg’s angle. The morphology of the prepared NTs was characterized using field emission scanning electron microscopy (Hitachi, FE-SEM S4800). The cross-sectional images were obtained by mechanically scratching the samples to examine the length of tubes. The chemical analysis of the synthesized TiO$_2$ NTs were carried out by energy-dispersive X-ray spectroscopy (EDX) using EDAX Genesis, fitted to the Hitachi FE-SEM S4800.

All electrochemical measurements IPCE, IMPS, OCP, and Mott–Schottky (M–S) analysis were carried out in a three-electrode cell configuration, with Ag/AgCl (3 M KCl) as the reference electrode, platinum sheet as the counter electrode, and the TiO$_2$ NTs as the working electrode. All experiments were performed in 0.1 M Na$_2$SO$_4$ aqueous solution as an electrolyte. Moreover, all assessments either in dark or light (IPCE, IMPS, OCP, and M–S) were carried out after the stabilization of current at a given potential.

The IPCE analysis was investigated using a LOT-Oriel 6365 with 150W Xe arc lamp equipped with a 1/8m Oriel cornerstone 7400 monochromator as a light source with a constant potential 0.5 V using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) in the presence of aqueous solution as an electrolyte. The IPCE value for each wavelength was obtained using Equation (2).

$$IPCE = \left(\frac{J_{ph} \times \eta n}{P \times \lambda}\right) \times 100$$  \hspace{1cm} (2)

where $J_{ph}$ is the photocurrent density (mA cm$^{-2}$), $P$ is the power density of incident light (W cm$^{-2}$), $\eta n$ is the photon energy of the incident light (1240 eV nm$^{-1}$), and $\lambda$ is the wavelength of the light (nm).

Intensity-modulated photocurrent spectroscopy (IMPS) analysis was carried out under constant potential 0.5 V using a Zahner IM6 (Zahner Elektrik Kronach, Germany) in the presence of UV-modulated light-emitting diode ($\iota = 358$ nm). The frequency analyzer (FRA) was used for frequency modulation. The photocurrent and photocurrent of the cell were examined using an electrochemical interface and send feedback to FRA. The frequency range of oscillations was 0.1–1 kHz with varying power densities of the light emitting diode (LED) (171.3, 85.5, and 9.7 μW cm$^{-2}$). The incident light intensity on the cell was examined using a calibrated Si photodiode. The corresponding charge transport time ($t_{rs}$) constants were investigated using Equation (3), which is inversely proportional to specific frequency ($f_{IMPS}$).

$$t_{rs} = \frac{1}{2f_{IMPS}}$$  \hspace{1cm} (3)

The OCP decay analysis was also investigated by illuminating TiO$_2$ NTs for 10 s and then the light was switched off. The OCP decay of photoinduced electrons as a function of time was recorded during relaxation from the irradiation steady-state to the dark equilibrium over a period of 20 min.

The M–S analysis was done using a Zahner IM6 system (Zahner Elektrik, Kronach, Germany) under dark conditions at a fixed frequency of 1 Hz. The applied voltage was in the range from 0.5 to –0.4 V with an amplitude of 10 mV. The donor density ($N_d$) was obtained using Equation (4).

$$N_d = \frac{2/\varepsilon_0\varepsilon_0}{d(1/C^2)/dV}^{-1}$$  \hspace{1cm} (4)

where $\varepsilon_0$ is the dielectric constant of vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$), $\varepsilon$ is the permitivity of vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$), and $C$ is the capacitance obtained from the electrochemical impedance at each potential (V). However, $d(1/C^2)/dV$ values were calculated from the slope of the linear parts of the M–S plots.$^{[38]}$

3. Results and Discussion

A series of TiO$_2$ NT samples were produced by the anodizing Ti as described in Experimental Section. The samples were then annealed using different thermal ramping rates.

3.1. Morphology and Crystal Structure

The surface morphology of the as-formed and annealed TiO$_2$ NTs was investigated using FE-SEM. The cross-sectional SEM of the as-annealed sample shows that the NTs used here are 6.7 μm in (see Figure 2a). The tube layers are made up of closed tubes with smooth inner and outer wall morphologies and have well-defined tube tops. Moreover, tubes show a typical honeycomb closed-packed arrangement of discrete NTs. To obtain crystallized tubes, the anodized TiO$_2$ NTs were annealed at 450°C for 1 h in air different ramping/cooling rates.$^{[39]}$ Figure 2b–e shows the morphology of tubes annealed with ramping rates of 50, 10, 1, and 0.1°C s$^{-1}$ (T-50, T-10, T-1, and T-0.1). Figure 2a shows that the tubes maintain their geometry to a large extent. Namely, the tube length, tube diameter, and the outer wall remain virtually unchanged. However, the tube tops exhibit an initiation layered$^{[40]}$ and some titane decoration$^{[41,42]}$ which can be ascribed to the modifications when converting the amorphous tubes into the crystalline form.$^{[43]}$ From the top-view SEM images of crystalline NTs, the diameter and thickness of the NT walls were found to be in the range of 41–45 nm.

