



Nanocoral architecture of TiO₂ by hydrothermal process: Synthesis and characterization

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ABSTRACT

TiO₂ thin films with novel nanocoral-like morphology were successfully grown directly onto the glass and conducting fluorine doped tin oxide coated glass substrates via multi-step hydrothermal (MSH) process. Titanium chloroalkoxide [TiCl₂(OEt)₂(HOEt)₂] precursor was used in an aqueous saturated NaCl in presence of 1 mM HCl catalyst and HNO₃ peptizer at 120 °C. Reaction time varied from 3 to 12 h. The morphological features and physical properties of TiO₂ films were investigated by field emission scanning electron microscopy, high resolution transmission electron microscopy, X-ray diffraction, Fourier transform IR spectroscopy, Fourier transform Raman spectroscopy, room temperature photoluminescence spectroscopy and X-ray photoelectron spectroscopy. The surface morphology revealed the formation of TiO₂ corals having nanosized (30–40 nm) polyps. The photoelectrochemical properties of the TiO₂ nanocoral electrodes were investigated in 0.1 M NaOH electrolyte under UV illumination. The results presented in this study highlight two major findings: (i) ability to tune the photoelectrochemical response and photoconversion efficiency via controlled thickness of TiO₂ nanocorals and (ii) the substantial increase in short circuit photocurrent (J_{sc}) due to the improved charge transport through TiO₂ nanocorals prepared via MSH process. This approach would be quite useful for the fabrication of nanocoral architecture that finds key applications in photocatalysis, dye-sensitized solar cells and hybrid solar cells.

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1. Introduction

Titanium oxide (TiO₂) nanostructures such as nanorod/flower/wire/tube-arrays have attracted much attention owing to their large surface area requirements in dye-sensitized solar cells (DSSCs), electric and photocatalytic systems. Building on to the extensive work directed towards the spherical nanoparticles, the assembly of shape-controlled nanostructure has recently been gaining importance, both for fundamental scientific research and technological applications. Ever since the first synthesis of TiO₂ nanotubes in 1999 [1], they have been extensively studied due to their remarkable physico-chemical properties such as high chemical stability, mechanical resistance and high optical transmittance in the visible–IR spectral range. TiO₂ is an important functional semiconducting material with numerous applications in a photocatalysis [2], self-cleaning material [3], electrode in DSSCs [4], Li-ion battery materials [5], sensors [6] and so on. Number of approaches have been reported to fabricate TiO₂ single crystal [7], nanorod; wire [8]; tube-arrays [9–12]/nanospheres that include template-assisted method [13], electrochemical anodic oxidation method [14], spray pyrolysis technique (SPT) [15], chemical vapor

deposition (CVD) [16], hydrothermal method [17], anodized aluminum oxide (AAO) template-assisted sol–gel method [18], AAO template-assisted electrodeposition method [19], electrochemical anodic oxidation of pure titanium sheet [19–21], eggshell membrane template [22], electrospinning [23] and chemical treatment of fine TiO₂ particles [19,24–26,8]. However, achieving precise control over the size and morphology of the grown TiO₂ nanostructures and their further self-organization is still a daunting task. Recently, a complicated hierarchical morphology of TiO₂ nanotube has been achieved by anodization of metallic Ti foil [19]. In spite of these significant achievements, exploring a facile approach for fabricating novel nanocoral architectures with controllable morphology is sparse. Chu et al. [27] synthesized ordered TiO₂–Ru and TiO₂–RuO₂ nanorod arrays using AAO templates by cathodic electrodeposition. However, upon removal of AAO templates, the nanorod arrays tend to collapse due to the huge surface tension among the nanorods [28–30]. In addition, the large-scale industrial preparation of multidimensional (MD) TiO₂ nanomaterials with a controlled methodology is an ambitious task. In this scenario, hydrothermal method may provide a better opportunity for having control over the size and morphology of TiO₂. Kasuga et al. [31] first introduced a simple template-free method to synthesize TiO₂ nanotubes from amorphous TiO₂ and 10 M NaOH in a hydrothermal reactor at 110–150 °C, followed by washing with 0.1 M HCl.

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Recently, Kim et al. [32] reported hydrothermal synthesis of hierarchical TiO₂ nanoporous spheres for their efficient use in DSSCs. Still, there remains a difficulty of coating the synthesized powdered nanostructures on transparent conducting oxide (TCO) substrates. However, the films are relatively difficult to fabricate requiring Ti film deposition, an anodization step, and then crystallization by thermal annealing, which commonly degrades the conductivity of the TCO layer. Researchers have addressed this problem by employing a doctor-blade technique for deposition of hydrothermally synthesized nanostructures using organic binders. In this case, adherence of the films to the TCO substrates and elimination of organic binders from the deposited material requiring thermal annealing is an unsolvable problem. Moreover, post-annealing treatment causes increase in sheet resistance of TCO substrates and disrupting of initial structure of nanostructures, ultimately attenuating the resultant photocurrent in DSSC.

Addressing the above mentioned obstacles, we report here for the first time, the novel synthesis of TiO₂ nanocorals directly onto the glass and TCO substrates using a modified hydrothermal process. Our synthetic process is performed at relatively low temperature (below 130 °C) without affecting conductivity of the TCO substrates.

High surface area of the photoanode is one of the key elements for efficient fabrication of DSSCs, which enable effective loading or adsorption of dye molecules for harvesting maximum portion of illuminated light. Therefore, it is expected that owing to highly porous morphology such nanocoral nanostructures could provide both great adsorption for the dye molecules and efficient electrolyte diffusion at the same time.

