Fabrication of Tantalum Oxyfluoride and Oxynitride Thin Films via Ammonolysis of Sol-Gel Processed Tetraethoxo (β -diketonato) Tantalum (V) Precursors for Enhanced Photocatalytic Activity

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Abstract

In the present report, the generation of Tantalum oxyfluoride and oxynitride upon ammonolysis of the gel obtained from modified tantalum-alkoxo complexes is reported. To the best of our knowledge, this is first report of the formation of tantalum oxyfluoride thin films via ammonolysis of the β -diketone modified tantalum-alkoxo complex $[\text{Ta}(\text{OEt})_4(\text{CF}_3\text{COCH}_2\text{COCH}_3)]_m$. The integration of nitrogen and fluorine in lattice sites of metal oxides leads to significant reduction in the band gap, resulting in their activation under visible light. Moreover, in this report the effect of the modified alkoxide precursors and ammonolysis on the photo-physical properties of Ta_2O_5 thin films have also been investigated and compared with the results obtained from films fabricated from unmodified tantalum (V) ethoxide. ^1H NMR, ^{13}C NMR and elemental analyses confirmed successful modification of tantalum (V) ethoxide to $[\text{Ta}(\text{OCH}_2\text{CH}_3)_4(\text{CH}_3\text{COCHClCOCH}_3)]_m$ (**1**), $[\text{Ta}(\text{OCH}_2\text{CH}_3)_4(\text{CF}_3\text{COCH}_2\text{COCH}_3)]_m$ (**2**) and $[\text{Ta}(\text{OCH}_2\text{CH}_3)_4(\text{CH}_3\text{COC}(\text{CH}_3)_2\text{COCH}_3)]_m$ (**3**). The fabrication of Ta_2O_5 thin films involved the spin casting of the gels of modified tantalum alkoxo complexes (processed by sol-gel method) on to glass substrate. X-ray photoelectron spectroscopy results show that nitrogen was incorporated into the ammonolyzed films fabricated from complex precursors (**1**) and (**3**), while the presence of fluorine as tantalum oxyfluoride was confirmed in the ammonolyzed film fabricated from complex (**2**) precursor. The optical characterization insinuate band gap narrowing from 3.55 eV for undoped film prepared from tantalum (V) ethoxide to 3.47 eV for undoped film prepared from $[\text{Ta}(\text{OEt})_4(\text{CF}_3\text{COCH}_2\text{COCH}_3)]_m$ and 3.05 eV for ammonolyzed film obtained from $[\text{Ta}(\text{OEt})_4(\text{CF}_3\text{COCH}_2\text{COCH}_3)]_m$ precursor. Furthermore, enhanced photocatalytic efficiency of the films is demonstrated by degradation of methylene blue dye.

1. Introduction

The discovery of photocatalytic properties of titanium dioxide by Honda-Fujishima paved way for the development of technologies with a huge potential applicability towards environmental remediation such as purification of water via degradation of dyes and pesticides, oxidation of volatile organic compounds and CO_2 reduction on various types of photocatalytic materials [1-6]. Over the past decades, nanoparticles and thin films of TiO_2 have been examined widely for their photophysical properties establishing TiO_2 as a benchmark photocatalyst [7-10]. However, thin films of group V metal oxides (Nb_2O_5 and Ta_2O_5) are of significant technological relevance owing to their excellent photophysical properties (comparable to that of benchmark photocatalyst) and favorable chemical, thermal, mechanical properties [11]. Also, they have a number of other potential uses in advanced electronics as high- κ dielectric materials or as diffusion barriers [11-15] Recently, Ta_2O_5 has been established as a robust memristive material [16-19].

