

Syntheses and Characterization of 1-D Titanium Glycolate microstructures: Effect of Dilution and Addition type on the Morphology of microstructures

ShilpaShinde¹, Abha Dhomane², Mahesh Subramaniyam³

^{1,3} (Dorf Ketal Chemicals (I) Pvt. Ltd, India)

² (Chemistry Department, K.V Pendharkar College/ Mumbai University, India)

Corresponding Author: Mahesh Subramaniyam

Abstract: Titanium glycolate is synthesized by the reaction of titanium butoxide with monoethylene glycol. This is a quick and convenient method for the preparation of titanium glycolate; the glycol acts as both reactant as well as solvent in the reaction. None of earlier studies reported in prior art have attempted a detailed investigation into factors influencing the transition of the multidimensional Ti glycolate structure to the one dimensional (1-D) Ti glycolate structure, though previous studies report the formation of titanium glycolates possessing different shape and size characteristics (i.e. micro-rods, whiskers, wires, and so forth) at varying syntheses conditions. This paper reports the transition of multi-dimensional to 1-D Ti glycolate structures (transition from micro-rods to nanowires) through a detailed investigation of key process parameters which direct the formation of a 1-D structure. The characterization of the as-prepared titanium glycolates has been conducted using various analytical techniques viz. Scanning electron microscopy (SEM), Thermo-gravimetric analyses (TGA, TGA-MS); Inductively Coupled Plasma – Optical Emission spectroscopy (ICP-OES), Fourier Transform Infrared spectroscopy (FT-IR) and Elemental analysis (CHNS).

Keywords: Ti alkoxides, Monoethylene glycol, 1-D microstructures

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I. INTRODUCTION

The use of titanium glycolate as esterification catalyst and 1-D titanium glycolate as template for making titania (TiO₂) [1] has been reported in prior art. One dimensional (1-D) nanostructures (such as rods, wires, whiskers, belts and tubes) are intriguing materials as they possess unique electronic, optical and magnetic properties [2]. 1-D glycolate microstructures are particularly well known for their unique electronic and optical properties, associated with the structural anisotropy exhibited by these entities [1].

The use of titanium for synthesis of 1-D titanium microstructures with high aspect ratios is a challenging prospect, owing to the isotropic crystal structure of titanium [1]. Monoethylene glycol has strong reducing properties and relatively high boiling point (~197 °C) and is widely used as reactant-solvent in the so called 'polyol synthesis' of metal nano-particles. Primary diols like monoethylene glycol react via alkoxide interchange, at the two terminal ends (of the diol), yielding insoluble, solid glycolates and corresponding derivatives [3]. There are some reports concerning syntheses of Ti glycolates in prior art. G. Shenet *et al* have synthesized titanium glycolates, as spheroidal and flattened granules, at elevated temperatures and low molar ratios of titanium alkoxides to monoethylene glycol [4]. However, formation of 1-D Ti microstructures has not been reported by them. X. Jiang *et al* synthesized Ti nanowires by complexation of titanium butoxide and ethylene glycol at reaction temperature of 170 °C. They report the spontaneous aggregation of chain like Ti-species into nanowires of uniform diameter. However the authors have not commented on formation of stable 1-D Ti microstructures especially at lower reaction temperatures or lower dilution [2]. H.K. Yuet *et al* have reported the synthesis of titanium glycolates, at room temperature, via the polyol process, wherein titanium alkoxide and polyethylene glycol are mixed vigorously and the mixture aged to settle down as white precipitate. Microrods were generated by this process. However, the authors do not throw any light on formation of 1-D titanium microstructures at low dilution [1]. The current work presented herein, merits in the detailed investigation into effect of key process parameters viz. dilution, mode of addition and reaction temperature on the transition of multi-dimensional titanium species to corresponding 1-D titanium glycolate structures (such as the transition from Ti micro-rods to Ti-nanowires).

II. EXPERIMENTAL METHOD

2.1 Chemicals and Materials

Ti^{IV} butoxide (TnBT; M. W.= 340.321) was sourced from Dorf Ketal Specialty Catalysts LLC, Texas, USA. Monoethylene glycol (MEG; M. W.= 62.07) was sourced from Reliance Industries, India.

2.2. Instrumentation

Scanning electron microscopy (SEM) images are taken using a field-emission microscope (TESCIN) operated at acceleration voltages of 5 - 30kV. Thermo-gravimetric (TGA) measurements are performed on a Mettler-Toledo TG-851 instrument. Measurements have been done at heating rate of 10°C/min in nitrogen atmosphere. TGA-MS analysis is performed using Perkin Elmer MS Clarus-600 analyzer. The FT-IR spectra are obtained using a Perkin-Elmer 91499 infra-red spectrophotometer in the range of 4000 to 500cm⁻¹. Elemental analysis has been performed on Thermo Fischer Scientific CHNS-O Flash EA 1112 series analyzer. Ti content was estimated using Perkin Elmer ICP OPTIMA 7000DV. The possible structure formation of the synthesized complexes was drawn using ISIS draw software (2.1.3D, MDL Information Systems Inc.).

