Effect of Titania Colloid Solution Concentration on Hydrophobicity of Well-Aligned TiO_2 Nanorods Synthesized via Hydrothermal Method

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ABSTRACT

Among one dimensional nanomaterials, TiO_2 nanorods have found important applications in various industries due to optical, photocatalyst and self-cleaning properties. In this research, at first TiO_2 nanorods were synthesized on a glass substrate by hydrothermal method. Then a thin film of TiO_2 particles was dip coated (as seed layer) on the substrate. After that, hydrothermal synthesis of TiO_2 nanorods with 0.05 and 0.1 mol concentrations was carried out on the seed layer. Morphology and microstructure of the seed layer and nanorods were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) and atomic force microscopy (AFM). Hydrophobicity of nanorods was studied by contact angle instrument. Results revealed that nanorods synthesized on the glass substrate without seed layer are not aligned at all and have the average diameter of 120 nm, whereas nanorods synthesized on the seed layer are well-aligned with 30nm average diameter. The result obtained from contact angle instrument showed that nanorods synthesized with 0.05mol concentration have larger contact angle (157^o), compared to those synthesized with 0.1mol concentration which have 115^o contact angle.

1. Introduction

Recently, one dimensional (1D) semiconductor structures such as nanorods and nanowires have attracted much attention of the researchers. Among 1D nanomaterials, due to their optical, electric and catalyst properties, TiO_2 nanorods have found important applications in various industries, for example as gas sensors, dye-sensitized solar cells (DSSC) and litium batteries as well as in water treatment and water decomposition for hydrogen production [1-6]. Controlling the wettability of the solid surface is very crucial for many industrial applications and biological processes such as prevention of sticking of snowflakes on antennas, self cleaning glasses, and so on. Hydrophobicity on a surface is obtained by decrease of the effective contact area between the surface and water. Solid surface wettability depends on two factors: surface energy and surface roughness, which can be achieved by coating the surface with low surface energy materials and developing a

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regular structure [7]. Up to now, few studies have been carried out for synthesis of TiO_2 nanorods via electrochemical deposition, chemical vapor deposition (CVD) and hydrothermal method. Electrochemical and chemical vapor deposition methods consist of using metal catalysts, high temperature and vacuum technique, which render the process to be expensive and complex. In comparison, one of the best ways for synthesis of TiO_2 nanorods is hydrothermal method, because of the low temperature of the process, rapid reaction and mass production. Superhydrophobic surfaces with contact angle larger than 150° and contact angle hysteresis smaller than 10° have been the target of interest for many researchers. A large number of reports have demonstrated that roughness along with low surface energy is necessary for obtaining superhydrophobicity. On the other hand, some reports stated that without modification by low surface energy materials, we can obtain superhydrophobicity on a hydrophilic substrate only by roughening [8-11]. Even though many researches have been carried out on synthesis of TiO_2 nanorods, investigating the synthesis parameters which affect hydrophobicity is still a serious challenge for the researchers. In the present research, the effect of concentration on nanorods and hence their hydrophobicity has been studied.

2. Experimental

2. 1. Materials

All chemical materials were provided with maximum purity from Merck Company (Germany). All aqueous solutions were prepared by using deionized water. Glass slides used as substrate were cleaned firstly by acetone and ethanol, then put in an ultrasonic and finally washed by deionized water.

2. 2. Preparation of colloid solution for seed layer coating

At first, 1mol titanium isopropoxide was dissolved in a mixture of 3mol glacial acetic acid and 2mol acetylacetone and stirred for 1 hour to obtain the precursor solution. In the second stage, a solution of 0.5 mol of double-distilled water, 2.2 mol ethylene glycol and 0.54 mol ethanol was added to the mixture and stirred for 15 minutes. The solution was aged at room temperature for 24 hours to yield a stable and homogeneous colloid solution to be used for coating. The obtained solution was coated on the glass substrate by dipping at the speed of 10 centimeters per second. The coated substrate was air dried and then annealed for 1 hour at 500ºC.

2. 3. Hydrothermal growth of TiO_2 nanorods

In order to obtain the precursor solution, at first, 0.05 mol (sample B) and 0.1 mol (sample C) titanium trichloride was stirred in concentrated sodium chloride solution for 10 minutes. The solution was then transferred to a Teflon container and the coated substrate was dipped into the solution, then hydrothermal growth was carried out in an autoclave at 160ºC for 3 hours. Following the synthesis procedure, the autoclave was cooled down at room temperature, then the substrate was taken out and washed with deionized water and cooled down.