Although, for the past few years the group V transition metal oxide investigations were focused on the properties and behaviour of oxides of niobium. However, recent investigations showed that oxides of tantalum has exceptional photocatalytic potential and can be an alternative of TiO_2 [20-27]. Furthermore, most investigations involved Ta_2O_5 photocatalyst in powder form, making it unfeasible to separate and

recycle the photocatalyst after reaction [28-30]. In this perspective, exploring Ta₂O₅ based photocatalytic thin films is of great significance [31]. Thin films in nanometer range have attracted a lot of attention due to significant changes in physico-chemical properties due to the high fraction of surface atoms in nanostructured materials, resulting in increased surface to volume ratio of these structures. Ta₂O₅ thin films can be applied to surfaces to change the physical and chemical properties of a material. Therefore, visibly active photocatalysts like tantalum oxynitride (TaO_xN_y) or tantalum oxyfluoride (TaO_xF_y) coated as films on different substrates, offering high surface to volume ratio have persistently been investigated for environmental remediation technologies [25-31].

Sol-gel process has been widely applied in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, nanotechnology and played a crucial role in preparation of novel organic-inorganic hybrid materials OIHMs [32-34]. The mechanism of sol-gel can simply be defined as generation of oxide networks through progressive condensation reactions of molecular precursors in liquid medium [33, 35]. In general, sol-gel process can be categorized into two methods: the inorganic method and the organic method.

The inorganic method involves the creation of networks in continuous liquid phase through metal oxide colloidal suspensions known as sols and then gelation. Whereas, widely used organic approach involves: (i) the preparation of a solution of metal alkoxide precursor M (OR)_n in an alcohol or other low molecular weight organic solvent which is miscible with water. Here M represents a network forming central metal atom such as Ti, Si, Nb, Ta, Al, Fe, B etc. and R is typically an alkyl group with general formula C_nH_{2n+1}; (ii) hydrolysis of the homogenous solution to form sol; (iii) condensation and polymerization of sol to form chains and particles; (iv) growth of particles followed by agglomeration of polymer structure followed by the formation of network resulting in thickening of solution known as gel; (v) drying and (vi) thermal treatment. Traditional Ta₂O₅ thin films fabrications via sol-gel processing have used tantalum alkoxides as most common precursors due to their high propensity towards water. Hydrolysis followed by condensation of tantalum alkoxides result in the formation of oxopolymers finally generating an oxide network upon calcination. The higher electrophilicity and coordination expansion of central tantalum atom due to the presence of high number of facile alkoxy groups make them highly susceptible to hydrolysis. Since, slower hydrolysis of the precursor in the sol-gel process is the most influential factor for the formation of homogenous materials therefore controlled hydrolysis has been achieved through increased steric hindrance offered to the substitution of alkoxy groups by hydroxyl groups via increasing the alkyl chain length of the alkoxy group or by using alkoxy precursor with secondary or tertiary alkyl group [36, 37]. Since, complex reactions are involved in lengthening of the alkyl chain of the alkoxy group, therefore substitution of some alkoxy groups by nucleophilic reagents like β-diketones, organic acids and glycols has been widely used to control the rate of hydrolysis of highly reactive metal alkoxides [36, 38-43]. Upon substitution, some of the coordination sites of the central metal atom are occupied by these ligands through less hydrophilic bonds or they impose other physical impedances such as steric effect to efficiently hinder the substitution of alkoxy group by hydroxyl group. Although, these ligands do not

completely prevent the hydrolysis of the sites occupied by remaining alkoxy groups but effectively reduce the rate of hydrolysis.

More importantly, the photocatalytic efficiency of Ta₂O₅ has limited utilization due to its high band gap energy profile (3.9 eV), rendering it active only under ultraviolet region of electromagnetic spectrum which constitutes only a small fraction (<5%) of the total spectrum [44]. To enhance the photocatalytic efficiency of Ta₂O₅, several novel materials were developed by doping with metal atoms (Mo, W) or non metal atoms (N, C) and fabricating various mixed oxide as improved photocatalysts [20-29]. Moreover, the recombination of photogenerated electron-hole pairs is a major drawback, because it reduces the quantum efficiency of photocatalytic activity as it has faster kinetics than surface redox reactions [45].