2.3 Synthesis of Titanium Glycolate complexes

1-D Titanium glycolate complexes have been synthesized at different molar ratios of TnBT and MEG. Molar ratios for [TnBT: MEG] of 1:10, 1:50, 1:500, 1: 1200, 1:1600, 1: 1750 and 1:2000 have been evaluated in the preparation of the 1-D materials. The effect of glycol dilution on the morphology of 1-D titanium glycolate complexes is thereby investigated. Typically, for a [TnBT:MEG] molar ratio of 1:10, TnBT(128g; 0.376 moles) is charged into a round bottom flask using a glass dropping funnel. To this is added in drop-wise manner, MEG(234g; 3.76 moles) at room temperature, under constant stirring. The mixture is then heated to 175°C, using an oil bath, for 2h. Post-reaction, the reaction mixture is cooled to room temperature and vacuum filtered through Whatmann filter paper no. 41 using a Buchner funnel. The solid, white powder thus obtained is washed with aliquots of alcohol and then oven-dried at 120°C for 10 minutes. The solid is then transferred to a desiccator, following which it is characterized using FT-IR, TGA, ICP-OES, Elemental and SEM analytical techniques. Likewise, for other ratios of [TnBT:MEG], the corresponding weights are taken and synthesis performed as described above. In a similar manner, the effect of temperature on the morphology of the 1-D structures in high glycol diluted systems is investigated. The 1-D titanium glycolate synthesis has been conducted for [TnBT: MEG] molar ratio of 1:1200 (as described above) at varying temperatures (viz. 110, 135 and 175°C) and the morphology of product evaluated.

III. RESULTS AND DISCUSSION

As mentioned earlier, structural anisotropy of 1-D glycolate microstructures are responsible for their unique electronic & optical properties [1]. Also the use of titanium for synthesis of 1-D titanium microstructures with high aspect ratios is a challenging prospect, owing to the isotropic crystal structure of titanium [1]. Titania is an important oxide, actively explored as photo-catalyst. Titania / Titanium glycolate with 1-D morphology (in nano- or micron-dimensions) are expected to exhibit higher surface area than TiO₂ in the powder form, resulting in enhancement of optical and photo-catalytic properties of the materials. Rates of surface reactions are expected to be greatly enhanced in the presence of nano- or micron-sized Ti species.

The composition and structural elucidation of titanium glycolate microstructures synthesized at various temperatures and dilutions have been studied using TGA and FT-IR spectroscopic analytical techniques. TGA and TGA-MS investigations of the 1-D Titanium glycolates in N₂ atmosphere indicates weight loss (refer Figure 1). The weight loss region around 363°C corresponds to the decomposition of the bound glycol ligand. Total weight loss of 51.8% is observed which is in agreement with theoretical weight loss of 52, as reported in prior art [5]. Mass fragmentation of the major TGA-MS peak indicates the presence of ethylene oxide (M.W. = 44) indicating that this is the complexing ligand for the titanium glycolate molecule.

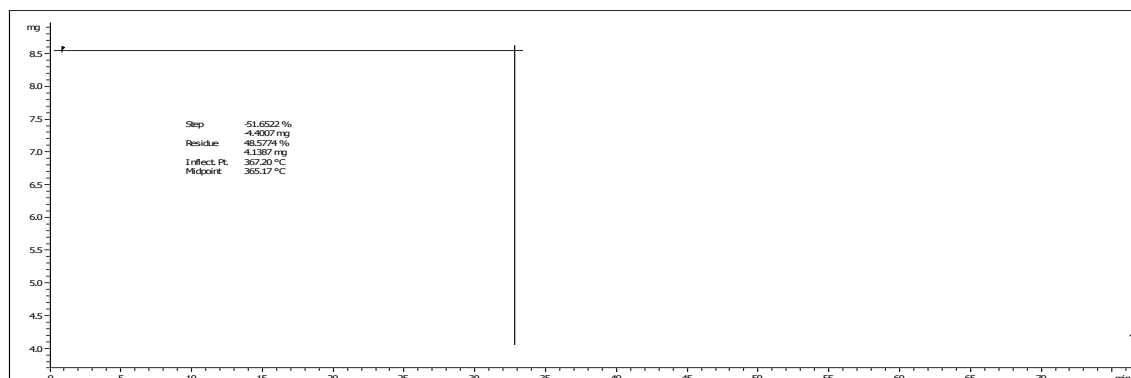


Fig 1: TGA spectra of Titanium glycolate

FT-IR spectra (Fig. 2) of the 1-D titanium glycolate, in the range of 4000 to 400 cm^{-1} confirm presence of various functional groups attributable to the monoethylene glycol and coordinated Ti species. Data for vibrations attributable to the following functional groups are given below.

