Designing TiO₂ nanostructures through hydrothermal growth: influence of process parameters and substrate position

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Abstract
Synthesis conditions and processing parameters profoundly affect the growth and morphology of nanostructures. In particular, when nanostructures are fabricated through a chemical technique such as hydrothermal, the process parameters such as reaction time, temperature, precursor concentration, and substrate orientation play a crucial role in determining the structure-property relationships. In this work, we report the hydrothermal growth of Titanium dioxide (TiO₂) nanostructures as a function of these parameters and show that specific morphologies can be obtained by a variation of these parameters. A systematic study is carried out to understand the influence of reaction time (from 0.5 h to 3.0 h), reaction temperature (180 °C–200 °C), titanium precursor concentration (0.25 ml and 0.50 ml in 20 ml solution of HCl and deionized water) and substrate orientation (horizontal and tilted at an angle), and we show that significant variation in morphology—from nanowires to nanorods and then dandelions can be achieved. In particular, we demonstrate that high surface area multidirectional growth of nanorods leading to flower-like nanostructures or dandelions resulting from precipitation during the hydrothermal process. This is in contrast with previous reports on similar structures, where the role of precipitations was not analyzed. The work shows a possibility to control such growth by manipulating substrate position inside the autoclave during the hydrothermal process and will be useful for surface-dependent applications.

1. Introduction

TiO₂ is extensively used in applications such as photocatalysis and solar cells, biomedical coatings, chemical sensors, etc [1] owing to its good chemical and thermal stability, excellent photoactivity in the UV region, and biocompatibility. Several nanostructures of TiO₂ have been investigated in the recent times [2]. In particular, one-dimensional nanostructures such as nanorod, nanowire, nanofibre, etc show unidirectional charge transport and also play a role in minimizing recombination of the photogenerated charge carriers [3–5]. Literature review shows that one-dimensional nanostructures can be fabricated using various techniques such as electrochemical anodization [6], electrospinning, vapor phase growth, template-assisted method [7], lithography [8], etc. Among these, the hydrothermal technique allows the growth of crystalline materials at relatively lower temperatures compared to that of the thermal annealing process. In the case of TiO₂, the hydrothermal technique is used to grow vertically aligned crystalline nanorods on FTO coated glass substrate [9]. In addition, the hydrothermally grown TiO₂ nanorods have minimal grain boundary defects because of their single-crystalline nature.

The crystallinity, morphology, electronic and optical properties of materials critically depend on the synthesis conditions. In the case of a hydrothermal technique, the synthesis conditions include the time and temperature of the reaction, properties of the solution and the nature of the precursor used. So far, several studies are reported on TiO₂ nanorod arrays grown at various reaction temperatures (mostly <200 °C) and...
durations (>2 h) using different precursor concentrations [9–12]. The obtained nanostructures are explored for several applications. However, slight variations in these parameters result in significant alterations of the properties of TiO₂ nanorods. In addition, for substrate-assisted growth, the nature and placement of substrate play an important role as the TiO₂ nanorods grow through self-assembly and the orientation of the substrate also influences the precipitation phenomena. Kumar et al. showed vertical TiO₂ nanorod arrays and dandelion structure formation for vertical and horizontal orientation of the FTO substrates [13]. Liu et al. reported precursor concentration-dependent morphology variation from nanorod arrays (for 0.045 ml TBOT) to microflowers on top of nanorod arrays (for 0.090 ml TBOT) during the hydrothermal reaction [14]. Tao et al. showed the formation of TiO₂ nanorods on the conductive side and nanoflowers on non-conductive sides of the FTO coated glass substrate when it was placed at 30° to 40° inclination against the wall of an autoclave with the conductive side facing up [15]. Ahmad et al. reported reaction time-dependent TiO₂ nanoflower formation on nanorods which was observed after 3 h of reaction time [16]. Issar et al. showed that the TiO₂ nanoflowers form with increasing hydrothermal temperature, where nanoflowers were observed for more than 180 °C temperature [17]. It is, therefore, evident that both aligned and oriented nanorods, as well as multidirectional growth of flower (dandelion) type structures, can be achieved by a variation of the hydrothermal process parameters. However, a systematic study of the effect of these parameters on resultant morphologies has not been reported. In this work, we have studied the variation of reaction time, temperature, precursor concentration, and effect of substrate position on the growth of TiO₂ nanorod and related dandelion structures. The morphology, crystallinity, optical properties and photocurrent behavior of these samples are investigated and a structure-property correlation has been achieved.