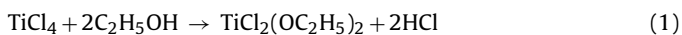
2. Experimental

2.1. Materials and chemicals

All the chemicals were of analytical reagent grade and used without further purification. Titanium tetrachloride (TiCl₄) (99.98% Spectrochem, India), absolute ethanol (AR, Changshu Yangyuan Chemicals China, 99.9%), concentrated HCl (35.46%, Thomas Baker), and concentrated HNO₃ (38%, Thomas Baker). The aqueous solutions were prepared using double distilled water. The glass substrates were ultrasonically cleaned using detergent followed by chromic acid/methanol treatment and finally cleaned with acetone. The F:SnO₂ coated glass plates (~12 Ω/cm, 1 cm × 3.5 cm × 7 cm) were used as substrates or supports to TiO₂ films for photoelectrochemical measurements.

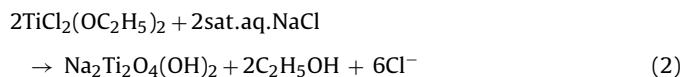
2.2. Preparation of TiO₂ photoanodes

In a typical experiment, the hydrothermal inorganic precursor solution was prepared by mixing 0.05 M TiCl₄ carefully with absolute ethanol in ice-cold bath forming yellow colored titanium chloroalkoxide [TiCl₂(OEt)₂(HOEt)₂] solution, as per reaction (1).

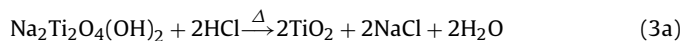


A small amount of 0.001 M concentrated hydrochloric acid (HCl, 36%, Thomas Beaker) was added as a catalyst and pH of solution was adjusted to 2.1 using nitric acid (HNO₃, 38%, Thomas Beaker) as a peptizer. Hydrochloric acid is believed to play a dual role here: (1) tailor the pH value of the reaction solution and retard hydrolysis of the precursor in the presence of water at low temperatures; (2) reduce the surface energy of the crystal plane side wall, promoting anisotropic growth in the (1 0 1) direction. The transparent solution thus prepared was further mixed with saturated solution of 6.8 M NaCl (Extra pure, Thomas Baker). The addition of water causes the hydrolysis of the inorganic moieties, producing in situ ethanol and

HCl, the latter being the reason for the high stability of the solution.



The final solutions are very acidic and stable for several months at ambient temperature (20–25 °C) or 1–2 weeks at 30 °C. The solution was stirred for 30 min using magnetic stirrer and transferred into a polytetrafluoroethylene (Teflon)-coated 25 ml vessel. The cleaned glass or TCO substrate was immersed into this solution vertically. It was then sealed and maintained at 120 °C for 3 h (at 1.5 kg/cm² pressure) designated as T₃. These processes are shown below:



where by Na⁺ ions are exchanged with H⁺ in a dilute HCl bath.



The TiO₂ nanocorals took place as shown in reaction (3b).

Upon completion of the reaction, the autoclave was allowed to cool at room temperature and the deposited film was rinsed in double distilled water and finally dried at room temperature. The same T₃ film was immersed again in fresh precursor and maintained at 120 °C for 3 h and designated as T₆. The samples deposited by following similar procedures with 9 and 12 h deposition time were designated as T₉ and T₁₂ respectively. This process is referred as multi-step hydrothermal (MSH) process. The TiO₂ film was whitish, uniform, crack-free and adherent to the substrates, whose adherence was checked by a scotch tape test.

2.3. Characterizations

The structural properties of the TiO₂ films were studied from X-ray diffraction (XRD) patterns recorded using an X-ray diffractometer (Philips, PW 3710, Almelo, Holland) operated at 25 kV, 20 mA with Cu Kα radiation (λ = 1.5406 Å). In addition to this, infrared (IR) spectroscopy was also used to confirm the TiO₂ phase. For this, the powder collected from the deposited films was characterized by infrared spectrometer (PerkinElmer, model 783, USA) in the spectral range of 450–4000 cm⁻¹ with a resolution of 1 cm⁻¹. To record IR spectrograms, a pellet was prepared by mixing KBr with the collected TiO₂ powder in 300:1 proportion and then pressing the pellet between the two pieces of polished steel. The Raman spectra of the films were recorded in the spectral range of 35–4000 cm⁻¹ using Raman spectrometer (Bruker MultiRAM, Germany Make) Nd:YAG laser source with excitation wavelength of 1064 nm and resolution 4 cm⁻¹. UV–vis absorbance spectra of TiO₂ thin films were obtained using a UV–vis spectrophotometer (UV3600, Shimadzu, Japan). The room temperature photoluminescence (RTPL) spectra of the films were recorded by using JASCO F.P.-750 Model, (Japan) spectrofluorometer with excitation energy 317 nm using 1000 W Xenon lamp. The scanning speed was 1200 nm/min, the PMT voltage 700 V and the width of excitation slit and emission slit 10.0 nm. The surface morphology of the films was examined by analyzing the scanning electron microscopy (SEM) images recorded using a scanning electron microscope (Model JEOL-JSM-6360, Japan), operated at 20 kV. TiO₂ film was coated with 10 nm platinum layer using Polaron scanning electron microscope sputter coating unit (Japan) before recording the SEM images. Field emission scanning electron microscope (FESEM) (Model Hitachi S4800, Japan) was employed for closer insight into the TiO₂ morphology. An X-ray photoelectron spectrum was studied by using XPS, VG Multilab 2000, Thermo VG Scientific, UK. The thickness of the resulting nanocoral TiO₂ thin films was estimated using surface profiler (Ambios XP-1) and also from FESEM cross-sections.

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