2. 4. Characterization

The crystal structure of the nanorods was characterized by X-ray diffraction (XRD, Philips). Morphology of the seed layer and nanorods was analyzed by scanning electron microscopy (SEM, Leo). Roughness and topography of the coating surface was studied by atomic force microscopy (AFM). Water contact angle (4ml deionized water) on nanorods was measured by contact angle instrument (CA, PLUS 15 OCA) at room temperature.

3. Results and Discussion

3. 1. Morphology and microstructure of TiO_2 nanorods

Improving the substrate affects the morphology and alignment of TiO_2 nanorods to a great extent.

Fig 1 shows the SEM image of TiO_2 nanorods grown on the glass substrate without the seed layer (sample A). As can be seen, the nanorods have grown in a completely non-aligned manner, with low density and without any specific orientation. Moreover, their diameters are large, with an average of about 150-300nm. The image shows that due to the absence of nucleation

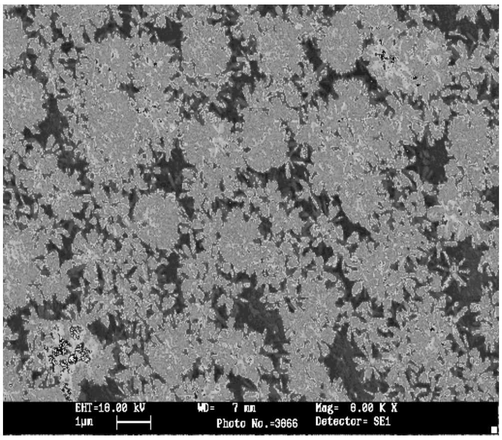

Fig. 1. SEM image of TiO_2 nanorods on the substrate without the seed layer

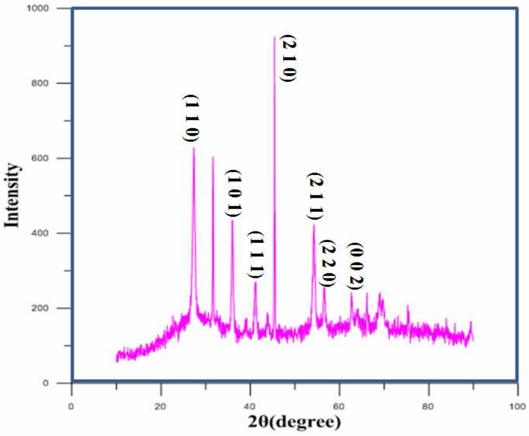

Fig. 2. X-ray diffraction pattern of TiO_2 nanorods on the substrate without seed layer

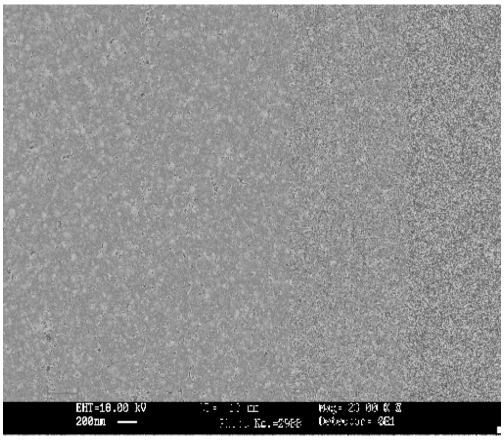

Fig. 3. SEM image of the seed layer for TiO_2 nanoparticles which has been annealed at 500ºC

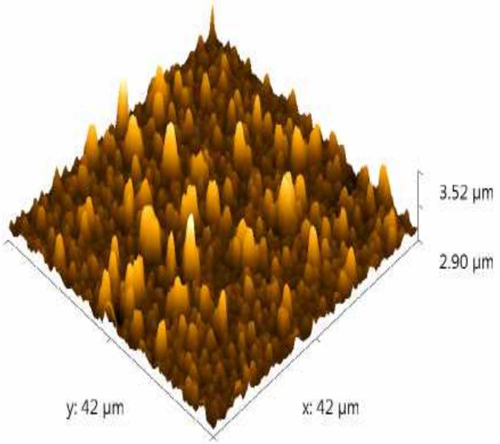

Fig. 4. AFM image of the seed layer for TiO_2 nanoparticles

areas on the glass substrate, the density of nanorods is low and the growth has occurred quite randomly. Fig 2 shows the X-ray diffraction pattern of TiO_2 nanorods which have been synthesized on the glass substrate without seed layer. The peak intensity and position of XRD spectrum is related to rutile phase; due to non-alignment of nanorods the diffraction has occurred in different planes, and because of the low density of nanorods, diffraction has taken place with low and different intensities.

