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Effect of High Temperature on Titanium Nanotube Arrays by Electrochemical Method

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Abstract

In recent years, elevated Titanium nanotube arrays were prepared influorine free based material. The effects of voltageand time, chemical composition and pH of the electrolyte on anodization process were reported. By using Ethylene glycol withNH_4Fsolutionanddeionizedwatert,elevated nanotubeof length430nmresulted at after1.5hranodization time at 65V voltage after 1.5hr. After annealing at 450'C, X-RD method was used for elemental analysis of the sample and SEM was done to study the structural morphology of the anodized sample.

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Keywords:*TitaniumNanotubeArrays,ElectrochemicalMethodetc.*

1. Introduction

Inthemostrecentdecade,low-dimensionalnanoauxiliarymaterialshavepulledinexpandinginvestigative and innovative consideration because oftheirphysicalpropertiesandtheirpotentialapplications(FujishimaandHonda,1972).Dimensionalityhasapivotalparti ndecidingthepropertiesandexecutionofnanomaterials.Subsequently,thecontrolofsizeandstateofnanomaterials is of extraordinary significance. Rather thansize control, control of the state of nano basic materialsis more troublesome and testing. The tubes, pieces orwires in the nano scale locale have novel properties.The revelation of carbon nano tubes by Iijima (1991)with their different fascinating properties has spurredthemissionforthecombinationofnanotubularstructuresofdifferentsubstancesandconcoctionmixes, for example, V2O5, SiO2, TiO2, Fe2O3, ZrO2 andMoO3.Amongthesematerials,titaniumdioxide(titania) has pulled in incredible enthusiasm since thedisclosure of its photograph affectability by Fujishimaand Honda (1972) and because of its solid photographoxidizing potential, high substance dependability, non-lethality and minimal effort (Guozhong, 2004). Titanianano tubes have enhanced properties contrasted withwhatever other type of titania for applications in waterandairrefinementphotographcatalysis,detecting,waterphotographelectrolysisforhydrogenera,photovoltaics,p hotographelectrochemicalsunoriented cells, gadgets, optics, tissue building and sub-atomicfiltration.Theboundlessinnovativeutilization

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of titania is impeded by its wide band-crevice (3 eV foranatasestageand3.2eVforrutilestage),whichrequiresbright(UV)illuminationforphotographsynergist initiation. Since UV range represents just alittleportion(8%)ofthesunpoweredrangecontrasted with noticeable light (45%), any movementin the light absorbance of titania from the UV towardsunmistakablerangedistrictwillenhancethephotograph synergist and photograph electrochemicalutility of the material. Titania band hole can be limitedbydopingwithdiversenonmetalparticles,forexample, N, C and S and distinctive metal particles, forexample, Fe, Mo, Ru, Os and V (Shen et al., 2006; Wu etal.,2005;YuanandSu,2004).Thisstudygoesforexaminationoftheimpactofdiverseanodizationparameters on titanianano tubes morphology created influidethyleneglycol asbasedelectrolytes.

Overview

Thegoalofthisthesisistostudythesynthesisoftitanium nanotubes using electrochemical anodizationtechniques, create hybrid materials by the addition ofothernanoparticulatecomposites,andfurthermoreapproach some solar energy harvesting applications ofthesenewmaterials.Theimportantelectrochemicalparameterscontrollingthegrowthofthenanotubeshavebeenextensivelystudiedandoptimized.Also,appropriatepost-fabricationprocessingconditionssuch as heat treatment conditions have been optimizedfortheproductionofcrystallineanatinetitaniumnanotubesoffersaliteraturesurveyonthedevelopmentoffabricationmethodsfortitaniumnanotubes.

Amechanisticexplanationofthesynthesisprocessmuch faster and withradically different results thanthe anodization in fluoride ions containing electrolytesisalsopresedescribesthechallengesencounteredwhen titaniana nan tubes powders for crystallizationpurposes,andhowrelatedparametershavebeenadjustedforoptimalpresentsourresultsonphotovoltaicpropertiesoftitanianananotubesandmodified titanium nanotubes. A custom experimentalsetup, easy to adapt for both photovoltaic and photocatalyticmeasurementshasbeendevelopedandsubsequently used for these studies. Finally, provides asummaryoftheresultsanddescribes futureoutlook.