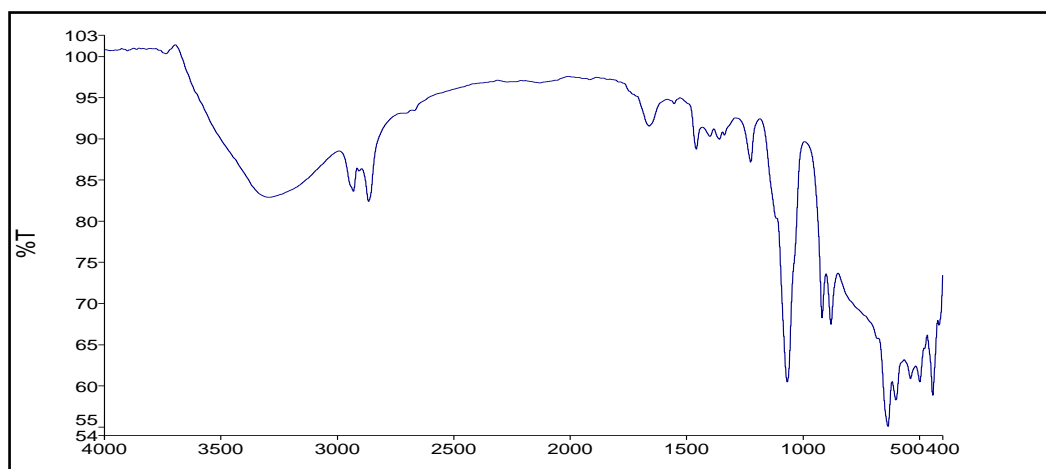
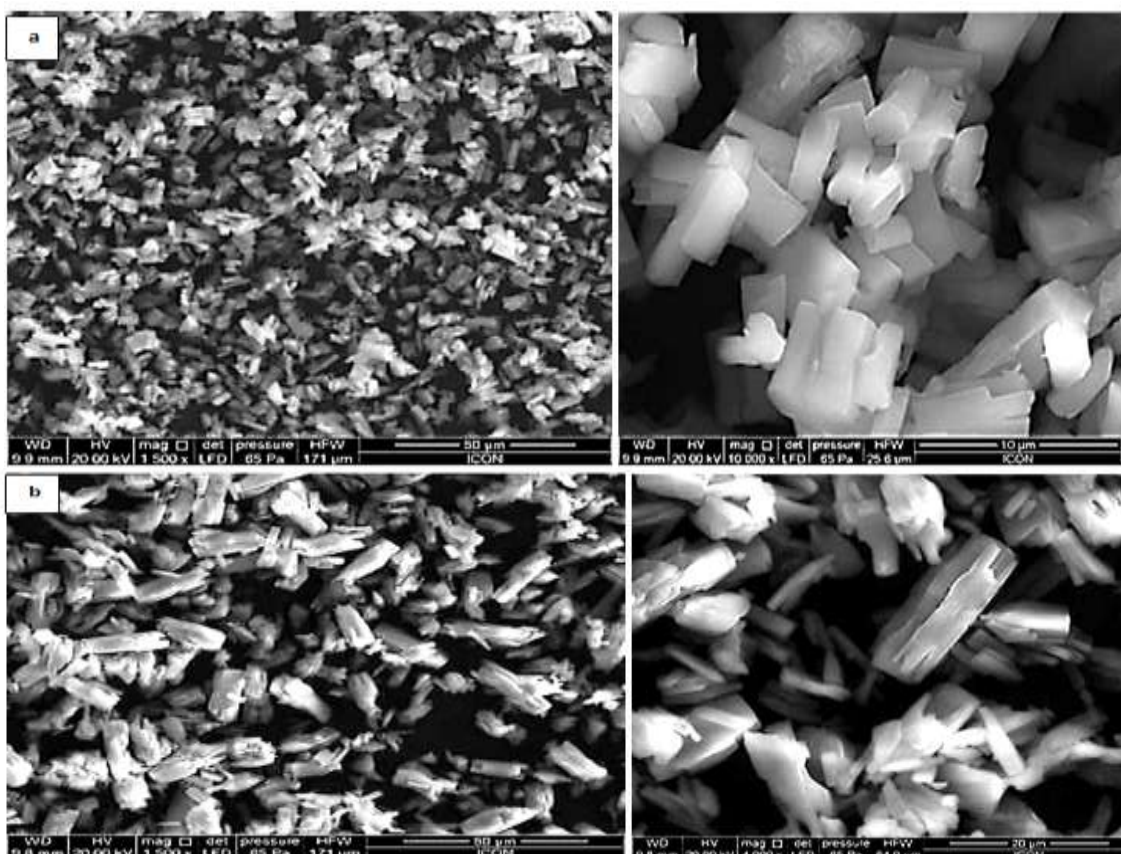


Fig 2: IR Spectra of Ti (OCH₂CH₂O)₂

The FT-IR bands located at 3384 cm^{-1} and 1659 cm^{-1} may be assigned to the –O-H stretching and –O-H bending modes respectively. FT-IR bands at 2929 and 2867 cm^{-1} may be assigned to the symmetric and asymmetric C-H stretching vibrations of ethylene glycol. FT-IR bands at 633 (shoulder) and 601 cm^{-1} may be assigned to Ti-O stretching. The FT-IR data confirms the formation of the titanium glycolate molecule [6].

Scanning Electron Microscopy has been used to characterize the Ti glycolates and evaluate any change in morphology of nano- or microstructures. The synthesis of the 1-D Ti glycolate microstructures has been described elsewhere. Essentially the glycolates are formed as solid, white residue after heating a mixture of Ti butoxide and MEG for 2h at 175°C. Normal mode of addition is adopted. Micrographs for the materials are given below



