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Rapid growth of highly ordered TiO_2 nanotube arrays assisted by field supporting effect of weak organic acids

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Abstract: In the present work, Titania (TiO_2) nanotubes are synthesized through electrochemical anodization of Ti foils in ethylene glycol electrolyte containing oxalic acid or malonic acid as agents of field supporting effect. The additional constituent in the anodizing electrolyte is found to have strong control over the growth of the TiO_2 nanotubes. A comparison of TiO_2 nanotubes formed with and without the presence of weak organic acids revealed higher growth rate and better morphology of the TiO_2 nanotubes samples grown in the presence of weak organic acids. The structural, morphological and compositional analyses were made using XRD, FE-SEM and EDX respectively. The improved properties of the 1D TiO_2 nanotubes obtained through the change in anodizing electrolyte chemistry yield promising results with large scope in sensing, solar cell and photocatalytic applications.
Keywords: titania; nanotubes; anodization; morphology; organic acids.

Introduction and Experimental:

Titania (TiO_2) in nanometer scale has been reported with different morphologies; for instance nanospheres, nanoparticles, nanorods, nanowires and nanotubes (NTs). Among the mentioned morphologies, NTs of TiO_2 has attracted the interest of several researchers around the world due to its large surface-to-volume ratio, optical characteristics and electrical properties [1]. These abilities make TiO_2 NTs a potential material in various application fields like sensing, solar cell and photocatalysis [2]. Moreover, the fabrication of TiO_2 NTs employing electrochemical anodization has made significant contribution to the increasing attention with its ability to precisely control the NTs architecture [2-4]. In the present work, investigation on the growth of TiO_2 NTs is carried out by altering the electrolyte chemistry by separately adding oxalic or malonic acid to the ethylene glycol based electrolyte solution. Compared to that of electrolyte without these weak organic acids, excellent increase in the length of NTs is observed with the presence of these additional electrolyte constituents.

Highly ordered TiO_2 NTs were synthesized via potentiostatic electrochemical anodization of Ti foil. In a typical procedure, a two electrode system was utilized and the reactions were conducted at 30 V for a constant period of 1 h at room temperature. Degreased Ti foil and Pt mesh were used as anode and cathode respectively. The main constituent of the electrolyte was ethylene glycol along with 0.3 wt% NH_4F and 2 vol% DI H_2O. To this combination 1 wt% of additives, either oxalic or malonic acid was included to study their effect in the growth of the NTs. The TiO_2 NTs samples obtained from these electrolyte combinations were labeled as OT and MT, respectively. For comparison, one of the samples was formed without the addition of these weak organic acids and thus achieved TiO_2 NTs was named ET. The as-obtained samples were annealed before characterization. The crystallinity and structure of the formed TiO_2 NTs were analyzed by Rigaku Smart Lab X-ray diffractometer (XRD) with CuKα (λ = 1.54060 Å) radiation. The morphological and elemental characterization was investigated with Carl Zeiss Supra 55 Field Emission Scanning Electron Microscope (FESEM) attached with Energy Dispersive X-ray Analysis (EDX).

Results and Discussion:

XRD pattern of the as-anodized TiO_2 NTs samples with oxalic acid (OT), malonic acid (MT) and bare (ET) are shown in Figure 1a, b and c, respectively. The annealed samples display distinct peaks with planes (101) (004) (200) (211) and (204) confirming the formation of anatase phase in all the three samples, indexed to a standard JCPDS data (21-1272). Additional peaks (103) (112) (105) are from the Ti foil beneath the TiO_2 NTs indexed to a JCPDS card (44-1294). The results are in line with the reported data [5]. Although the patterns reveal good crystalline nature of all the samples, MT (Figure 1b) seems to demonstrate better intensity of peaks compared to its counterpart OT (Figure 1a). However, the sample ET showed much less intensity of the peaks formed.

Figure 2a, b and c illustrates the cross-sectional TiO_2 NTs FESEM images corresponding to the samples OT, MT and ET. Figure 2c is found to possess poor growth of TiO_2 NTs with 1.9 μm/h. On the other hand, efficient growth of the TiO_2 NTs was seen in the samples OT and MT (Figure 1a and b). Both the samples are observed to possess higher growth rate, however MT possessed better growth in length with 12.8 μm/h than OT with 6.9 μm/h. The rapid growth may be attributed to the field supporting effect and the good oxidizing capacity of the weak organic acids. Another study earlier with lactic acid is reported to be the fastest growth in any combination of electrolyte [6]. The report supports the fact related to the present study, that these additional electrolyte components play an important role in the formation and growth of the highly ordered TiO_2 NTs array. The top surface morphology of the samples OT, MT and ET are depicted in Figure 3a, b and c, respectively. It is clear that the accelerate growth in OT and MT has not affected the tubular morphology of the TiO_2 NTs. The images of OT and MT further reveal that the architecture comprising of wall thickness and pore size is uniform when compared to ET and earlier reports [3, 7]. Figure 4 portrays the EDX spectra of the samples OT (Figure 4a) and MT (Figure 4b) are seen to possess little amount of carbon as impurity may be due to the use of weak organic acids in the electrolyte [8]. In contrast, ET is found to be free of carbon impurities.

In summary, the present study confirms the rapid growth of TiO_2 NTs in the samples OT and MT with the presence of oxalic acid and malonic acid, respectively. The faster growth, in turn is found not to affect the surface morphology of the TiO_2 NTs. Good crystallinity with slarge intensity and small amount of carbon impurity were observed in the samples OT and MT. However, ET is observed to have slower growth rate, nevertheless without the presence of carbon impurity. The findings strongly suggest that room for further improvement is available in the production of higher quality TiO_2 NTs.