To confirm the conversion of the amorphous phase to anatase, XRD patterns of the annealed samples were examined. The XRD patterns of T-50, T-10, T-1, and T-0.1 are shown in Figure 2f. The sharp diffraction peaks of annealed tubes at 450 °C for 1 h in air at different heating rates at 25.3°, 37.0°, 38.1°, 48.1°, 54.0°, 55.1°, 62.8°, 68.9°, 70.5°, and 75.1°, are indexed to (101), (103), (004), (200), (105), (211), (204), (116), (120), and (215) (PDF)CFDS # 01-084-1285) of anatase TiO$_2$ NTs.$^{[43,44]}$ However, peaks at 40.1°, 53.0°, and 76.1° are indexed to (101), (102), and (210) of titanium substrate.$^{[43,44]}$ This illustrates that the annealing treatment changes the original amorphous phase of TiO$_2$ NTs to a well-crystallized anatase phase. The crystal size of all samples was calculated using the Scherrer Equation (1) by taking the
FWHM of (101) anatase reflex at $2\theta = 25.3^\circ$, which is given in Table 1. The results show a similar degree of crystallization to anatase with a crystallite size of $\approx 20-23$ nm.

To evaluate the chemical composition of the TiO$_2$ NTs in dependence of the annealing ramping rate, EDX measurements were carried out. Figure 2g–j shows the EDX spectra of T-50, T-10, and T-1, indicating the presence of carbon, oxygen, fluorine, and titanium. The presence of carbon in TiO$_2$ NTs originates from the electrolyte and environment.\textsuperscript{[45]} Table 1 shows the percentage of different elements present in the TiO$_2$ NT matrix.

### Table 1. Crystallite size and percentage of different elements present in T-50, T-10, T-1, and T-0.1 NTs.

| Samples | Crystallite size [nm] | Titanium [at%] | Carbon [at%] | Oxygen [at%] | Fluoride [at%] |
|---------|----------------------|----------------|--------------|--------------|----------------|
| T-50    | 22.9                 | 45.57          | 2.32         | 51.14        | 0.96           |
| T-10    | 22.5                 | 46.59          | 2.88         | 50.16        | 0.37           |
| T-1     | 20.9                 | 47.12          | 2.14         | 50.39        | 0.35           |
| T-0.1   | 21.3                 | 48.18          | 2.01         | 49.67        | 0.15           |

To examine the photoresponse of annealed TiO$_2$ NTs at different ramping rates at 450 °C for 1 h in air, the IPCE measurements were taken under monochromatic light illumination, as shown in Figure 3a. The IPCE values calculated from photocurrent analysis as a function of incident wavelength are highest (37%) for T-1, followed by T-0.1 (31%), T-10 (19%), and T-50 (10%). The results indicate that increasing the heating time leads to enhancement in the IPCE values up to T-1, and then reduction in IPCE values is observed. This improvement in the IPCE values with heating time may be due to the introduction of point/structural defects.\textsuperscript{[46]} To see the effect of heating and cooling times, we annealed samples at different heating, cooling times and observed that only heating rate matters. The IPCE data were further plotted for the evaluation of the bandgap ($E_g$) of TiO$_2$ NTs annealed at 450 °C for 1 h in air for different ramping/heating rates. Figure 3b shows the graph of $(\text{IPCE} \times h\nu)^{1/2}$ versus photon energy ($h\nu$), which was used to calculate the bandgap, as shown in Table 2.\textsuperscript{[47,48]}

### 3.2. Photocurrent (IPCE) Analysis

To examine the kinetics of electron–hole recombination and charge transport (mobility and trapping) of TiO$_2$ NTs annealed at 450 °C for 1 h in air at different ramping/heating rates, IMPS measurements were carried out. IMPS is a perturbation...
technique, which uses sinusoidal oscillation of intensity of illuminated light to provide information on the transport times of photogenerated charge carriers, viz. holes to the semiconductor/electrolyte junction and electrons through the tubes to the back contact.\(^{[49]}\) Figure 2c–e shows the normalized IMPS spectra of the as-prepared TiO\(_2\) NTs annealed at different ramping rates at 0.5 V with different power densities of LED (171.3, 85.5, and 9.7 \(\mu\)W cm\(^{-2}\), respectively) by plotting the photocurrent efficiency response in complex Nyquist diagram. All the spectra show one semicircle, whereas a second semicircle of the opposite sign can be discerned in some cases at high light intensities. Figure 3f shows the photogenerated charge transport time constants \((t_{\text{rs}})\) of the TiO\(_2\) NTs annealed at different ramping/heat- ing rates obtained from IMPS analysis and calculated using Equation (3). The results show that T-1 has the highest photocurrent efficiency, and also exhibits the shortest transport time. This indicates a smaller extent of charge trapping/detrapping in T-1.\(^{[50]}\) Therefore, T-1 exhibits less recombination of electrons and holes during illumination, indicating less interfering electronic defects in the structure. Thus the enhanced charge transport or lower recombination may be ascribed to less point/structural defects.\(^{[51,52]}\)