2. Experimental section

2.1. Substrate cleaning
Commercially available glass substrate of 25 mm × 75 mm × 2.2 mm dimensions with a conductive coating of fluorine doped tin oxide (FTO) was used as substrate. Those were cut into pieces of sizes 10 mm × 20 mm and ultrasonically cleaned in ethanol and deionized (DI) water each for 2 min. Finally, these were dried under airflow.

2.2. Sample preparation
TiO₂ nanostructures were synthesized by a hydrothermal method. At first, a 20 ml solution comprising hydrochloric acid (HCl (37%)) and DI water at a 1:1 volume ratio was prepared. Titanium (IV) butoxide (TBOT) was added (0.25 or 0.50 ml) dropwise in the above solution and stirred for 30 min before using it for the hydrothermal reaction. The homogeneous precursor solution was transferred to a Teflon-lined stainless steel autoclave (150 ml) and the cleaned FTO substrates were placed submerged in it. The hydrothermal reaction was carried out for four durations, i.e., 0.5 h, 1.0 h, 2.0 h and 3.0 h keeping all other parameters constant. Further, the reaction was carried out at two different temperatures such as 180 °C and 200 °C. The effect of substrate position was investigated by keeping the substrate in (i) horizontal position and (ii) at an angle with the wall of the Teflon container. At last, all as-prepared samples were washed with DI water and finally dried under airflow.

2.3. Characterizations
The surface morphology was analyzed by Field Emission Scanning Electron Microscope (FESEM) (Model: FEI Inspect F50). The dimensions of nanostructures were measured from FESEM images using ImageJ software. X-ray Diffraction (XRD) patterns recorded using PANalytical X-ray Diffractometer, operating at 40 kV and 30 mA anode current using CuKα (λ = 0.154 nm) radiation, was used to identify the phase and crystal structure. The optical absorption spectra were measured from Perkin Elmer LAMBDA 950 UV–vis-NIR Spectrophotometer in Diffused Reflectance Spectroscopy (DRS) mode equipped with an integrating sphere accessory. Photocurrent measurement was carried out using CH Instrument Electrochemical Analyzer (CHI6054E model) and using Oriel Newport 300-Watt Xenon lamp with AM 1.5 G filter as a light source.

3. Results and discussion

3.1. Effect of hydrothermal reaction parameters
Hydrothermal reaction parameters, such as temperature, time, and precursor concentration, strongly affect the nucleation, growth, and crystallization of the material under process. Scanning Electron Microscopy (SEM) is a very useful tool for the study of morphology and stepwise process of nanostructure formation. The effect of the hydrothermal parameters on the morphology variation is discussed in this section, where the experiments were carried out placing the substrates aligned at an angle with the FTO side facing down.
3.1.1. Reaction time

