

STRUCTURAL PROPERTIES OF REINFORCED TiO₂ NANO-RODS WITH AMMONIA AND DEVELOPED BY HFCVD

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ABSTRACT

A sediment process has come to existence under condition of heated filament thermal at pressure of 1torr, for development of titanium dioxide layer formed by nano-particles and nano-rods. By controlling the time of the operation process and the concentration of titanium in solution, we were able to produce a range of structures and morphology that are applied in a wide variety of technologies from Solar cells to water refinement or are used in nano-electric and/or phonetics according to their monodimensional and congruent structures.

Keywords: Nano-Rods, TiO₂, Nanoparticles, SEM, Tetraisopropoxide

INTRODUCTION

Photochemical reactions catalyzed by semiconductors have been extensively investigated. The photogenerated electrons and holes migrate to the semiconductor surfaces where they can induce reduction and oxidation of adsorbed molecules. Titanium dioxide (TiO₂) is one of the most popular and promising materials in photocatalytic application (Ohtani *et al.*, 1997). TiO₂ is commercially available and easy to prepare in the laboratory. The crystal of TiO₂ exists in different forms, such as rutile, anatase, and brookite (Fox *et al.*, 1993). Anatase and brookite are thermodynamically metastable and can be transformed irreversibly to most stable and condense rutile phase at high temperatures (Kominami *et al.*, 1999). A number of methods have been used to prepare TiO₂ nanoparticles, such as chemical precipitation (Scolan *et al.*, 1998), microemulsion-mediated hydrothermal (Wu *et al.*, 1999), hydrothermal crystallization (Wu *et al.*, 2002), (Yang *et al.*, 2005) and (Zho *et al.*, 2005), and sol-gel (Wang *et al.*, 1999). Sol-gel is one of the most successful techniques for preparing nano-sized metallic oxide materials with high photocatalytic activities. By tailoring the chemical structure of primary precursor and controlling the processing variables, nanocrystalline products with very high level of chemical purity can be achieved. In sol-gel processes, TiO₂ is usually prepared by the reactions of hydrolysis and polycondensation of titanium alkoxides, Ti (OR)_n to form oxopolymers which are then transformed into an oxide network. To control the hydrolysis process in order to obtain homogeneous titanium oxide networks, some of the chelating reagents such as diol, carboxylic acid, or diketone compounds are added (Wu *et al.*, 2002). The condensation is usually accomplished by gelization and calcination. Condensation pulls together the constitute particles of the gel into a compact mass, thus building up the metal oxide crystal. Calcination, on the other hand, is especially important for removing the organic molecules from the final products and completing the crystallization. However, high temperature calcination results in aggregation and/or phase transformation and affects the microstructures as well as the properties of TiO₂ nanoparticles (Su *et al.*, 2004). Hydrothermal synthesis is a “soft solution chemical processing” which provides an easy route to prepare a well crystalline oxide under the moderate reaction condition, i.e. low temperature and short reaction time (Pookmanee *et al.*, 2004). Due to the potential to yield high-purity and homogeneous fine crystalline powders, hydrothermal process has gained considerable popularity in preparing ceramic samples with controlled particle size and morphology. In this study, hydrothermal process replaces calcination heat treatment was employed following the sol-gel steps to prepare the TiO₂ nanoparticles. The effect of hydrothermal temperature and duration on the microstructural evolution, crystal phase, surface area, and photocatalytic capability of the

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TiO₂ powders was investigated. To examine the photocatalytic efficiency of the synthesized TiO₂, degradation of methylene blue, a prototype molecule, in water, was studied. It has been reported that methylene blue is degraded in aqueous dispersions of TiO₂ under UV illumination (Schattka *et al.*, 2002). Based on this investigation, we examined closely the formation mechanism of TiO₂ nano-particles and nano-rods in the HFCVD process with the aid of SEM observation.

Experimental Procedure

In this work a CVD heated filament inside a chamber was used to provide nano-particles and TiO₂ rods as shown in Figure1. Filament of tungsten (W) with length of 1.5cm has been applied. Space between the filament and the substrate is 1.5cm and constitutes of a chemical compound with Ti{OCH(CH₃)₂}₄ formula that is a titanium alkoxide (IV) named titanium tetraisopropoxide and is used as the source of gas.