Fig 3 shows the SEM image of the glass substrate coated by TiO_2 nanoparticles which has been heat treated at 500ºC. The coating is completely even and without any cracks. The size of the particles is about 50nm.

Fig 4 shows the seed layer annealed at 500ºC. The growth of nanorods has occurred in columnar and uniform manner.

SEM and AFM images in fig 3 and 4 show that the seed layer has a uniform surface and can play the role of a template for growth of well-aligned TiO_2 nanorods.

Fig 5 shows SEM images of well-aligned TiO_2 nanorods with 0.05mol concentration synthesized on the seed layer by hydrothermal method (sample B).

The nanorods have appropriate orientation and a fairly good alignment and have grown with a uniform distribution of density on the seed layer. The average diameter of nanorods is about 25nm and their average length is in the range of 1 micrometer.

Nucleation and the speed of the nanorods growth are highly dependent on the concentration the precursor solution. Fig 6 shows the SEM images of well-aligned TiO_2 nanorods with 0.1mol concentration (sample C). The figures

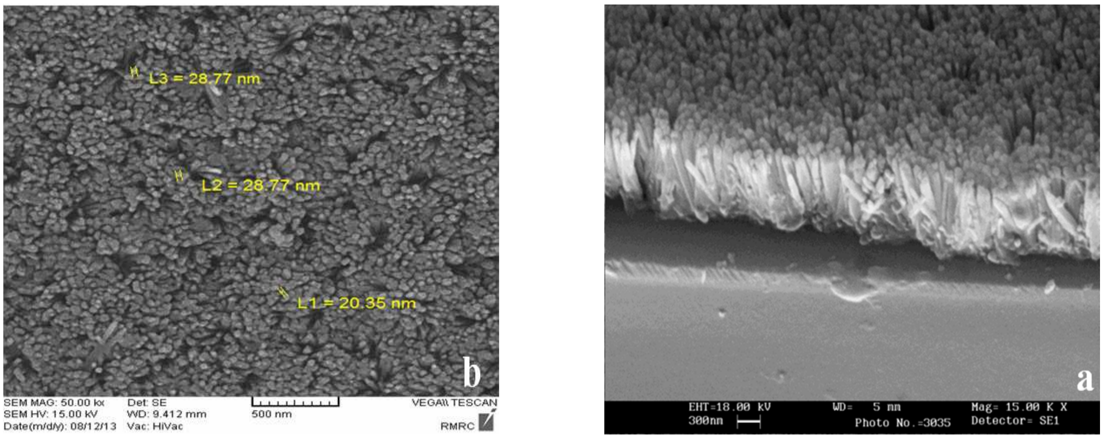

Fig. 5. SEM images of TiO_2nanorods with 0.05 mol concentration: (a) cross view, (b) top view