Figure 1 shows the FESEM images of TiO$_2$ nanostructure arrays grown on FTO coated glass substrates at different reaction times such as 0.5 h, 1.0 h, 2.0 h and 3.0 h. In these experiments, 0.5 ml of TBOT was added to the mixture of DI water and HCl, having a total volume of 20 ml and the reaction was carried out at 200 °C. The top view images along with cross-sectional views for different time durations are presented. As seen from the images, 0.5 h reaction time shows nanorod with a tetragonal shape having an average length of $\sim 1.8 \mu$m and width of $\sim 190$ nm, measured using ImageJ software. This is in contrast with few reports such as by Ahmad et al (hydrothermal reaction at 150 °C using 6 ml of TBOT in a solution of 120 ml of HCl and 120 ml DI water) [16], where neither nanorods nor nanoparticles were obtained until a reaction time of more than 2 h. Most of the reports such as that by Yoon et al (at 180 °C using 0.4 ml TBOT in 14 ml of HCl and 14 ml of DI water) [3], Kumar et al (at 120 °C–180 °C using 1 ml of TBOT in a 1:1 mixture solution of HCl and DI water) [13] showed the nanorod formation occurred only after 2 h. However, in our study, the specific reaction conditions such as temperature (200 °C) and concentration (0.5 ml of TBOT in a solution of 10 ml HCl and 10 ml DI water) ensure that the nanorods are formed within 0.5 h of reaction time. When the reaction time is increased to 1.0 h, the alignment of the nanorods appears to be more ordered, with an average length of $\sim 1.9 \mu$m. Also, the edges of the individual nanorods appear to be sharper and well-defined. Further increment of reaction time to 2.0 h leads to longer and wider nanorods (length $\sim 3.3 \mu$m and width $\sim 300$ nm). Finally, the reaction time of 3.0 h results only in a minor increment of the length ($\sim 3.4 \mu$m). To further examine the effect of reaction time, the hydrothermal process was carried out for 4.0 h. This, however, resulted in the TiO$_2$ layer being peeled off from the FTO coated glass substrates.
glass substrate. The peeling off may be caused by the simultaneously occurring growth and dissolution processes. A more extended period leads to saturation of growth rate and dissolution at the FTO-nanorod interface. Moreover, a strain caused by the lattice mismatch at the FTO-TiO$_2$ nanorod interface is responsible for weak adhesion that leads to dissolution resulting in the peeling of the TiO$_2$ nanorod array film from the FTO substrate [18].

3.1.2. Reaction temperature

Figure 2 presents the FESEM images of TiO$_2$ nanorods on FTO coated glass substrate prepared at two different hydrothermal reaction temperatures, i.e., at 180 °C and 200 °C. The reaction time was kept constant at 2 h and the titanium precursor concentration was kept at 0.5 ml. It is observed that only a 20 °C difference in reaction temperature results in a significant difference in the final morphology of the TiO$_2$ nanorods. In both cases, a tetragonal shape is observed; however, a higher temperature (200 °C) yields sharper and well-defined nanorod morphology. This is attributed to the faster decomposition of TBOT at a higher temperature that accelerates the growth process [19, 20]. Moreover, these images suggest that thinner nanowires combine to form nanorods. At 180 °C, although individual thinner nanowires coalesce together to form larger structures, the growth process becomes more complete with the rise of reaction temperature to 200 °C. Sharper and well-defined morphology signifies an ‘all-round’ growth achieved at the higher temperature.