2. Experimentalsetupandmethods

The trials were done in a two terminal electrochemicalcell where the two anodes were set 4 cm separated.Titaniumfoil,overwhichtitianananotubesweredeveloped, was utilized as anode while platinum foilwas the counter cathode. An immediate current powersupply (Bio-Rad Laboratories, model 400, Irvine, CA)was utilized as a wellspring of consistent potential. TheDC power supply was furnished with an informationsecuring framework and a cutting edge calculation andinterface for continuous observing of electrical currentand voltage amid the trials. A ultrasonic shower wasutilized for degreasing of titanium foil and last cleaningofmanufacturednanotubes.

The ultrasonic waves were additionally utilized forunsettlingoftheelectrolyteamidtheanodizationproceduretoenhancethenatureofnanotubesbyblending at minuscule level. The pH ofthe electrolytewas measured utilizing an Orion 5-star in addition toBenchtopmultimeter(ThermoelectronCorp.,Waltham,MA).Allexaminationsweredidatroomtemperature around 25 °C. The morphology of titanianananotube clusters was contemplated utilizing Hitashi S4500 field outflow SEM. The cross sectional picturesweretackledmechanicallytwistedspecimenswheretitania nanotube layers were freed from the supportingTi foil. All tests were did under a smoke hood.Titaniumfoils (0.89 mm thick, 99.7% virtue, Alfa Aesar, WardHill, MA) cut into 1.4 cm distance across plates. The Ticircle was mounted in a Teflon holder so that stand outface ofit was presented to the electrolyte. Glycerol (A.R., 99.5%, Caledon Laboratory Ltd.,George town, ON),ethylene glycol 99.5 % with water lingering ~ 0.4%.(CaledonLaboratoryLtd.,Georgetown,ON),NH4F,NH4NO3, urea (All three chemicals were A.R. 98 %, J. T.BreadcookboughtfromMallinckrodtBakerInc.,Pillipsburg, NJ) and deionized water were utilized as apartoftheinvestigationswithnofurthertreatment.

Titanium foil circles were degreased by sonicationinmethanoltookafterbywashingwithdeionizedwater. At that point, they were synthetically cleaned innitricandhydrofluoricacidsarrangement(5.6Mand 3.3M,separately)for10sec.