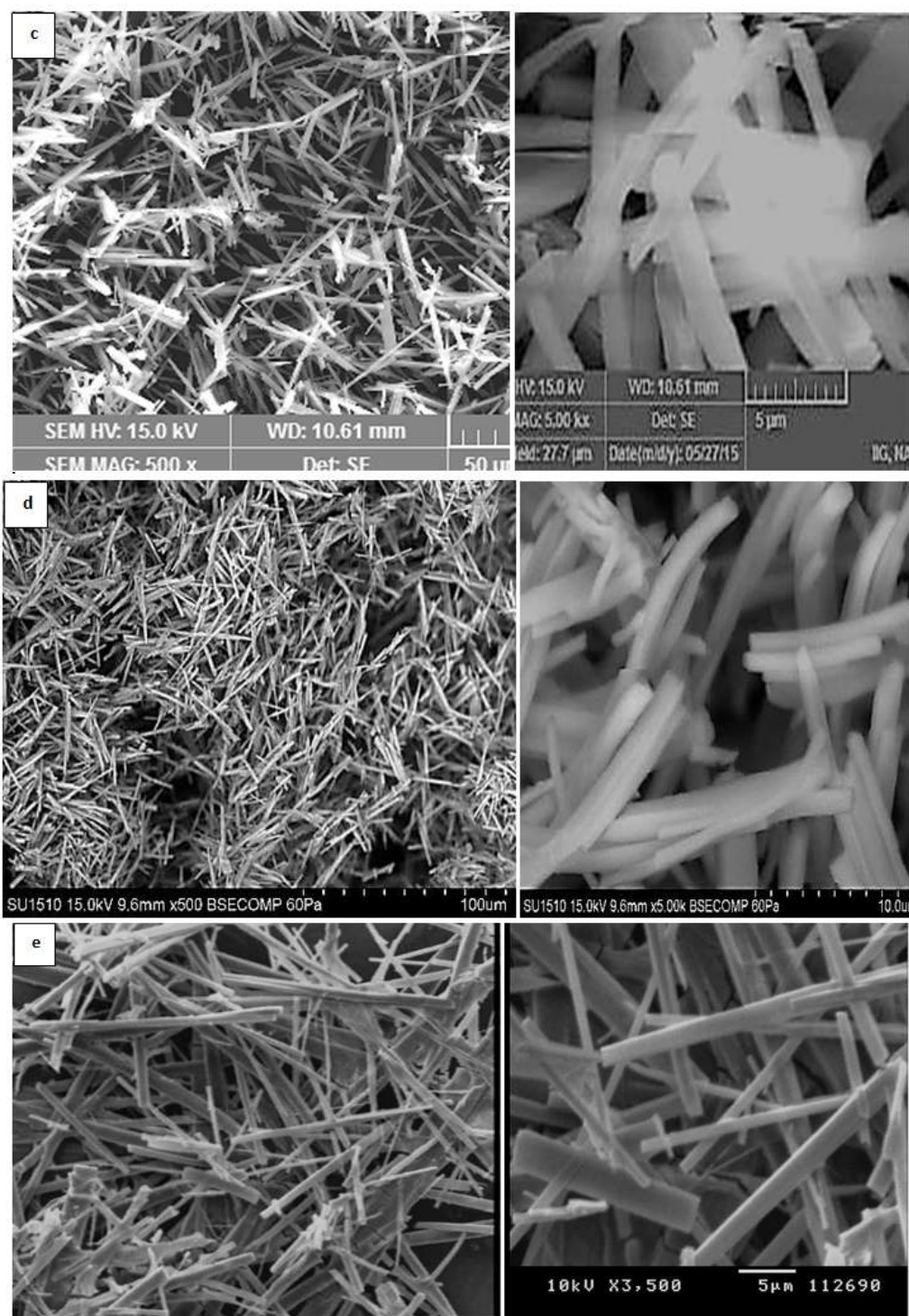


Fig 3 (a - e): SEM images of complexes prepared from titanium butoxide and ethylene glycol (agitation for 2hours at 175°C) in normal mode at dilutions (a) 1:10, (b) 1:50, and (c) 1:500 (d) 1:1200 (e) 1:1500

3.1 Ti glycolate syntheses at varying dilution (increasing glycol content) and low temperature addition methodology:

Dilution has a marked effect on the morphology of the Ti glycolate microstructures as evinced from the SEM micrographs. As the [TnBT: MEG] increased (i.e. at increasing dilution) we see a spectacular transition from a micro-cuboid structure ([TnBT: MEG = 1:10]) to a 1-D microstructure (See micrographs 3 (a -e)). The SEM images of Fig. 2 (c) ([TnBT: MEG = 1:500]) and Fig. 2 (d) (TnBT: MEG = 1: 1200)) shows the formation of micro-rod with typical longitudinal length scale of around 25 μ . At [TnBT: MEG = 1:1500], aspect ratio improves and bundle of nanowires is observed.

Thus one may infer that in the presence of progressive dilution, there is an increase in the length of the crystal indicating a progressive growth towards the 1-D morphology. At higher concentrations of titanium alkoxide (or lower glycol dilution), small cube-like structures with dimensions of $4.6 \times 2\mu$ (possessing a relatively low aspect ratio) are formed. With the gradual increase in the dilution ratio of ethylene glycol, transition in the morphology of the solid is observed. At 1:50 molar dilution for [titanium alkoxide: MEG], is observed a mixture of 1-D structures with dimensions varying from 8 - 25μ in length and 1.6 - 8.7μ in width. At higher dilutions of [TnBT: MEG] viz. 1:500 and 1:1200, we observe nano-rods with typical longitudinal length scale of 20 - 25μ . At higher dilutions nanowire bundles are observed. Aspect ratio is higher and the corresponding surface area will be higher. Summarized below in Table 1 are the characteristics of titanium glycolate microstructures obtained at various dilutions with low temperature (Normal) addition methodology.

Table 1: Morphology transition at various glycol dilutions at low temperature addition

Mole ratio of TnBT: MEG	Morphology	Length (μ)	Width (μ)	Aspect Ratio	Yield (%)
1:10	Small cuboid structures	~ 4.6	2	2.3	85
1:50	Short un-uniform cuboidal micro-rods	8.6 to 24.7	1.6 to 8.7	2.8 to 5.3	98
1:500	1D structures (micro-rods)	~ 20	~ 2	10	96
1:1200	1D structures (bundle of nanowires)	~ 25	~ 1	25	95
1:1500	1D structures (bundle of nanowires)	~ 40	1-2	20 - 40	74
1:2000	No solids obtained	-	-	-	-

It is interesting to note that, irrespective of the dilution used, when TnBT and MEG are brought into contact with each other, at room temperature the mixture appears as clear to slightly hazy solution. This haziness disappears on slightly warming the mixture. If the mixture were further heated to higher temperatures, the haziness reappears albeit at different temperatures for various dilutions. The temperature at which the haziness is found to reappear is detailed in Table 2, below:

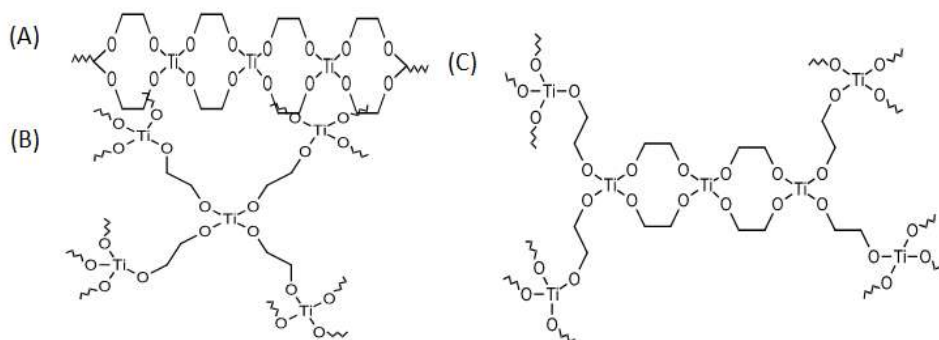
Table 2: Haze Point for various glycol dilutions:

Ratio (TnBT:MEG)	Temp ($^{\circ}$ C)
01:10	70
01:50	80
1:200	140
1:500	150
1:1200	165
1:1500	175

The dynamic transformation from the cuboidal to the 1-D Ti microstructures is energy driven. To explain the difference in energy required for formation of various morphologies, at varying dilution, one must take into account, albeit on molecular level, the environment of any $Ti(OCH_2CH_2O)_2$ unit cell at varying dilutions. While the chemical transformation is intrinsic to the transformation from cuboidal to 1-D shape, physical packing constraints to any Ti-intermediate morphology formed initially, will vary with progressive dilution. At lower dilutions, constraint on the sphere of propagation will result in a comparatively closer packing of the Ti glycolate units[7]. As a result, a lower intermolecular distance between any 2 adjacent Ti alkoxy units and a greater concentration of frequently interacting, cohesive Ti units would lead to precipitation of a stable solid with cuboidal or micro-rod morphology. At lower dilution, energy requirement to bring about this cohesion between two Ti glycolate units leading to precipitation will be low and hence, as expected precipitation of the solid Ti glycolate microstructures (cuboids, micro-rods) is observed at low temperature. On the other hand, for progressively higher dilutions, though the sphere of propagation is not limiting, energy requirement to bring about this cohesion between the Ti units will be higher and the precipitation will occur at higher temperatures, which is observed in Table 3. It has been reported in prior art that nano-domains spontaneously self-assemble into configurations that minimize the total free energy of the system [8]. The transition of cuboidal to 1-D microstructures (cuboids to wires, See Figs.a to d) is a direct result of the higher surface energies of the end surfaces, which constitute the growth front of the progressive intermediate morphologies (cuboid \rightarrow micro-rod \rightarrow wire). Further uptake of molecules, possessing enhanced mobility at higher temperatures, followed by their diffusion to this growth front will lead to transition to morphologies possessing increasing surface area[9, 10].

At very high dilutions, the Ti alkoxy units will be distanced apart owing to which the cohesiveness between them will be negligible and this may result in negligible or zero precipitation. Hence in order to obtain a microstructure at very high dilutions, a very high energy requirement will need to be fulfilled and the current experimental conditions may not be able to provide the same.

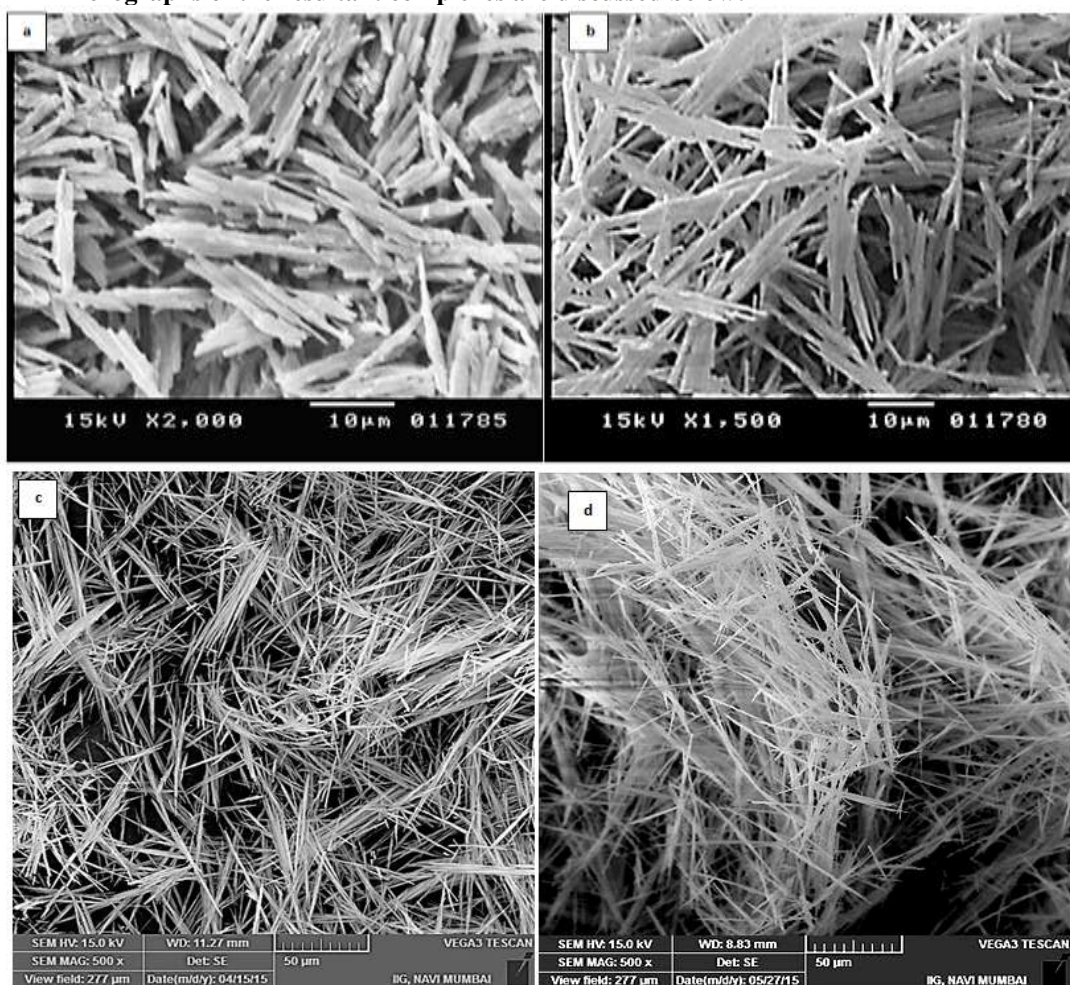
From the analysis, we can conclude that the probable titanium glycolate structures form at different dilution, as shown in Fig 4. Proposed structures for Titanium glycolate at different EG dilution may be:



3.2 Ti glycolate syntheses at varying dilution (increasing glycol content) and high temperature (reverse) addition methodology

Titanium glycolate microstructures were also prepared by reversing the mode of addition i.e. by using the high temperature mixing methodology. Monoethylene glycol is heated to 175°C and then TnBT slowly added to the heated ethylene glycol. A haze started appearing after 50% addition of the total TnBT taken. Different dilutions of monoethylene glycol were considered as a variant in this experiment.

The SEM Micrographs of the resultant complexes are discussed below:



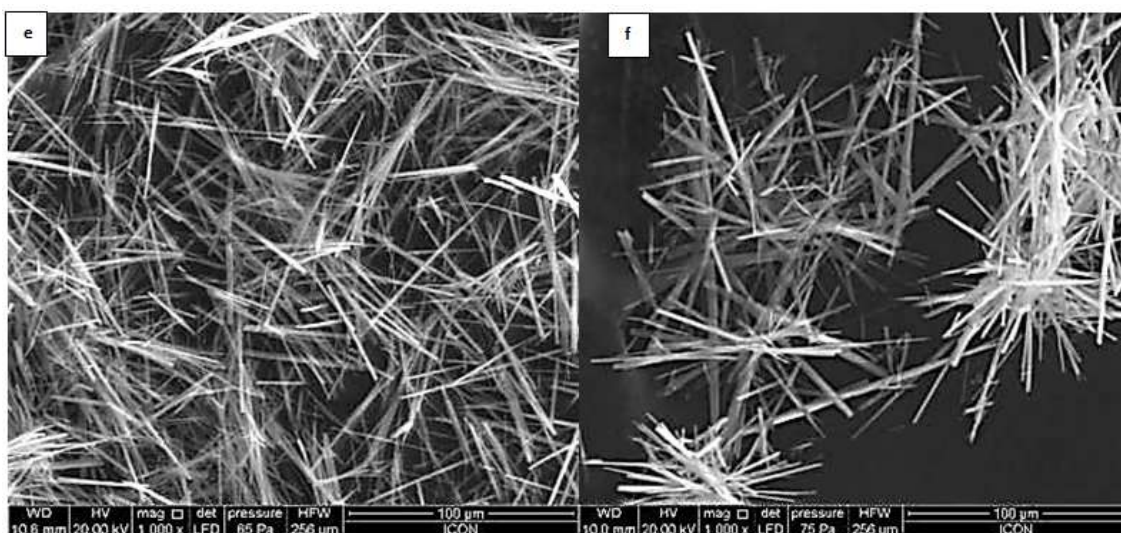


Fig. 5 (a – f): SEM images of complexes prepared by high temperature (Reverse) addition methodology (a) 1:10, (b) 1:50, and (c) 1:500 (d) 1:1200 (e) 1:1500 (f) 1:1750

1-D microstructures prepared by high temperature (Reverse) addition methodology are obtained in face of [TnBT + MEG] dilutions as low as 1:10(Fig a). Details of the same are given in Table 3, shown below:

Mole ratio of TnBT: MEG	Morphology	Length (μ)	Width (μ)	Aspect ratio	Yield (%)
1:10	Small un-uniform rods	5 to 10	1	5	83
1:50	Short nanorods	10 to 15	0.8	12.5	90
1:500	nanowires	60 to 70	0.8	75	91
1:1200	nanowires	70 to 80	0.8	87.5	91
1:1500	Mixture of small and big nanowires	18 to 60	0.9 to 1.4	Avg. =31	68
1:1750	Mixture of small and big wires	19 to 79	1.4 to 3.4	Avg=18.2	Fine haze observed
1:2000	No solid	-	-	-	Nil

Table 3: 1-D microstructures prepared by high temperature (Reverse) addition methodology

As is evinced from the SEM micrographs, at lower [TnBT + MEG] dilutions 1:10 and 1:50, short, non-uniform rods are observed (see Figs. a and b). At progressively higher [TnBT + MEG] dilutions 1:500 and 1:1200, there is a transformation of micro-rods into fine nano-wires (see figures b, c and d). Microstructures with an aspect ratio > 25 can be termed as nanowires[11].At higher [TnBT + MEG] dilutions viz. 1:1500 and 1:1750, there appears to be likely breakage in the nanowires. Such a phenomenon has been described earlier by Priya S. etal (see Figs. e and f) and a mixture of big and small wire-like structures are observed[12]. The aspect ratio also decreases at these dilutions. Enhanced aspect ratios may indicate a build-up in the surface areas of the materials. If so, then for [TnBT+MEG] dilution of 1:1200, the surface area for the nano-wires will be the highest. Given that higher surface area structures have unique benefits, an open ended question remains as to whether nano-wires can be tailored, at least in principle, to provide desired greater lengths and hence larger surface areas than reported herein through control on the mode of addition, temperature and dilution parameters.