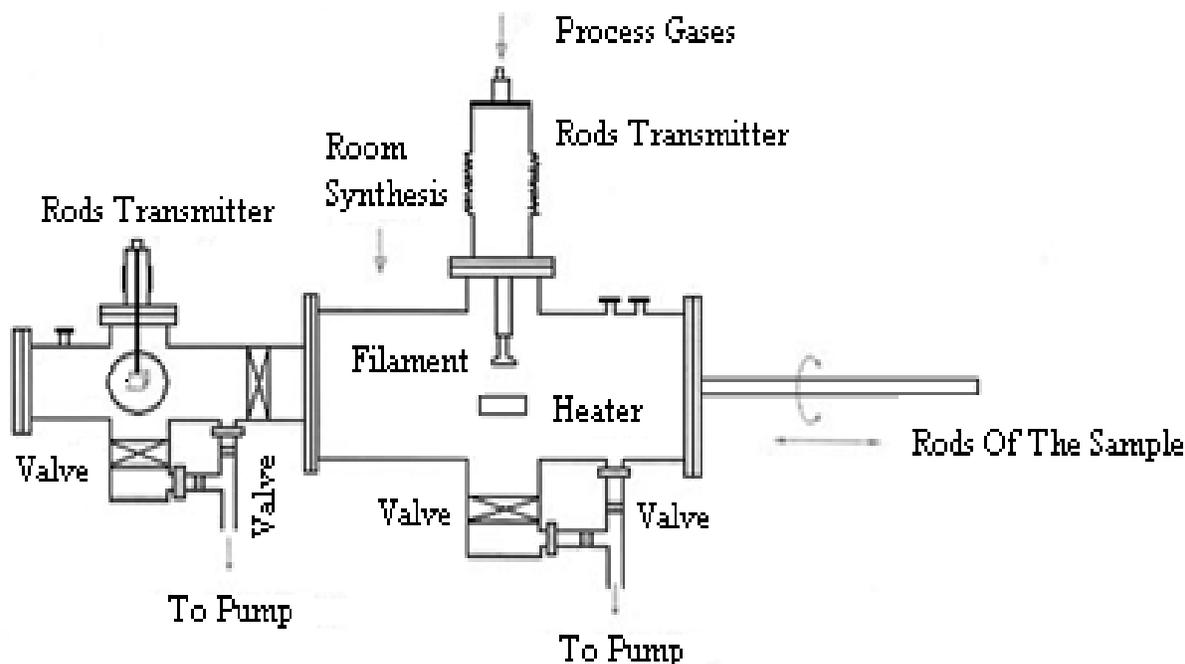


Figure 1: An HFCVD apparatus

This material is ultrasonized on silicon substrate through three stages in order to remove contaminants and then for 2.5min, Nickel catalyst is deposited on it by PECVD. Before performing the development, etch gases (NH₃, H₂) injected into the system under pressure 5torr, then before and after etching, AFM is done.

Two precursor substances TTIP, TTIP + EtOH are sequestered under thermal filament heat by the HFCVD machine. By entering vapors of TTIP + EtOH, TTIP into the chamber with argon and ammonia gases, as diluents and reducer respectively, and after lapses of times 900 s and 1800 s, development is done at temperatures of 550 °C and 650 °C degrees.

Methods and tools for data analysis following the completion of the process are for identifying the SEM, AFM, DotMapping. This low-cost Process does not require sophisticated control, and is under TTIP convection flow and vapor diffusion in chamber.

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RESULTS AND DISCUSSION

TiO₂ morphology reinforced with ammonia, and SEM image of nano-particles and nano-rods seen in figures 2 and 3 respectively. By passing the current from filament in electronic gun, some electrons are sent.

Figure 2a is the resulted image of TTIP vapors at a temperature of 550 °C and time of 900 s by entering Ar and NH₃ gases under currents of 63.2sccm and 13A and the voltage of 5 V and figure 2b obtained from the combination of EtOH + TTIP vapors at 550 °C and 900s by entering Ar and NH₃ gases under currents of 63.2sccm and 13.3A and the voltage of 5V. Comparing the two figures *a* and *b*, we conclude that the surfaces of both samples are granular while the grain at surface of sample *a* is greater.

In figures 3a and 3b, SEM is observed at temperature of 650 °C and time of 1800s which under flow of Ar, NH₃ gases 63.2 sccm, Voltage 5V, figure 3a contains TTIP vapors, the length of the nano-rods is 714.70nm and their diameter is 420.42nm, the current is 12.3A and the figure 3b contains EtOH + TTIP vapors, the current of 12A, and the length of 15.98 μm and diameter of 0.73 μm.

