Morphology and structural properties of titanium dioxide nanorods array prepared via hydrothermal method with various amount of precursor

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ABSTRACT: Titanium dioxide rutile nanorods array were fabricated on fluorine-doped tin oxide (FTO) substrate with different volumes of precursor. Prior to that, preliminary research has been done on FTO substrate from two different companies to prevent a peel-off problem of the nanorods. Atomic force microscopy confirmed higher surface roughness on the FTO from Sigma Aldrich when compared to the FTO from SPD Laboratory. Rutile phase of the fabricated nanorods were confirmed with X-ray diffraction analysis, while morphology of the nanorods were analyzed by using FESEM analysis which shows increased diameter and thickness with increasing volume of precursor.

Keywords: *Titanium dioxide; Rutile; Hydrothermal*

1. INTRODUCTION

Titanium dioxide (TiO_2) is one of the most consumed nano-material in the world along with carbon and silver [1]. Being a material with outstanding properties such as high stability and chemical properties, great accessibility and low cost, TiO_2 is used in wide variety of applications majorly photocatalysis, photovoltaics, and cosmetics. TiO_2-based devices usually shows a great performance in nanometre scale. To accommodate this, numerous morphologies of TiO_2 were fabricated such as nanosheets, nanoparticles, nanoflowers, and nanorods [2]. Among them, nanorods have an advantage in exhibiting excellent electron transport due to its one-dimensional structure. This helps in minimizing the recombination of the electron and providing a direct pathway from the substrate. Rajaei et. al. studied the different morphologies for dye-sensitized solar cells applications. The three morphologies studied were nanoparticles, mesoporous TiO_2 nanorods, and solid TiO_2 nanorods. Power efficiency of the DSSCs showed that solid TiO_2 nanorods gave a higher efficiency of 8.8% [3].

Transparent conducting oxide (TCO) is an electrically conductive material that has low absorption of light. FTO has excellent electrical conductivity and optical properties, with high heat stability and chemical inertness. One of the important factors to good use of FTO films was its light-trapping ability, and for that, surface roughness is varied. To fabricate nanorods, adequate roughness was needed to prevent a peel-off from the substrate. It is also to ensure that the growth of the TiO_2 nanorods were of a high quality nanorods.

In this study, TiO_2 nanorods were fabricated on FTO substrates from Sigma Aldrich with different volumes of precursor using one-step hydrothermal reaction method.

2. METHODOLOGY

30 mL of concentrated hydrochloric acid (HCl) (Wako Chemical, 100% purity) was dissolved in 30 mL of DI water and vigorously stirred on the magnetic stirrer for 10 minutes. Then, 1mL of titanium tetrabutoxide (TBOT) (Wako Chemical) was added dropwise using a capillary tube. After stirring for 15 minutes, the solution was poured into a steel-made autoclave with Teflon-made liner for hydrothermal reaction. The hydrothermal reaction was performed at 150°C for 16 hours in the electric oven.

The roughness of the FTO substrate were characterized using atomic force microscopy (AFM). Field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7601F) was used to analyze the TiO_2 nanorods morphology, and the structural characterization of the samples was determined by using X-ray diffraction spectroscopy (XRD) with diffraction angle fixed at 0.5° (thin-layer XRD, Rigaku RINT Ultima III)

3. RESULTS AND DISCUSSION

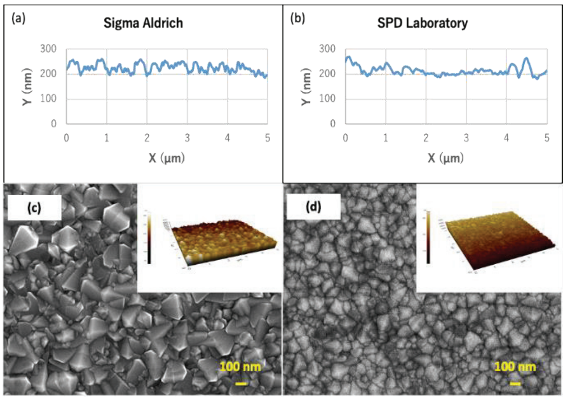
3.1 Comparison of FTO substrates from different manufacturers

Figure 1 shows AFM images of the FTO substrates for (a) Sigma Aldrich and (b) SPD laboratory. From these images, FTO substrate from Sigma Aldrich shows the presence of abundant high peaks as corresponded to FESEM images in Figure 1 (c) while SPD laboratory's FTO substrate gives only a few high peaks, leading to a smaller roughness. Table 1 shows the R_a values of FTO substrate from both Sigma Aldrich and SPD Laboratory. Sigma Aldrich's FTO substrate shows a higher R_a value at 18.42, compared to SPD Laboratory's at 15.78.