Nevertheless, in order to effectively exploit of solar energy and indoor artificial illuminations, the development of visible-light active Ta₂O₅ thin films via a simple and time-saving approach at moderate temperature has become imperative [46]. To the best of our knowledge, this is the first report of the fabrication and application of tantalum oxyfluoride thin films via ammonolysis of modified tantalum-alkoxo complex [Ta(OEt)₄(CF₃COCH₂COCH₃)]_m. Furthermore, a comparative investigation of the effect of modified precursors and ammonolysis on structural, optical and photocatalytic properties of sol-gel derived tantalum pentaoxide thin films systematically prepared from β- diketones [3-Chloro-2,4-pentanedione, 3,3-Dimethyl-2,4-pentanedione, 1,1,1-Trifluoro-2,4-pentanedione] substituted tantalum (V) ethoxide precursors has also been discussed.

2. Experimental

Tantalum (V) ethoxide and β-diketone derivatives were purchased from Sigma Aldrich and used with no further purification. All reactions were carried out under a dry argon atmosphere by using standard Schlenk techniques. All solvents were dried and degassed prior to use.

2.1. Synthesis of Complexes

[Ta(OCH₂CH₃)₄(CH₃COCHClCOCH₃)]_m (1). 3-Chloro-2,4-pentanedione (201.84 mg, 1.5 mmol) was slowly added to a solution of Ta(OCH₂CH₃)₅ (609.37 mg, 1.5 mmol) in toluene (5ml) with constant stirring. The mixture was stirred for 12 h and the solvent was removed in vacuo to give a yellow liquid in 85% yield. Elem. anal. *calc.* C = 38.30, H = 6.67 and *exp.* C = 37.96 and H = 6.24. IR (cm⁻¹) ν_{C=O} = 1690 s ; ν_{C=C} = 1560 m; ν_{C-O} = 1060 s & 1045 m; ν_{Ta-O} = 640 m

[Ta(OCH₂CH₃)₄(CF₃COCH₂COCH₃)]_m (2). 1,1,1-Trifluoro-2,4-pentanedione (231.135 mg, 1.5 mmol) was added to Ta(OCH₂CH₃)₅ (609.37 mg, 1.5 mmol) following the procedure as stated above for the synthesis of compound [Ta(OCH₂CH₃)₄(CF₃COCH₂COCH₃)]_m which was a light yellow liquid with 86% yield. Elem. anal. *calc.* C = 36.37, H = 6.34 and *exp.* C = 35.86 and H = 5.12. IR (cm⁻¹) ν_{C=O} = 1680 s ; ν_{C=C} = 1560 m; ν_{C-O} = 1060 m & 1020 m; ν_{Ta-O} = 670 m

[Ta(OCH₂CH₃)₄(CH₃COC(CH₃)₂COCH₃)]_m (3). Similarly, 3,3-Dimethyl-2,4-pentanedione (192.25 mg, 1.5 mmol) was slowly added to Ta(OCH₂CH₃)₅ (609.37 mg, 1.5 mmol) to synthesize **[Ta(OCH₂CH₃)₄(CH₃COC(CH₃)₂COCH₃)]_m** as a colourless liquid with 90% yield. Elem. anal. *cal/c*. C = 44.89, H = 8.04 and *exp*. C = 43.86 and H = 7.62. IR(cm⁻¹) $\nu_{C=O}$ = 1640 s ; $\nu_{C=C}$ = 1550 m; ν_{C-O} = 1060 m & 1000 m; ν_{Ta-O} = 670 m

2.2. Fabrication of Ta₂O₅ Thin Films:

Ta₂O₅ sol was prepared by dissolving the precursor alkoxide [**1**, **2**, **3**] (1.0 mmol) in ethanol (3 ml) with constant stirring for 3h. 1ml of deionized water was added to the resultant clear sol under vigorous stirring to obtain gel. The resultant homogenous gel was spin casted onto glass substrate at 1500 rpm for 60 sec. The spin casting procedure was repeated in order to obtain uniform films. Two sets of the films were prepared from precursors **1**, **2** and **3**. One set of films (**A**), (**B**) and (**C**) were calcined under oxygen (40ml/min) at 500 °C for 1h and the other set was subjected to ammonolysis (40ml/min) under identical conditions and re-designated as **NA**, **NB** and **NC** respectively.