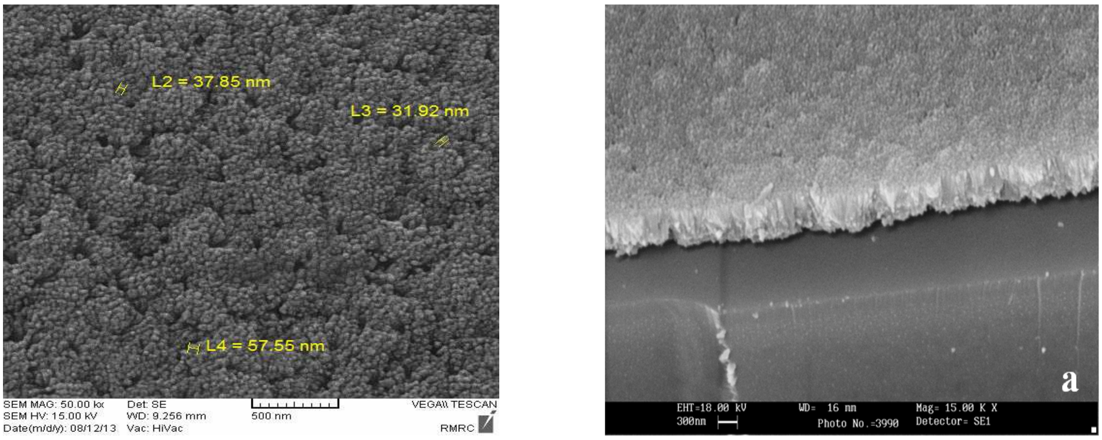

Fig. 6. SEM images of TiO_2 nanorods with 0.1 mol concentration: (a) cross view, (b) top view

show that with increase of the precursor concentration from 0.05 to 0.1mol, the growth density of nanorods has dramatically increased, so that nanorods are entirely interconnected and dense. With increase of concentration, the average diameter of nanorods has reached to 45nm. These results reveal that applying a precursor with high concentration can enhance the speed of nucleation of nanorods on the seed layer and therefore nanorods with very high density and large diameter can be synthesized.

Fig 7 shows the X-ray diffraction pattern of TiO_2 nanorods at 0.05 and 0.1mol concentrations. Diffraction has mainly occurred in (002) and (101) planes which are related to rutile phase. Nanorods synthesized with 0.1mol concentration show greater peak intensity compared to those synthesized with 0.05mol concentration. It demonstrates high density of nanorods at 0.1mol concentration and is in agreement with SEM images in fig 5 and 6. Also, in both concentrations, the number of diffractions in different planes is much lower, compared to the diffractions for the nanorods grown on the substrate without seed layer, which is due to excellent alignment of nanorods in the presence of seed layer. Moreover, because of high growth density of nanorods in both concentrations, diffraction intensity is also much higher.

3. 2. Hydrophobicity of well-aligned TiO_2 nanorods

Wettability experiments were carried out on a sample coated by TiO_2 seed layer annealed at 500ºC as well as two samples of TiO_2 nanorods with 0.05 and 0.1mol concentrations (samples B and C) which had been grown in a well-aligned manner on the seed layer. Hydrophobicity images of the three samples can be observed in fig 8, 9 and 10. As can be seen, wettability angle on the

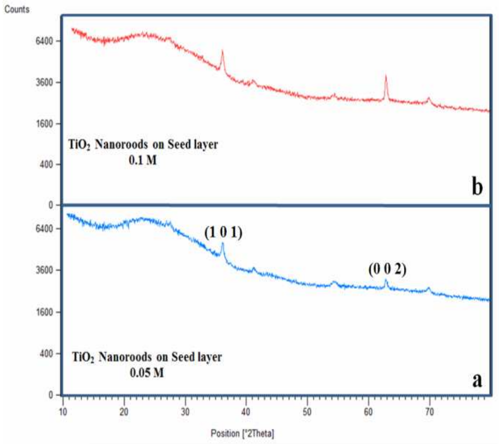

Fig. 7. X-ray diffraction pattern of well-aligned TiO_2 nanorods at (a) 0.05 and (b) 0.1 mol concentrations

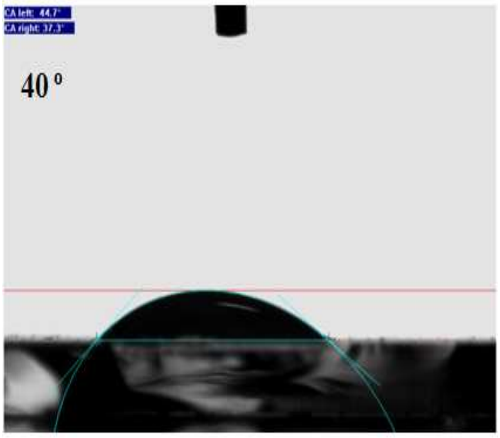

Fig. 8. Water drop on annealed TiO_2 seed layer (sample A)