3.1.3. Precursor concentration

In order to analyze the effect of precursor concentration on the rod morphologies, two different concentrations were chosen, namely 0.25 ml and 0.50 ml of TBOT in 20 ml of solution. Figure 3 presents the FESEM images of the TiO$_2$ nanorod arrays prepared at 200 °C for 2 h using the above-mentioned concentrations of the precursor. Figure 3(a) shows a relatively random alignment of nanorods with a range of size (cross-section) distribution. Notably, both thinner (resembling nanowires) and thicker 1D nanostructures are observed having an average length of ~1 μm. When the concentration of TBOT is doubled, keeping all other parameters unchanged, several thinner nanowires are combined to form wider nanorods preserving the tetragonal shape. As a result, the distribution of nanorods becomes denser and vertically aligned on the FTO substrate. This can be attributed to the thicker growth of individual nanowires caused by higher concentration and then the adjacent ones fusing together to form wider nanorods. Further, at 0.50 ml concentration, the average length of the nanorods increases to ~3 μm, which suggests that the precursor concentration has a synergetic influence on both the density and the growth rate of TiO$_2$ nanorods.
In principle, during a hydrothermal reaction, molecules of the precursor go through a hydrolysis process by reacting with the aqueous solution followed by nucleation and growth at a certain temperature. In addition, the vaporized form of the solution creates a higher pressure that also helps in the nucleation and growth process \[1\]. The nucleation and growth mechanism determine the morphology of the material \[2\]. Since hydrolysis of the precursor leads to nucleation, a higher precursor concentration naturally results in more nucleation sites. As the reaction proceeds with time, growth takes place along certain preferred directions that are governed by surface energy consideration. In the case of TiO\(_2\) nanorods grown by hydrolysis of the precursor leads to nucleation, a higher precursor concentration naturally results in more aligned TiO\(_2\) nanorods. The result also confirms the dandelions are in rutile phase. Since the dandelion structure, such additional peaks appear in the XRD pattern, which are not observed in the case of substrate-assisted growth. However, in the case of TiO\(_2\) nanorods grown by hydrothermal process, growth is preferred along (002), which is also evident from the XRD data shown in the subsequent section. Also, the reaction temperature affects the reactivity and hydrolysis of the precursor and usually, an optimum value of temperature is required to achieve efficient nucleation and growth process. Although a higher reaction temperature stimulates the decomposition of the precursor and increases the reactivity towards hydrolysis, a monotonous increase in temperature may not lead to a desired morphology of the material. Thus, hydrothermal variables such as temperature, time and precursor concentration control the overall nanostructure formation.

3.2. Effect of substrate placement

So far, we have discussed the influence of intrinsic parameters related to a hydrothermal process. However, in the case of substrate-assisted growth, the exposure of the substrate surface with the solution is of primary importance as that controls the extent of nucleation and subsequent growth. In order to analyze the effect of substrate position inside the autoclave, three sets of experiments were carried out. In the first two experiments, the substrate, immersed into the solution, was placed aligned at an angle \(30^\circ\)–\(40^\circ\) with the wall of the vessel, keeping FTO coated side facing down and facing up respectively (schematically shown in figure 4). In the third experiment, the substrate was placed horizontally on the floor of the autoclave with the FTO side facing up. The FESEM images of the resultant growth are shown in figure 5. When the substrate is aligned at an angle with the FTO side facing down, tetragonal-shaped TiO\(_2\) nanorods are observed, as shown in figure 5(a), which resembles the normal growth of the nanorods discussed in the previous sections. The inset of figure 5(a) presents the corresponding magnified image. When the FTO side is facing up, flower-like morphologies (dandelions) appear on top of the nanorods (figure 5(b)). It is observed that a number of spike-shaped nanorods are grown and such ‘secondary’ nanorods appear to be originating from the top of the ‘primary’ nanorods grown directly on the substrate (figure 5(d)). When a number of secondary nanorods nucleate on top of primary nanorods, dandelion-like structures are formed. It is also observed that the width of the nanorods in the dandelion structure is higher than the nanorods grown from the FTO substrate. Each nanorod in the dandelion is thicker than each of the vertically oriented nanorods. Further, the density of such dandelions significantly increases when the substrate is placed horizontally as shown in figure 5(c). The inset of figure 5(c) shows the corresponding magnified image. A cross-section FESEM image showing the vertically grown nanorods and the dandelion structures is presented in figure 5(d).

Figure 6 shows a schematic description of the substrate configuration and the evolution of the resultant morphologies during the hydrothermal processes carried out under the present work.