Ta₂O₅ thin film prepared as control and designated as **D** was prepared from Ta₂O₅ sol. This sol was prepared by dissolving the parent tantalum (V) ethoxide (1.0 mmol) in ethanol (3 ml) with constant stirring for 3h. 1ml of deionized water was added to the resultant clear sol under vigorous stirring to obtain gel. The resultant homogenous gel was spin casted onto glass substrate at 1500 rpm for 60 sec. The spin casting procedure was repeated in order to obtain uniform film and was calcined under oxygen (40ml/min) at 500 °C for 1h.

2.3 Characterization:

¹H NMR and ¹³C NMR spectra were recorded using a Bruker Advance II 400 MHz NMR spectrometer and are referenced to TMS. IR spectra were recorded using Perkin-Elmer System 2000 FT-IR spectrometer. The crystal structures of the Ta₂O₅ films were determined by X-ray diffractometer (Rigaku Smartlab, Japan) operated at 40 kV, 30 mA. Cu K α (λ = 1.541 78 Å) was used at X-Ray source. Topographical features of the films were investigated with AFM (Agilent technologies). The chemical environment of films was investigated by X-ray photoelectron spectrometer (PHI 5000 Versa Probe II), using Al K α source energy (1486.6 eV) and spot size of 200 micrometer with power of 50 W and 15 kV. The optical constants and thickness of the films were characterized using variable angle spectroscopic ellipsometer (VASE) (J.A. Woollam Co., Inc) at wavelengths ranging from 300 to 1000 nm at an angle of 70°. The optical transmittance was recorded using UV-Vis spectrophotometer (Shimadzu 3600+) along a range of wavelengths from 300 nm to 1400 nm. Absorption coefficient (α) was calculated using the equation

$$\alpha = 1/d \ln (1/T) \quad (1)$$

Where d and T respectively represents the thickness and transmittance of films [39].

2.3 Photocatalytic Degradation of Methylene Blue

The photocatalytic activities of the films were evaluated by the degradation of methylene blue (MB) over a period of 480 minutes at ambient temperature and pressure. The Ta₂O₅ film was immersed in 50 ml of MB solution (4mg/L). Prior to photocatalytic reaction the solution was kept in the dark for 30 min to establish the adsorption-desorption equilibrium. The reactor was a laboratory-built system comprising of a 300 W high-pressure mercury UV tube emitting near UV radiation with a peak wavelength of 365 nm. The distance between the light source and film was kept constant to achieve a constant light intensity on the film surface. The photocatalytic degradation was monitored by measuring the absorbance of the solution with a UV–Vis spectrophotometer. Factors like dye concentration, pH, temperature etc. were kept constant in all the experiments.

3. Results And Discussion

The reaction of tantalum (V) ethoxide, with the used β -diketone derivatives in 1:1 molar ratio, gave modified alkoxides [Ta(OEt)₄(β -diketonate)]_m (**1-3**) in good yields where m is the unknown nuclearity (the exact nuclearities of the complexes have not been determined in the present work). The ¹H NMR data for compounds **1**, **2** & **3** are tabulated in table 1 and ¹³C NMR values for these compounds are shown in table 2. The ¹H NMR of compound **3** shows three sets of triplet (δ 0.84, 1.04 and 1.07) and quartet (δ 3.72, 3.89 and 3.91) suggesting that in solution the molecule contains OEt ligands in three types of environments in an intensity ratio of 2:1:1. Singlets at δ 1.89 and 5.12 respectively indicate the presence of methyl and methine protons of the 3,3-Dimethyl-2,4-pentanedione ligand. Similarly, ¹H NMR spectra of compounds **1** & **2** also demonstrate octahedral structure for the precursor complexes. Moreover, the IR spectra of each complex exhibited bands for $\nu_{C=O}$ in the range of 1640 cm⁻¹ to 1690 cm⁻¹ and ν_{C-C} in the range of 1550 cm⁻¹ to 1560 cm⁻¹ insinuating the presence of the substituted β -diketonate ligand.