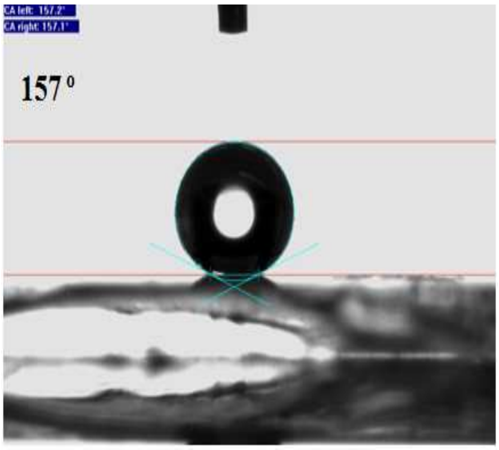

Fig. 9. Water drop on top of well-aligned TiO_2 nanorods with 0.05mol concentration (sample B)

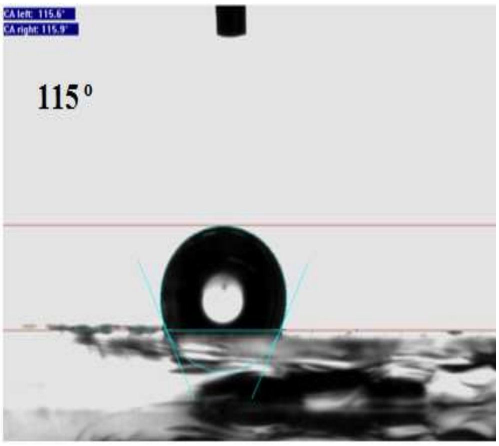

Fig. 10. Water drop on top of well-aligned TiO_2 nanorods with 0.1mol concentration (sample C)

seed layer is 40° which shows hydrophilicity of the surface. With growth of well-aligned TiO_2 nanorods on the seed layer, wettability angle on these nanorods reaches from 40° to 157° for 0.05 mol concentration (sample B) and 115° for 0.1mol concentration (sample C). Based on these results, it can be concluded that with growth of nanorods, due to increase of surface roughness and decrease of surface energy, the hydrophilic surface has changed into a hydrophobic one. The relationship between wettability behavior of well-aligned TiO_2 nanorods and 0.05 and 0.1 mol concentrations can be explained by Cassie equation [12]. According to Cassie equation, water drop is placed on a composite of the air and nanorod and the air trapped between nanorods prevents penetration of water into porosities of the surface.

$$\mathrm{Cos}\grave{e}\chi = \varphi\sigma(1+\mathrm{Cos}\grave{e}\sigma)\,1 \qquad [1]$$

Where θ_c is contact angle on top of nanorods according to Cassie model, $f_s$is fraction of nanorods in contact with water droplet and θ_s is contact angle on smooth, single-crystalline TiO_2 surface, which is 40° in this research. The only variable parameter in Cassie equation is f_s, or fraction of nanorods in contact with water droplet. F_s is dependent on diameter and density of nanorods. On the other hand, as it was mentioned in 3.1., the essential factor in diameter and density of nanorods is concentration. In 0.05mol concentration, the diameter of well-aligned TiO_2 nanorods is 25nm and in 0.1mol the diameter is 45nm, which means the increase of nanorods diameter with increase of concentration. Also, with increase of concentration, density of nanorods has dramatically increased and morphology consists of nanorods which are stuck together with very small distances between them. In such a morphology, the mechanism of air trapping which is the principal condition for Cassie model does not occur; therefore, it causes the conspicuous increase of f_s in Cassie equation and hence decrease of contact angle, so that according to Cassie's model the contact angle reaches from 157° (for sample B) to 115° for sample C.

4. Conclusions

1. By using sol-gel method, a thin film of TiO_2 was coated on glass substrate as seed layer with anataz phase and 50nm grain size.
2. TiO_2 nanorods with rutile phase were synthesized on the substrate via hydrothermal method. Results revealed that seed layer plays a fundamental role in controlling morphology and diameter of nanorods. In the absence of seed layer, non-aligned nanorods with random orientation, low density and average diameter of 100nm are formed on the substrate. When the substrate is coated with seed layer, well-aligned nanorods with high density and average diameter of 25nm will grow on the seed layer.
3. Nanorods synthesized with 0.1mol concentration have larger diameter (40nm) and much higher density compared to nanorods synthesized with 0.05mol concentration, which have diameters of 25nm.
4. The result obtained from contact angle instrument showed that nanorods synthesized with 0.05mol concentration have larger contact angle (157°) compared to those synthesized with 0.1mol concentration, with contact angle of 115°.

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