In order to determine the crystalline phases of samples without and with dandelion growth, XRD was performed and the data are presented in figure 7. It is observed that in both cases rutile phase of TiO\(_2\) is formed with peaks at 36.61°, 44.19°, 54.79°, 63.30°, 65.98° and 69.59° corresponding to (101), (210), (211), (002), (221) and (301) planes respectively (ICSD data file with Ref. code 01-073-1765). However, the presence of dandelion structures results in additional peaks of rutile phase at 27.98°, 39.75°, 41.84°, 57.12° and 64.59° corresponding to (110), (200), (111), (220) and (310) respectively. This can be attributed to the formation of dandelions, which are the combination of multidirectional TiO\(_2\) nanorods. Because of the random orientations of the nanorods in the dandelion structure, such additional peaks appear in the XRD pattern, which are not observed in the case of aligned TiO\(_2\) nanorods. The result also confirms the dandelions are in rutile phase.

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The diffuse reflectance (%R) spectra of TiO$_2$ nanorod arrays without and with dandelion structures are shown in figure 8(a). The reflectance data show a higher value for nanorods with dandelion structures that can be attributed to enhanced scattering of light from the randomly oriented nanorods. Additional surfaces available to the light from dandelions lead to enhanced scattering and therefore, a higher diffuse reflectance from the samples. The Tauc plot obtained from the reflectance data using the Kubelka-Munk function [24] is shown in figure 8(b). The estimated band gap is $\sim$3.05 eV, which matches with the bandgap of the rutile TiO$_2$ [1]. It is understood that the presence of dandelion structures does not shift the band edge because of the relatively larger dimensions that do not result in charge carrier confinement. Also, a similar crystalline phase and absence of any impurities cause the absorption edge to remain unaltered.

Kumar et al compared the effect of substrate placement on the morphology of the nanostructures. They observed dandelion-type structures in the case of the horizontally placed substrate; however, the presence of TiO$_2$ nanorod arrays was not reported [13]. Recently, Issar et al showed nanoflower morphology due to an
Figure 7. XRD patterns of TiO$_2$ nanorod arrays without and with dandelion structures.

Figure 8. (a) Diffuse reflectance (%R) spectra and (b) Tauc plot of TiO$_2$ nanorod arrays without and with dandelion structures.
increase in reaction temperature to 200 °C[17]. However, in our study, dandelion-like structures are independent of temperature and are formed only when the substrate is placed with the FTO side facing up. On the other hand, Meinan Liu et al reported that after a certain precursor concentration (3 mM of TBOT) microflowers were formed on TiO2 nanorod arrays[14]. In our study, it is observed that dandelion structure is not formed even for higher concentrations of the precursor (0.25 ml and 0.50 ml, which are equivalent to 8.33 mM and 16.67 mM, respectively) if the substrate is placed keeping FTO side facing down (figure 3). It is important to note that the dandelion-like structure forms on top of the TiO2 nanorod arrays only when the substrate is either placed horizontally or tilted with the FTO side facing up. This indicates that the position of the FTO coated substrate plays a leading role in controlling the formation of the dandelion structure rather than the precursor concentration.

Subramanian et al [25] studied the growth of micrometer-sized cactus-like flowers of rutile TiO2 for DSSC applications. They suggested flower-like hierarchical morphologies grow as branches from a central nanorod structure during a facile hydrothermal process. They also hypothesized that both heating and cooling conditions play an important role in the growth of such flower-type morphologies. A similar mechanism has also been proposed by Ali et al[26], in which a central nanostructure gives rise to the growth of secondary branches. However, in our case, the dandelions grow not as branches from any nanorod but from the top surface of the primary nanorod arrays. Burungale et al reported the growth of hierarchical nanostructures from the pyramidal-shaped tip of TiO2 nanorods, in which the faces of the pyramid acted as nucleation sites for the growth of secondary nanorods. This resulted in the growth of secondary nanorods spreading out from the tip of primary rods [27]. In our case, however, FESEM images do not show pyramid-shaped tips; in contrast, the tips are square or rectangular-shaped facets as shown in figure 1. Therefore multidirectional growth of secondary nanorods is not feasible from the tips of the primary rods. Maria John et al [28] observed the growth of nanostructures similar to that observed in our case; however, the multidirectional growth mechanism was not analyzed in detail.