### 3.4. OCP Decay Analysis

To calculate the lifetime, transient photoconductivity, charge transfer efficiency, and recombination kinetics of photogenerated electrons, the OCP decay analysis was conducted. OCP decay analysis was done according to the technique reported by Zaban et al.\(^{[53,54]}\) Figure 4a shows that after turning off the illumination, the voltage shows an exponential decay as a function of time due to recombination of charge carriers. As shown in Figure 4a that T-1 exhibits the fastest electron transfer time among all samples, leading to a longer lifetime of charge carriers. Therefore, the number of free-electron which can migrate to the surface is highest for the T-1 sample. This is well in line with the findings from IMPS measurements and their interpretation in terms of point/structural defects in TiO\(_2\) NTs at an optimized annealing ramping rate.\(^{[52,55]}\)

### 3.5. M–S Measurements

To further examine the impact of the point/structural defects generated by the effect of ramping/heat- ing time on the TiO\(_2\) NTs, the flat band potential \((V_{\text{fb}})\) and charge carrier density \((N_d)\) of the prepared annealed TiO\(_2\) NTs were calculated using M–S analysis. Figure 4b shows the M–S plots of annealed TiO\(_2\) NTs at different ramping rates for 1/C\(^2\) as a function of the applied potential under dark conditions. Figure 4b shows that

#### Table 2. Bandgap, flat band potential, and charge carrier density of T-50, T-10, T-1, and T-0.1 NTs, respectively.

| Samples | Bandgap [eV] | Flat band potential \((V_{\text{fb}})\) [V] | Charge carrier density \((N_d)\) [cm\(^{-3}\)] |
|---------|-------------|--------------------------------|------------------|
| T-50    | 3.11        | 0.27                           | \(4.01 \times 10^{18}\) |
| T-10    | 3.09        | 0.21                           | \(5.37 \times 10^{18}\) |
| T-1     | 3.04        | 0.08                           | \(6.47 \times 10^{18}\) |
| T-0.1   | 3.07        | 0.17                           | \(5.65 \times 10^{18}\) |
all samples display a positive slope, indicating n-type semiconducting behavior with electrons as the majority carrier. The values of $V_{fb}$ were calculated from the X-intercept of the linear region of the M–S plot, by extrapolating the $1/C^2 = 0$ graph for TiO$_2$ NTs annealed at different ramping/heating rates. The calculated $V_{fb}$ values are shown in Table 2. The T-1 shows a lower $V_{fb}$ as compared with other NTs, suggesting more efficient charge separation and transport as discussed in previous work. Moreover, the $N_d$ of different TiO$_2$ NTs was also calculated using Equation (4) and shown in Table 2. The calculated $N_d$ values for all TiO$_2$ samples are found to be in the range of reported donor density values in literature for TiO$_2$ anatase (approximately $10^{17} - 10^{19}$ cm$^{-3}$).

4. Conclusion

In this work, a widely used electrochemical anodization method was applied to synthesize highly ordered TiO$_2$ NT arrays of $6.7 \mu$m length on a Ti foil in a fluoride-containing electrolyte. These NT arrays are amorphous—they were then crystallized to anatase at 450°C using different ramping/heating rates. Ramping/heating rates have a drastic impact on the IPCE of the different anatase photoelectrodes. The effect of annealing ramping/heating rates was investigated using XRD, EDX, IMPS, OCP decay, and M–S techniques. The experimental results reveal that among all samples, an optimum ramping rate (1°C s$^{-1}$) that exhibits the highest photocurrent activity. This beneficial effect can be ascribed to the most effective electron transport—shortest transport time—and the least amount of trapping states present in these tubes. Therefore, an optimal annealing temperature and heating/cooling time is necessary for TiO$_2$ to achieve a minimum of point defects and as a result, the anatase nanotubular structure of TiO$_2$ can yield a higher photocurrent activity. We also observe that the reported effects depend only on the heating rates. Remarkably, these effects have hardly been previously reported in the literature.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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electrochemical anodization, photoanodes, photoelectrochemistry, ramping rates, TiO$_2$ nanotubes

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