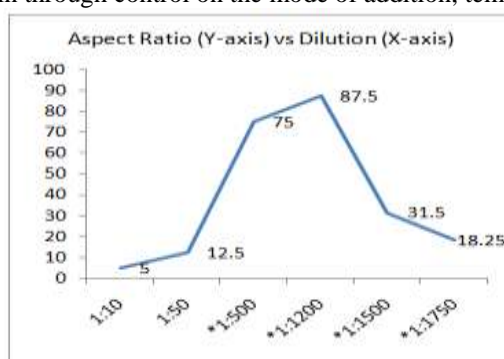


Fig. 6 –Aspect ratio versus Dilution

If the modes of addition are to be compared for a more desired route to synthesis of the 1-D nanostructures, the reverse or high temperature addition mode is most favorable. As is evinced from the comparative data in the Tables 2 and 4, corresponding to normal or low temperature mode of addition and reverse or high temperature mode of addition, respectively, the aspect ratio dramatically improves when the reverse mode of addition of reactants is used as the synthetic route. Aspect ratios for the reverse mode of addition are nearly twice that of the normal mode of addition especially at low dilution. At comparative higher dilution the aspect ratios tend to increase by nearly seven-fold for the reverse mode of addition. Also nature of the solids as evinced by the SEM micrographs show that for the normal mode of addition micro-rods are formed whereas for the reverse mode of addition 1-D nano-wires are formed and this morphology persists even at very high dilution. Further the solids formed by the normal mode of addition have a larger width and shorter length whereas the solids formed reverse mode have a smaller width and are comparatively greater in length. This indicates that the reverse mode of addition of reactants promotes growth towards a 1-D nano-structure of greater surface area, as supported by the aspect ratio data.

3.3 Ti glycolate microstructures are also synthesized at varying temperatures viz. 110, 130, 175 and 195°C, using the reverse addition mode of synthesis as under:

Ti glycolate microstructures are prepared at varying temperatures mentioned above, while maintaining a constant [TnBT: MEG] = 1:50

The SEM Micrographs of the resultant complexes are discussed below:

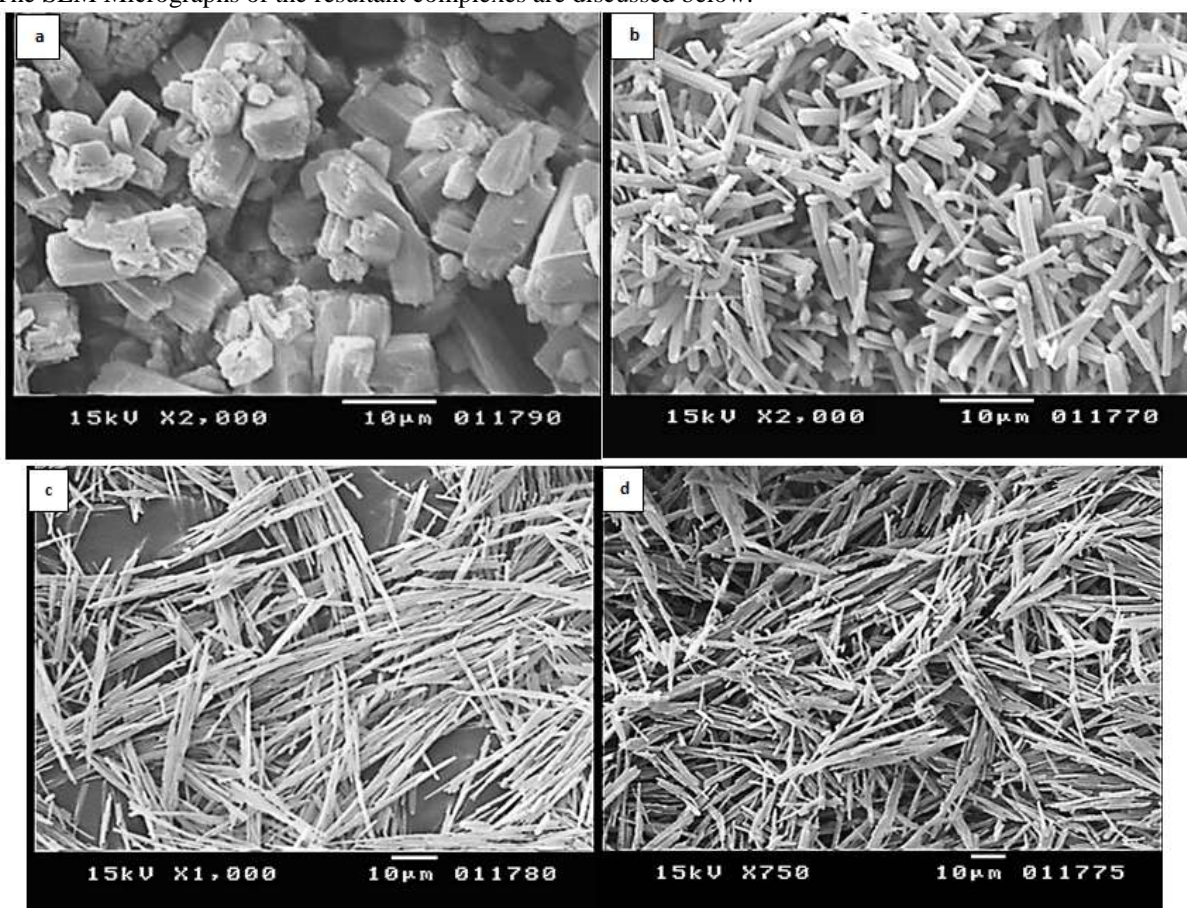


Fig. 6 (a – d): SEM images of complexes prepared at [TnBT: MEG] = 1:50 by reverse mode of addition methodology at varying temperatures (a) 110°C, (b) 135°C, (c) 175°C (d) 195°C

For lower dilution, on comparison of the solid Ti glycolate product obtained at lower temperatures of 110 and 135°C, at [TnBT : MEG] = 1: 50 in both cases, the SEM micrographs indicate the formation of well-defined cuboid structures and micro-rods (with cuboid contours) though possessing larger length and smaller width, respectively. If the synthesis of Ti glycolate is performed at higher temperatures i.e. 175 and 195°C at the same [TnBT: MEG] ratio = 1: 50, nanorods of high surface area are obtained. At 195°C there is not much change in the aspect ratio (as compared to product synthesized at 175°C) though very minor breaking of the nanorods is observed.