In a recent work, Maria et al [29] observed the growth of secondary nanorods in flower-type morphology and attributed to pyramidal-shaped tips similar to the report by Burungale et al. Further, Ahmad et al observed no nanoflowers formation up to a reaction time of 5 h; however, use of cetyltrimethylammonium bromide (CTAB) as a capping agent accelerated the growth rate and promoted the nanoflower formation at relatively shorter reaction time[30]. In contrast, we observed dandelion structures on top of the TiO2 nanorod array even at a much shorter duration of 1 h (figure S1 (available online at stacks.iop.org/NANOX/2/010028/mmedia) in supplementary material) without using any capping agent. This can be attributed to the faster growth rate.

In general, nanostructure formation through hydrothermal technique is controlled by nucleation and subsequent growth mechanism. At first, monomers formed by the hydrolysis of TiO2 precursor condense to initiate nucleation, which eventually acts as seed material to promote the growth process. FTO, with tetragonal crystal structure (a = b = 0.4687 nm) [31], shows a high degree of lattice match with that of rutile TiO2 (a = b = 0.4594 nm) [32]. This similarity in TiO2 and FTO lattice structure leads to single crystalline growth of individual TiO2 nanorods on FTO with particular alignment [18], which results in a uniformly oriented near-vertical nanorod arrays formation. In the present case, when the FTO side of the substrate is facing up (horizontal or tilted), the TiO2 nanorod array is formed. In addition, particles are deposited as a result of precipitation over the nanorod array, which act as secondary nucleation centers. However, the sinking or settling of precipitated particles on the TiO2 nanorod arrays is governed by gravitational force and the extent of precipitation, therefore, depends on the mass and the size of the clusters. The role of precipitates under the gravitational influence as the seed point of dandelion growth can be understood by considering the fact that no dandelions formed in case of the tilted substrate with FTO side facing down and a higher density of such dandelions grows in the case of the horizontally placed substrate as compared to that in the tilted substrate with FTO side facing up. Each of the precipitated particles on top of TiO2 nanorod arrays is actually polycrystalline in nature and therefore has different facets that support further growth of the secondary nanorods. Figure 9 shows a closer view of the initial stage of dandelion growth. The precipitated particle and the growth of few secondary nanorods are clearly observed in the image. It is also interesting to note that the lateral dimensions of the nanorods significantly increase during the secondary growth as compared to the primary nanorods grown directly from the FTO substrate. This can be attributed to the homogeneous nucleation of the TiO2 nanorods over the precipitated particles in contrast with heterogeneous nucleation on the FTO substrate. Homogeneous nucleation allows a wider base of similar material for the growth of secondary TiO2 nanorods and hence the lateral dimension of the nanorod increases. Peng et al [33] also observed a wider nanorod formation where TiO2 nanoparticle-coated FTO glass was used as a substrate. In that report, the formation of the dandelion-like structure on TiO2 nanorods was attributed to the adsorbed TiO2 nanocrystals in the intervening space of thinner nanowires (those combined to form nanorods), which acted as the secondary nucleation centers. They observed dandelion-like structure formation for substrate placed aligned at a certain angle (∼75° with the floor of the autoclave) with FTO side facing down. However, we do not observe any dandelion-like structure formation in the case of the tilted substrate with the FTO side facing down for a range of substrate alignment angles (∼10°–50°
with the wall of autoclave, i.e., ∼40°–80° with the floor of the autoclave) within experimental limitation. This can be attributed to the gravitational influence, which does not allow the particles to deposit as a result of precipitation on the downward FTO surface. No dandelion formation in the case of the substrate placed at a near-horizontal alignment (∼15° with the floor of the autoclave) having FTO side facing down was also observed by Peng et al which supports our discussion on gravitational influence. It is also important to note that although precipitation of particles do occur over glass surface (when FTO coated side is facing down), the absence of FTO or TiO₂ does not provide the required nucleation sites/stable anchoring of the particles for supporting further growth.