Table 1: Surface roughness, R_a of FTO substrates from Sigma Aldrich and SPD Laboratory

FTO	**R_a(nm)**

Sigma Aldrich	18.42
SPD Laboratory	15.78



3.2 *Effect of different amounts of precursor on the fabrication of TiO_2 nanorods*

Figure 2 shows the XRD pattern of TiO_2 nanorods prepared with different amounts of precursor TBOT. The peaks correspond to JCPDS 21-1276 of rutile-phased TiO_2. With 0.50 mL of TBOT precursor, FTO peaks at 37.7° shows the highest intensity. As the amounts of precursor increased, FTO peaks started to decrease. At 0.50 mL, only one rutile phase peak emerged for (101) plane. When the precursor amount increased to 0.75, 1.00 and 1.50 mL, rutile phase peaks for (002) plane started to be visible and its intensity continued to increase with increasing TBOT precursor. This shows that with higher amount of TBOT precursor used, the TiO_2 nanorods become more aligned.

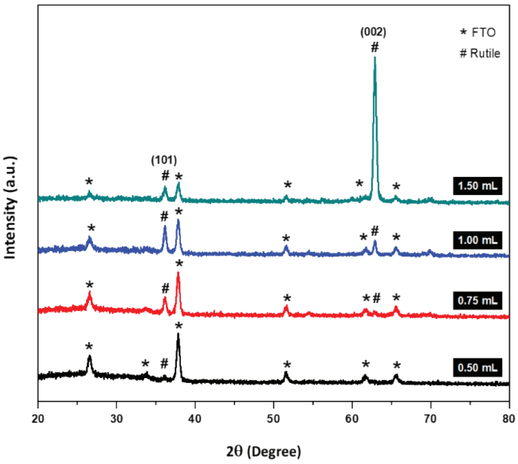
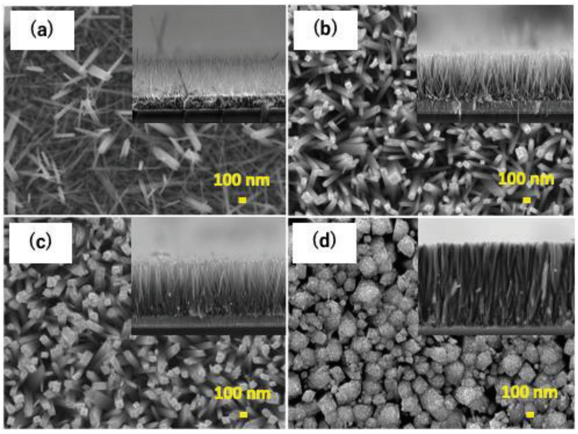


Figure 3 (a-d) shows the morphological images of TiO_2 nanorods fabricated with 0.25 to 1.50 mL of TBOT, respectively. Figure 3 (a) shows TiO_2 nanorods with irregular diameter fabricated using 0.25 mL of TBOT. When the amount of precursor increased to 0.50 mL, the diameter and thickness of the rods also increased as shown in Figure 3 (b). The same tendencies occurred when the volume of the precursor further increased to 1.00 and 1.50 mL, as shown in Figure 3 (c). Low precursor concentration resulted in non-aligned TiO_2 nanorods while higher concentration resulted in well-aligned rods. With low nucleation density, the nanorods can continue growing to a longer length at any angle without the possibility of running into each other. When nucleation density is high, nanorods that grow to the substrate surface normal have a high possibility of running into each other, thus stopping the non-vertical growth [4].



4. CONCLUSION

Early study on roughness of the FTO substrates shows that Sigma Aldrich's FTO has higher roughness, hence it is more suitable for the growth of TiO_2 nanorods. TiO_2 nanorods were optimized by varying the amounts of the precursor used with temperature and time fixed to 150°C and 16 hours. XRD spectroscopy shows that the TiO_2 nanorods were of pure rutile phase. Shown from FESEM images, diameter and thickness of the nanorods increased with increasing amount of precursor. The optimum amount of precursor was 1.00 mL of TBOT.

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