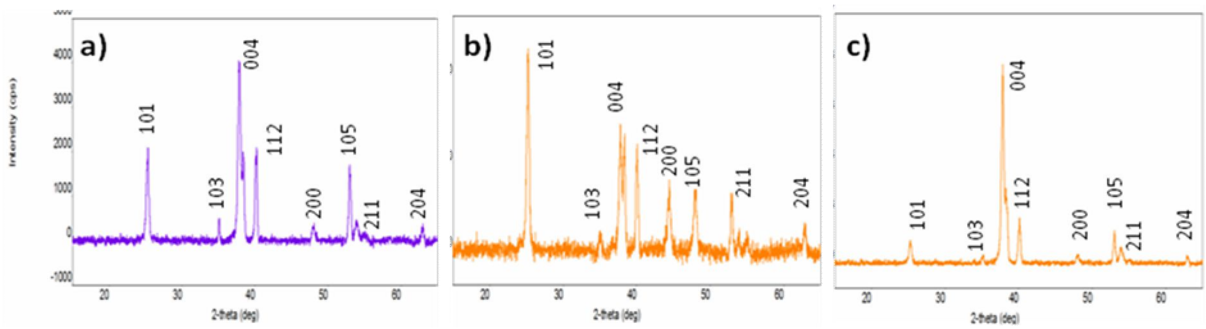

Figure 1 XRD patterns of the TiO_2 NTs a) OT b) MT and c) ET

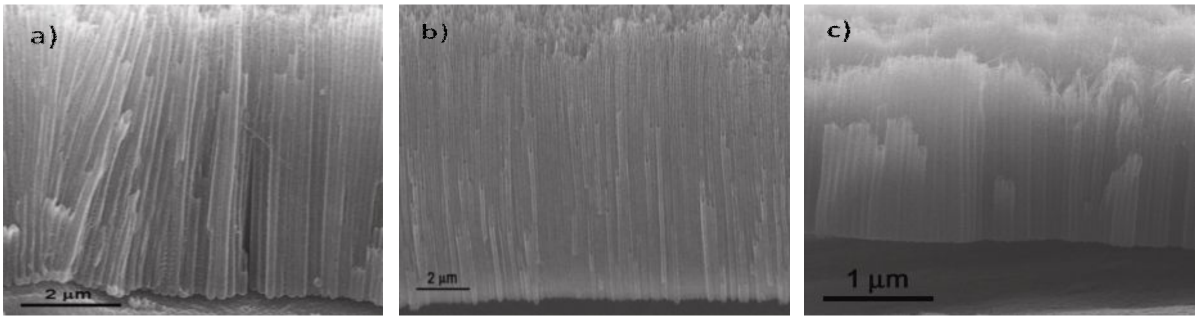

Figure 2 Lateral view of TiO_2 NTs grown a) OT, b) MT and c) ET

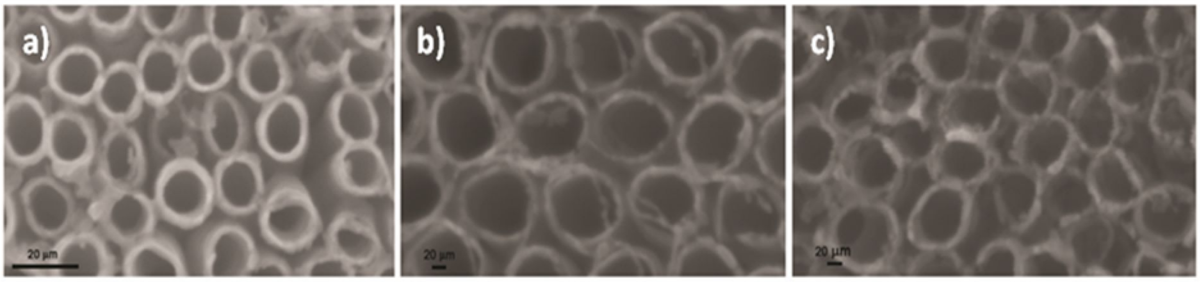

Figure 3 FESEM pictures of TiO_2 NTs in top-view. a) OT, b) MT and c) ET

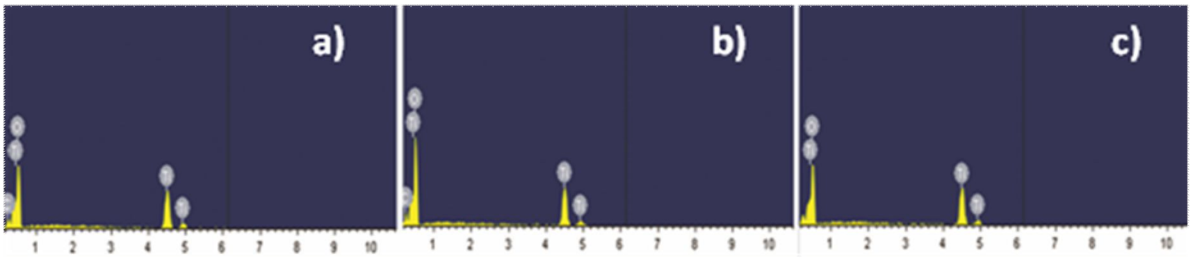

Figure 4 EDX spectra of a) OT, b) MT and c) ET

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