The role of precipitates in the growth of dandelions is further established by photocurrent measurements as shown in figure 10. The photocurrent is measured in 1 M KOH aqueous electrolyte solution using TiO₂ nanostructure (on FTO coated glass) as a working electrode, platinum as a counter electrode, and Ag/AgCl (in saturated KCl) as a reference electrode under one Sun (100 mW cm⁻²) illumination. In the case of TiO₂ nanorods arrays without dandelions, a photocurrent density of ∼0.78 mA cm⁻² is obtained at an applied potential of 0.6 V (versus Ag/AgCl) under AM 1.5 G conditions. However, in samples with dandelions, the photocurrent reduces to about ∼0.54 mA cm⁻² under similar conditions. It is evident that a higher surface area

Figure 9. FESEM images of the initial stage of dandelion formation from precipitates (at 200 °C for 2 h using 0.5 ml titanium precursor).

Figure 10. Photocurrent density versus time plot at an applied potential of 0.6 V (versus Ag/AgCl) for TiO₂ nanorod arrays with and without dandelion structures.
results from such morphologies, as reported by dye adsorption studies\cite{14, 25} and also through the diffused reflectance data reported in figure 8, lowering of photocurrent indicates loss of photogenerated charges through recombination, possibly at the dandelion-nanorod interfaces. Since the interface in the present case is a result of precipitation, it may not act as an ideal one for facilitating efficient charge transfer. However, such morphologies may find a useful application in surface-dependent phenomena.

It is therefore evident that although dandelion-type flower-like morphologies are reported through the hydrothermal growth of TiO$_2$ nanorods, the role of substrate placement in our case (as discussed in the previous paragraphs) points to a fundamentally different mechanism. Since the horizontal placement of the FTO coated substrate results in a higher density of dandelion growth, TiO$_2$ nanoparticles precipitated on top of the nanorods act as nucleation sites (higher chance of precipitation on a horizontally placed substrate compared to that on a tilted substrate).

4. Conclusions

We studied the effect of hydrothermal variables and substrate position on the growth process and resultant morphology of TiO$_2$ nanostructures grown on FTO coated glass substrate. The microscopic investigation shows that shorter and thinner nanowires of variable widths grow at 0.5 h, whereas both length and width increase with increasing reaction time up to 2 h, and then the growth rate saturates. On the other hand, lower process temperature (180 °C) and lower concentration (0.25 ml) of TBOT precursor results in thinner and variable-width nanowires with relatively random orientation, which gradually transform into well-aligned TiO$_2$ nanorods with sharper edges and tetragonal shape with an increase in temperature to 200 °C and a higher concentration of precursor (0.50 ml). We also found that substrate position plays an important role in the secondary growth of nanostructures on top of the nanorods. When the FTO side is placed facing down in a tilted configuration aligned with the wall of the container, only nanorods growth is observed, whereas having the FTO coated side facing up results in beautiful dandelion growth on top of the nanorods. The density of dandelions increases further when the substrate is placed in a horizontal position at the bottom of the container. The observation suggests the growth of dandelions on nanorods nucleate from precipitated TiO$_2$ particles onto the top of the nanorods. Enhanced diffused reflectance indicates an increase in the surface area of the TiO$_2$ nanostructures. However, in spite of an increase in the apparent surface area, the photocurrent density decreases in dandelion structures as compared to that in bare TiO$_2$ nanorods. We infer that a relatively defective interface between the dandelions and TiO$_2$ nanorods formed due to precipitation may result in inefficient separation of the photogenerated charges leading to a lower photocurrent. The observations suggest that the hydrothermal process has an intensive ability to control the nanostructure formation and the growth process by tuning the reaction variables and substrate position. The TiO$_2$ dandelion structure over the nanorods may be useful in surface-sensitive applications such as sensing and catalysis.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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