Electrochemicalanodization

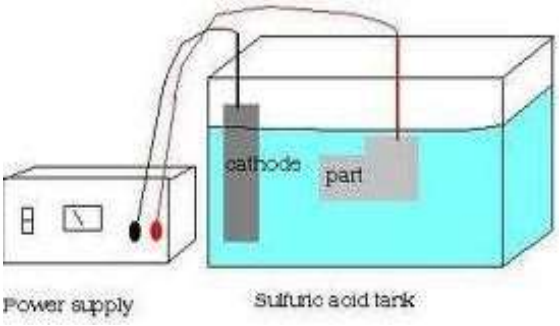

Figure2.1 AnodizingExperimentalsetupmodeldiagram-1

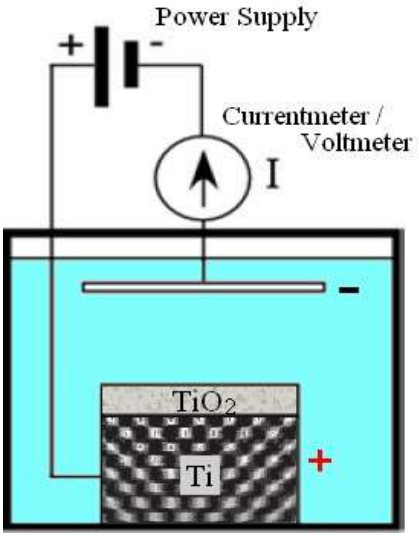

Figure2.2 AnodizingExperimentalsetupmodeldiagram-2

Titaniumdioxidenanotubesaresynthesizedbyanodizedmethod.Inthisstudy,thegrowthofnanotubesisanodizedonTif oils(purityof99.6%,thickness of 0.4 mm) by constant current at 15 mA inthe ethylene glycol solution containing 0.3 wt.% NH4Fand2vol.%deionizedwaterkeptat25°C.TheanodizedTiO2nanotubesareannealedinoxygenat350°Cfor60min.pl atinumplateasacounterelectrode. Structural Analysis shows - the XRD (x-raydiffraction) of nanotubes withdifferent growth ratesMorphologicalAnalysis.HRTEM(high-resolutiontransmission electron microscopy) reveals informationaboutthe particle sizeandshape.

Nanotubesarrayssynthesizedbyanodization

Early works on anodic titanium nano porous and nanotubular structures wereconducted during late 1990'sand early 2000'sby several research groups,mainlythose of E. Darque-Ceretti of the Ecole des Mines deParis, P. Schmuki of Friedrich-Alexander University inErlangenGermanyandthatofC.GrimesatPennsylvaniaStateUniversity.Zwilling&Darque-

Cerettiusedchromicacidcombinedwithasmallamount of hydrofluoric acid in their 1997 and1999trials. These were the first reports of the formation of anano porous structure in titanium. It was clear that thenanoporousstructureobservedonlyformedwhensufficient HF was added to the electrolyte mixture, Aspurechromic acidwasleadingtotheformationof athinbutstableoxidelayerwithnoapparentporestructure. In 2001 the Grimes group discovered thattitaniananotubescouldbegrownbyusinganelectrolyte consisting primarily of HF acid (0.5wt %)togetherwithhigheranodizationvoltages.

This finding revived interest in the anodization oftitanium.Grimesandco-workersinitiallyfocusedprimarily on promising sensor applicationsbut soonalsorealizedthepotentialofthesearraysinphotocatalytic applications. The group of P. Schmuki, using amixtureofsulfuricacidandasmallamountofHF(0.15wt%),reportedthesynthesis'tube-likestructures'in2003.Tubesupto500nmlongwereproducedby this method in about30-60 minutes ofanodization.

Titaniananotubessynthesis

As presented in the previous chapter, until recently itwas believed that fluoride ions are critical and maybeimpossible to replace as catalyst for the synthesis oftitanium nanotubes arrays by anodization, due to theiruniquepropertyofreactingwithtitaniumoxideformingtheTiF62-complexwhichwasfurthermoredissolvedintothesolution.Asaconsequence,allanodicnanotubesarraysreportedbefore 2007wereproducedinfluorideionscontainingelectrolytes.

Assumingthepossibilitythatchlorideionscouldhave similar catalytic properties, thus constituting (atleast) a less hazardous alternative to the highly toxichydrofluoricacid,severaltrialshavebeenperformedinourlaboratoryinthesummerof2006involvingsolutionsofvar iousacids(organicorinorganic)incombinationwithchlorinesaltsastheanodizationelectrolyte. While those trials resulted in the expectedformation of a thin oxide layer on the surface of theoriginaltitaniumfoil,followedin some casesbythequickformationofcorrosionpitsinvarious"weak"spotsonthesamplesurface,oronitsedges.

However, closer inspection of those corrosion pitsrevealed the presence of titanium nanotubes bundleswith lengths up to 50-60 microns and a cross section ofthe order of square microns.The successful synthesisof high aspect ratio titanium nanotubes in chloride ionscontaining electrolytes has been thus for the first timereported by our lab, and systematic studies have beenemployedforfurtheroptimizationoftheprocess.

Anodizationsetup

All the samples synthesized in our lab throughout thisworkwereproducedbyatwo-electrodeDCanodization process in a beaker containing the desiredelectrolyte,withtheinitialtitaniumfoilactingasthe

working anode, and a platinum mesh as the cathode.The electrodes were separated by a distance of 4 cm.The two-electrode configuration was preferred to thestandardthree-electrodeconfigurationforsimplicityandcosteffectivenessreasons,astheresultswereproventobesimilar.Theconstant voltagewasprovided by a computer-assisted Agilent 6811B powersupply (Agilent Technologies, Santa Clara, CA), whichwasalsoemployedforensuringandrecordingtheexternalcurrentwiththeaidofaLabVIEWprogram.