EDX analysis shows high density development area. In figure 4a which is containing TTIP vapors, it has been observed that titanium and carbon and also a signal of nickel there exist. In figure 4b which contains vapors of EtOH + TTIP, a reduced signal of titanium is shown and also there is a signal of Ni,C. In the spectra of EDX, the existence of nickel with Ti,O has been shown. In table 1, the weight percentage of the Ti,C elements is shown.

Due to existence EtOH, the weight percentage of carbon in solution EtOH + TTIP, is 18.95% more. The figures 5a and 5b containing TTIP, TTIP + EtOH vapors respectively which have been shown by DotMapping analysis. On the surface of nano-rods, scattering of titanium element is observed with red spots that the distribution of Ti in the figure 5a containing TTIP vapors. Due to the high purity of titanium in solution, TTIP is greater than 5b.

The Effect of TTIP Concentration

A solution of TTIP, TTIP + EtOH is applied by filament heating in order to be observed the concentration of titanium in the morphology. Characteristics of producing coatings are determined by SEM. Figures 2a and 2b at times of 900 s and temperature of 550 °C, the surface is granular. In a sample containing TTIP vapors, the particle size is larger. According to Figures 4a and 4b, it is observed that the concentration of titanium in the sample 4a is higher, while the concentration of C is lower, thus the concentration of Ti in TTIP of primary solution has a significant effect on the morphology of deposited nano-rods. As the increase of intended concentration, the density of nano-rods is intensively increased.

The Effect of Time

4 different coatings of composed solutions of TTIP, TTIP + EtOH, have been produced respectively, in time and temperature of 550 °C and 650 °C, 900 s and 1800 s. From 900 s to 1800 s, these nanostructures are alternately developed and their length increase as time increases. At 900 s, nano-particles cling together and form a dense network. After 1800 s, and the morphology of nano-particles changed, an increase is observed in length, and is turned into nano-rods.

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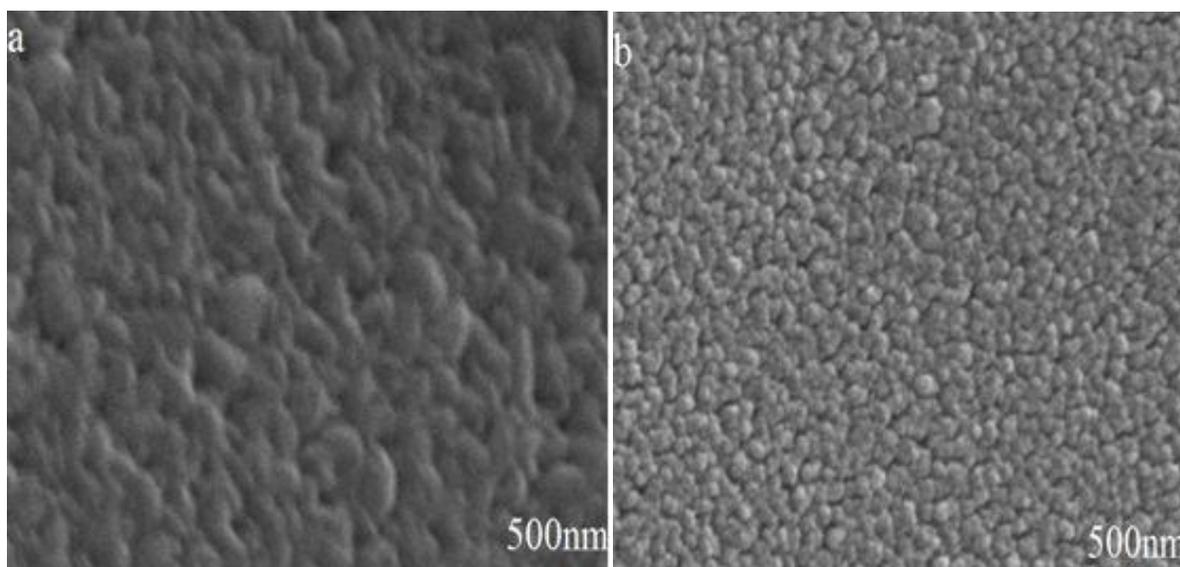


Figure 2: SEM micrograph of TiO₂ nano particles deposited with a) TTIP b) TTIP+EtOH