3.4 Ti glycolate microstructures are prepared at varying temperatures, mentioned above, while maintaining [TnBT: MEG] = 1:1200

The SEM Micrographs of the resultant complexes are discussed below:

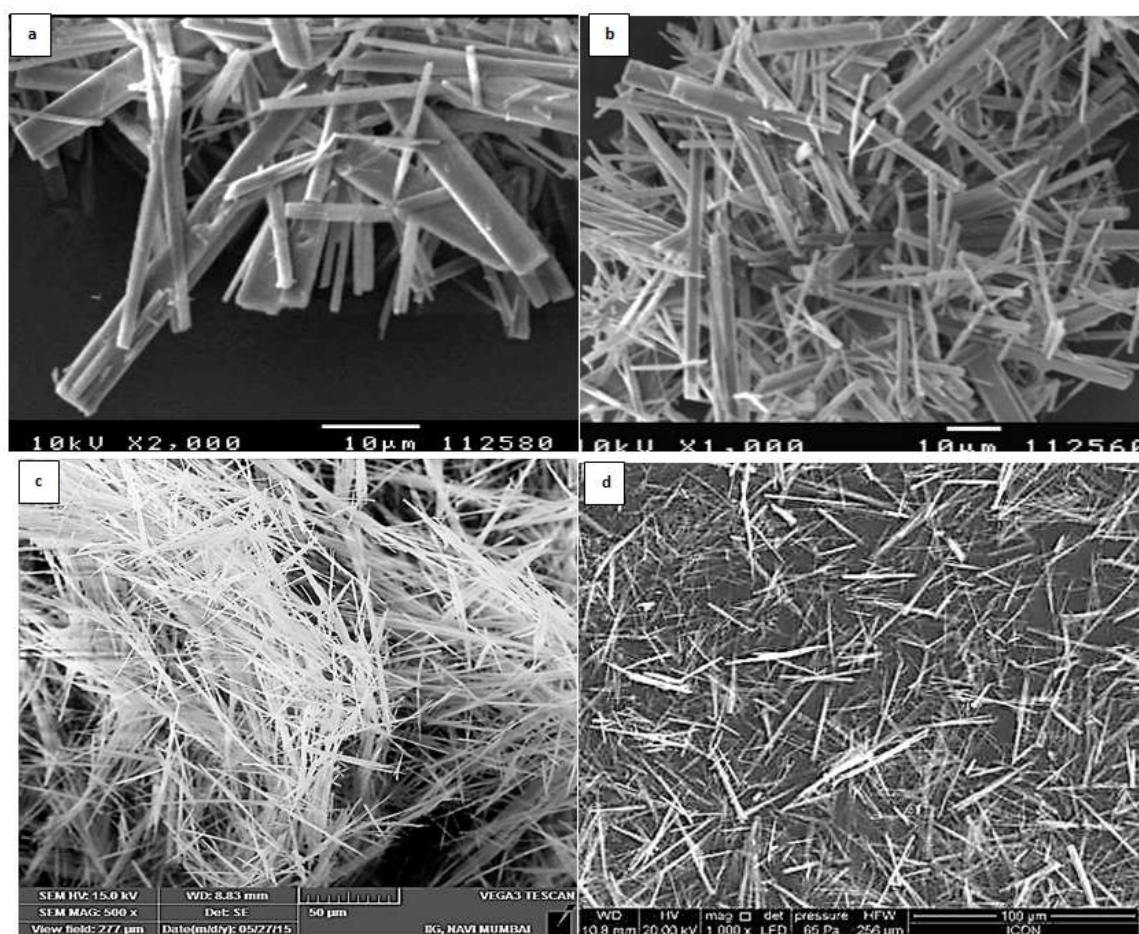


Fig. 7 (a – d): SEM images of complexes prepared using [TnBT: MEG] = 1:1200 dilution by reverse mode of addition methodology at varying temperatures (a) 110°C, (b) 135°C, (c) 175°C (d) 195°C

At higher dilution, it is interesting to observe that Ti glycolate product synthesized at lower temperature viz. 110°C and [TnBT : MEG] = 1:1200, comprises of a mixture of micro-rods (major) and nano-wire like component (minor). The 1-D nano-wire content is enhanced for the Ti glycolate product prepared at 130°C and [TnBT: MEG] = 1:1200. The Ti glycolate product prepared at 175°C and [TnBT: MEG] = 1:1200, comprises long 1-D nanowires possessing a high aspect ratio. However synthesis of Ti glycolate at 195°C yields a product that shows physical breaking of the nanowires.

IV. CONCLUSION

The key influencing critical process parameters studied are mode of addition, glycol dilution, and reaction temperature. Aspect ratios improve drastically for the reverse mode of addition methodology as compared to the normal mode of addition methodology. The study has found that the nanowire formation of high aspect ratio is possible only at a particular glycol dilution and that mode of addition of reactants and reaction temperature play a significant role on the formation of 1-D Ti microstructures. The transition of microrods to nanowires is favored by an increase in the dilution (mole ratio) of ethylene glycol, up to certain extent; however, as dilution increases, an adverse effect of dilution is observed. Well defined nanowires are obtained at a dilution of 1: 1200 (Titanium butoxide: MEG; mole/mole), but beyond this ratio of 1: 1200 mole/mole, structural changes lead to formation of micro-rods. A surprising finding was, at very high dilutions, well defined Ti glycolate microstructures are not precipitated out but a hazy composition is observed, which on allowing to stand, was composed of Ti glycolate entities of lower aspect ratio. In principle, the formation of nanowires of very high surface area can be effected by optimizing the reaction conditions i.e. using the reverse mode of addition methodology, working at higher dilutions at optimum temperature.

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