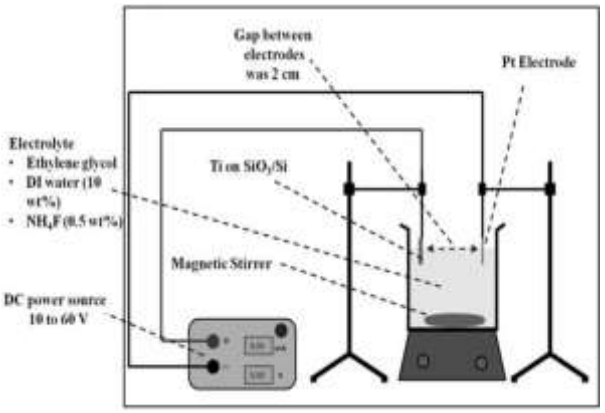

Figure2.3 AnodizingExperimentalsetupmodeldiagram-3

3. ResultsandDiscussion

As presented before, a first success in the synthesis oftitaniananotubesbyanodizationat12-20VDCinchlorideioncontainingelectrolyteswasobtainedthrough the use of various acid solutions (oxalic acid0.5M,formicacid0.5M,sulphuricacid0.05M)incombinationwithchlorinesalts(NH4Cl,KCl)inconcentrations varying from0.3 to 0.6M. KOH or NOAHwasalsoaddedsometimesinordertocontrolsolution's pH, and successful results were obtained forpH values in the 1.3 – 3.2 range. Micron size32bundlesof nanotubes averaging around 25 nm in diameter andwith a wall thickness round 5 nm were spotted both onselect attack areas on the sample and also forming aprecipitate on the bottom of the beaker as they werereleasedintothe solution.

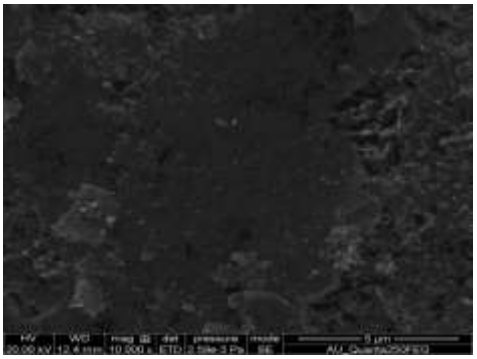

Figure 3.1 Scanning electron microscopy image oftitaniananotubes(sideview)fabricatedbyanodizingtitanium foil

Bycomparison,suchlengths(andcorrespondingaspectratios)areattainedinfluoridesonlyaftertensof hours of anodization. This motivated us to furthercontinueourstudyinordertooptimizetheanodizationparametersforbetter,moreuniformsamplecoveragewithformationsites,ideallyleadingtotheformationoforderednanotubesarrayswhilekeepingtheadvantagesofusingchlorineinsteadoffluorine. The nanotubes obtainedby anodization areamorphous, and further employment in solar

energyharvestingdevicesrequirescrystallization,routinelyacquiredbyannealing.Titanianano tubespowderssynthesizedbyanodizationoftitaniumfoilsinsolutions fluoride ions (resulting in long range orderedarrays with hexagonal orientation detached from thetitanium substrate as free standing films), or chloride(short range orderedbundles formed as a precipitatein the solution and subsequently dried for nanotubespowders)wereused.

Whileannealingtemperatureslowerthan300°Careinsufficientforcrystallizationtooccur,fortemperatureshigherthan400°Cthenanotubesmorphologyisaffected.Whiletheyarekeepingtheoriginalordering,theindividualtubesarechanginginto one dimensional nano particulate structures. Thisleaves a small window for annealing condition whichwould result in crystallization of the powders to thephase, while keepingthenano tube structure intact.Annealingtimemayalsoplayanimportantrole,assolid diffusion may occur after crystallization, possiblychanging thestructureat thenanoscale.