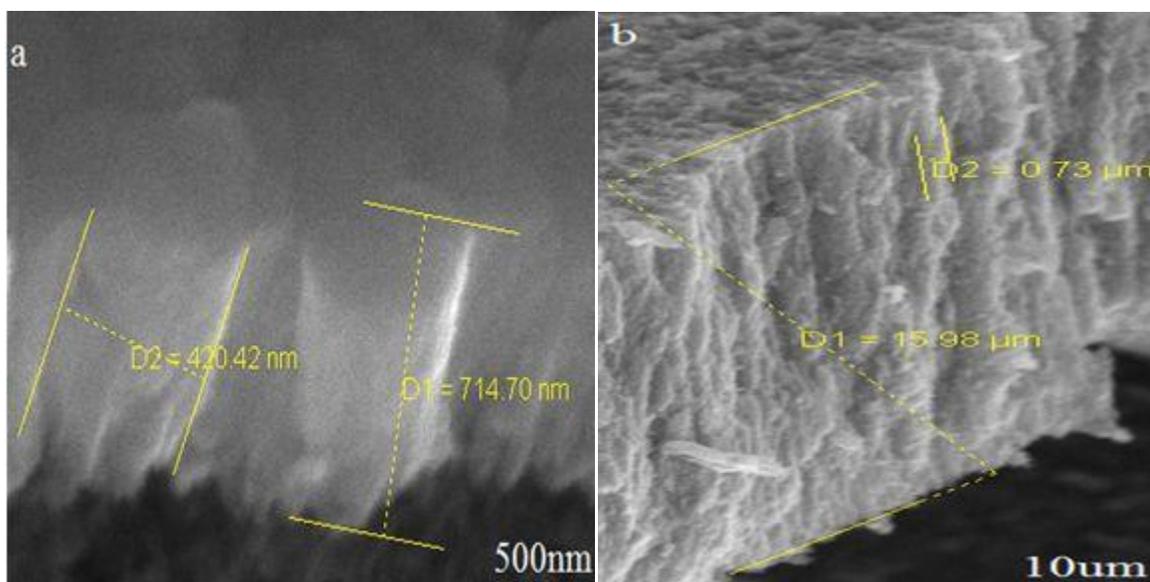


Figure 3: SEM micrograph of TiO₂ nano-rods deposited with a) TTIP b) TTIP+EtOH

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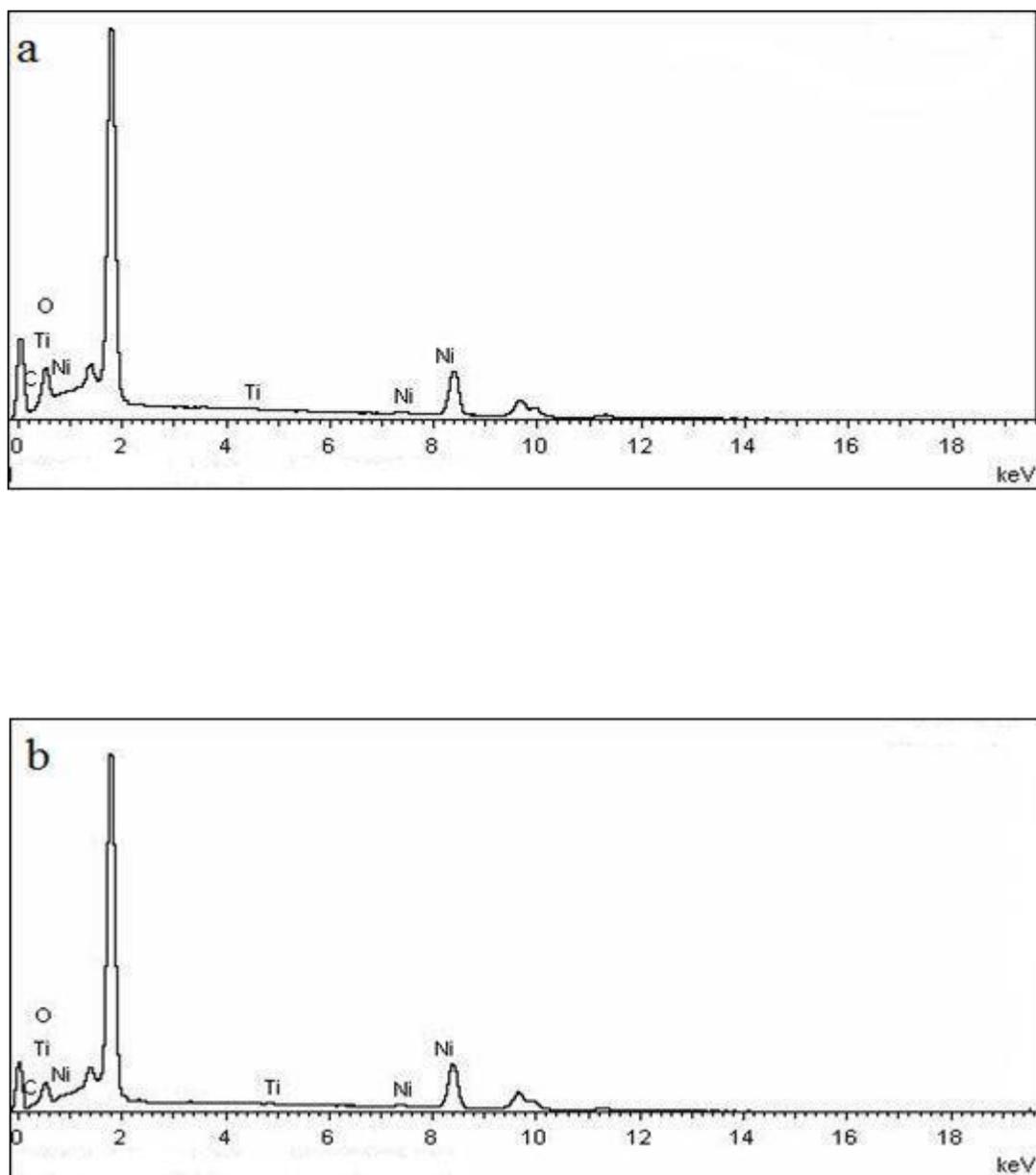