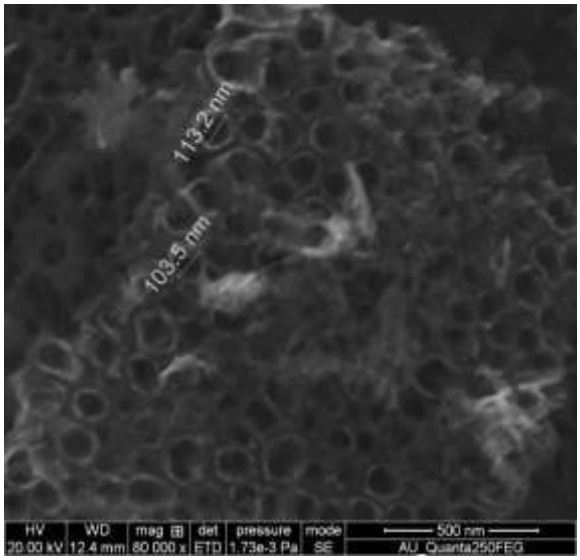

Figure3.2SEMviewsoftitianananotubespowderssynthesized byanodization

Differential scanning calorimeter studies revealed forall samples heated to a final temperature higher than350° that the phase transition occurs between 270°Cand 320°C,while for temperatureslower than260°Cno phase transition was observed .Subsequent trials attemperatures between 270°C and 300°C with a scanrateof1-2°C/minstillproduced(sometimespartially) crystalline structure asTEMthisstudyresults showthatthereisanarrowwindowintheannealingtemperature and temperature scanning ranges wherecrystallizationhappenswithoutdamagingthetubesstructure. Temperatures above 300°C are necessary forfull crystallization, while scanning rate values above 2-5°C/min,coupledwithtemperaturesabove350°Cdamagethenanotubestructureofthematerial,breakingitinto quasispherical particles.

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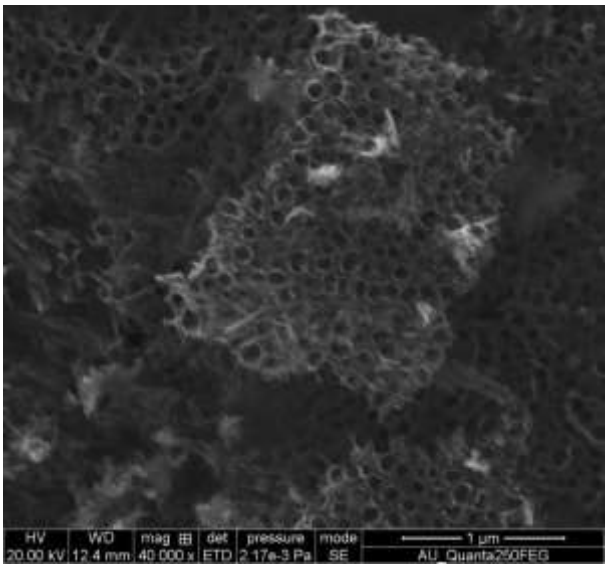

Figure3.3SEMviewsoftitanianananotubespowderssynthesized byanodization

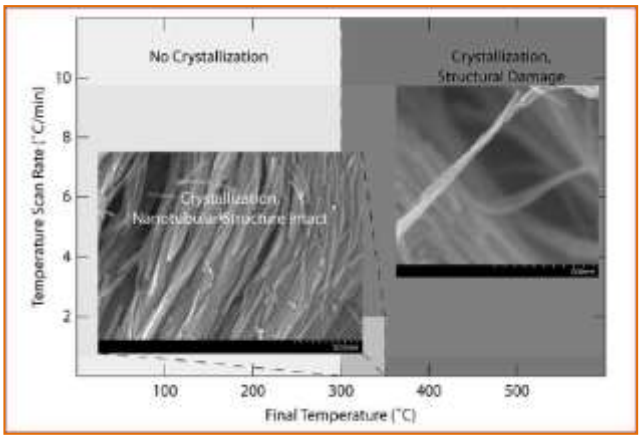

Figure3.4 Identification of annealing outcome forvariousparametersintheTemperatureScan/FinalTemperaturespace

Conclusion

Figure3.5 Identificationof UVtestreportinthewave/absorption

Richter,C.,Wu,Z.,Panaitescu,E.,Willey,R.J.,andMenon,L.(2007), Ultra-High- Aspect-Ratio Titania Nanotubes.

Throughout this study we investigated the synthesis oftitania nano tubes using electrochemical anodizationtechniques, created hybrid materials by the addition ofothernanoparticulatecomposites,andfurthermoreapproach some solar energy harvesting applications ofthese new materials. Our study on titania nanotubesarrays by anodization of titanium sheets has led to thediscoveryofelectrochemicalfabricationoftitanianananotubes by using chloride ions in place of fluorineions. The advantages of this methods are a much fastersynthesis (minutes with respect to tens of hours), andlowertoxicityofthesubstancesused.

A systematic study of the synthesis conditions fromjournals revealed clues to the mechanism of the newprocess,whilealsoprovidinguswithtoolsforoptimization.Doubleanodizationorusageofnon-aqueous electrolytes improved the synthesis process;yielding superior nanotubes with respect to individualmorphology, long range ordering and sample coverage.Afurtherinvestigationoftheannealingparametersallowed us to create crystalline nanotubes, suitable forsolar energy harvesting applications. Such applicationsincluded dye sensitized and CdTe sensitized solar cells,photo electrochemical water splitting, and controlledgold attachment to the nanotubes for

improved photocatalyticdevices(suchasphoto-assistedCOoxidations).

References

Feynman, R. (1960), There's plenty of Room at the Bottom(seeforexamplehttp:/www.its.caltech.edu/~feynman/plenty.html).Engineering&Science(Caltech).23(1). AdvancedMaterials.19(7):p.946-948

O'Regan, B. and Gratzel, M., A low-cost, high-efficiency solarcellbasedondyesensitizedcolloidalTiO2films.Nature,1991.353(6346):p.737-7

Richter, C., Panaitescu, E., Willey, R.J., and Menon, L. (2007),Titania nanotubes prepared by anodization in fluorine-freeacids.Journalof MaterialsResearch.22(6):p.1624-163

Panaitescu, E., Richter, C., and Menon, L. (2008), A Study ofTitaniaNanotubeSynthesisinChloride-Ion-ContainingMedia.JournalofTheElectrochemicalSociety.155(1):p.E7-E1

Friedman, A., Panaitescu, E., Richter, C., and Menon, L. (2008),High-aspectrationanonoodlesofaluminaandtitania.JournalofNanoscienceandNanotechnology,8(11):p.5864-586

Panaitescu, E., Nagesha, D., Fitchorov, T., Morris, J.S., Sridhar,S., and Menon,L.(2009)_Photovoltaic Properties of CdTeNanoparticles-DecoratedTitaniaNanotubesArrays.inNext-GenerationandNano-ArchitecturedPhotovoltaics, V.G. Stoleru,A.G. Norman, and N.J. Ekins-Daukes (editors),MaterialsResearchSocietySymposiumProceedings,vol.1121E,Warrendale,PA, N17.3

AbdElmoula, M., Panaitescu, E., Phan, M., Yin, D., Richter, C.,Lewis, L.H., andMenon, L. (2009), Controlled Attachmentof Gold Nanoparticles on Ordered TitaniaNanotube Arrays.JournalofMaterials Chemistry, p. accepted.

Richter, C., Jaye, C., Panaitescu, E., Fischer, D.A., Lewis, L.H.,Willey,R.J.,

Menon,L.(2009),Effectofpotassiumadsorptiononthephotochemicalpropertiesoftitaniananotubearrays.JournalofMaterialsChemistry:p.inpublication,doi:10.1039/b822501j..Choi,H.-L. And

Park, C. (1999), Effect of ultrasonic treatment on ripening oftitaniumoxalatesaltfromsolution.JournalofMaterialsScience,34(15):p.3591-3596