Figure 4: EDX analysis of TiO₂ nano-rods deposited with a) TTIP b) TTIP+EtOH

Table 1: table EDX analysis of TiO₂ nano- rods deposited with TTIP and TTIP+EtOH

Element	Weight% With TTIP	Weight% With TTIP+EtOH
C	6.19	25.14
Ti	1.64	0.06

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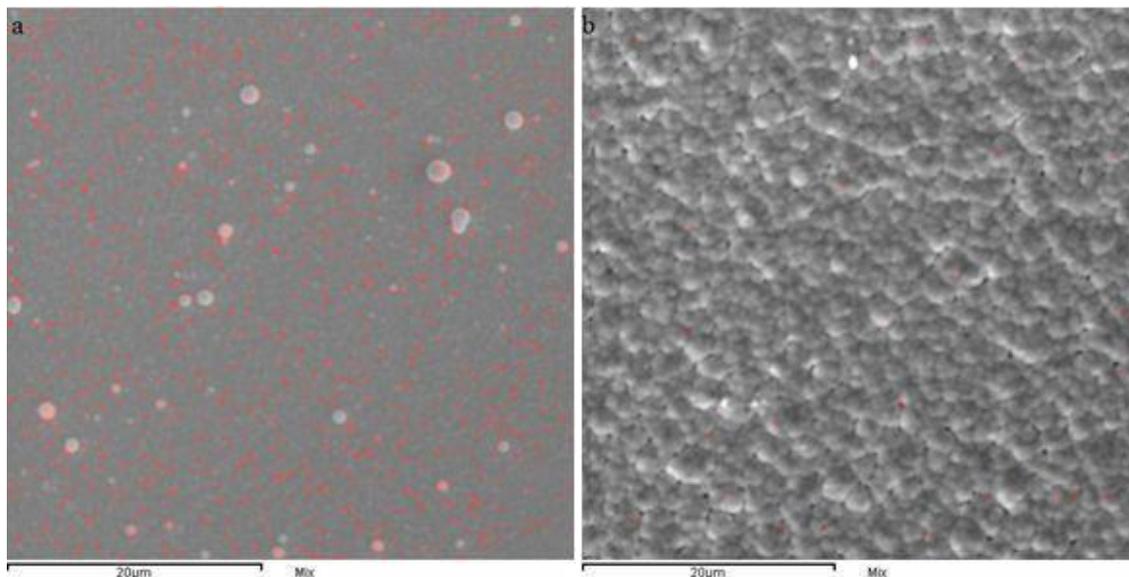


Figure 5: Dot Mapping analysis of TiO₂ nano-rods deposited with a) TTIP b) TTIP+EtOH

Conclusions

Sediment process under hot filament temperature is described in this paper and is a flexible method for combining titanium coatings with nano-particle and nano-rod structures. Ti concentration and distribution in the nano-rods developed with TTIP solution, is more. The length of nano-rods in TTIP + EtOH solution was longer and their diameters are less. Sedimentation time (900s-1800s) to produce these nano-particle and nano-rod coatings is much lower than the time required by other methods. This rapid kinetic precipitation, performing process at pressure of 1torr, and direct production of nano-particle and nano-rod coatings have made this method very attractive for future industrial applications.

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