The thicknesses of the films were investigated via variable angle ellipsometry. It was found that the thicknesses of the films were $\approx$ 200 nm. Moreover, the thickness of the glass substrate was observed to be 3 mm with a refractive index of 1.52.

3.1 X-Ray photoelectron spectroscopy analysis

The chemical environment of the fabricated films was determined through XPS. All the films calcined under oxygen flow as well as ammonolyzed films **NA** and **NC** insinuated same chemical environment. However a comparison between the XPS survey spectra of ammonolyzed films **NA** fabricated from synthesized precursor [Ta(OCH₂CH₃)₄(CH₃COCHClCOCH₃)]_m (**1**), **NB** fabricated from precursor [Ta(OCH₂CH₃)₄(CF₃COCH₂COCH₃)]_m (**2**) at 500 °C and film **B** fabricated from precursor (**2**) but calcined under oxygen flow is as shown in fig.1 (a). The spectra confirm the presence of Ta, O, N, F and C elements. The peak at binding energy of 286.0 eV is for C 1s which is used as reference.

Fig. 1 (b) illustrates the chemical state of Tantalum metal obtained for all the fabricated films. The presence of symmetric 4f peaks for Ta⁵⁺ and absence of Ta⁰ metal peaks, confirming the presence of

tantalum as Ta₂O₅. Moreover, the peaks at binding energy 26.29 and 22.72 eV confirms the presence of O–Ta–O 4f_{7/2} and O–Ta–N 4f_{7/2} [47]. However, for film **NB**, the peak for Ta-4f_{7/2} is shifted to high energies and appears at 29.21 eV. This shift may be attributed to high fluorine anion activity indicating a fluorinated oxide phase of tantalum (O–Ta–F) [48].

Notably, fig. 1 (c) shows the chemical environment of F 1s core electrons present in film **NB** with peak at 689.08 eV, confirming the substitutional fluorine atoms which occupied the oxygen sites in the lattice forming O-Ta-F bonds [49]. The fluorine atoms are believed to originate from the 1,1,1-Trifluoro-2,4-pentanedionate ligand upon degradation at high temperature.

However, the analysis of chemical environment of ammonolyzed film **NA** (Fig. 3d) confirms the interstitial nitrogen in Ta₂O₅ with a sharp peak at binding energy 402.00 eV and a weak intensity peak at binding energy 397.73 eV insinuating the binding of 1s electron of substitutional N atom in the environment as O–Ta–N in lattice of N-doped Ta₂O₅. Similar environment was observed for film **NC**. The XPS spectra observed above for undoped and N-doped thin films are also in concordance with our previous report [30].

The overall atomic percentage of doped nitrogen and fluorine atoms is tabulated in table 3.

3.2 Crystal structure analysis

The diffractograms of Ta₂O₅ thin films are shown in fig. 2. The films **A**, **B**, **NA**, **NB** and **NC** were amorphous. Diffraction peaks at 2θ = 23.41°, 46.59° for film **D** (control) were observed and respectively indexed to (-1 0 1) and (2 0 0) metastable triclinic crystal planes of H-Ta₂O₅ phase described by space group *P*^{*}₁ [JCPDS card no: 00-021-1198] [50]. Interestingly, diffractogram obtained for film **C** exhibit diffraction peaks for hexagonal as well as triclinic crystal structure of Ta₂O₅. The peaks at 2θ = 22.90°, 28.49°, 46.89°, 51.20° and 57.90° were indexed to (0 0 3), (2 0 0) (0 0 6), (2 2 0) and (2 1 1) hexagonal crystal planes of δ-Ta₂O₅ described by space group *P*6/*mmm* [JCPDS card no: 00-018-1304] [51] and peaks at 2θ = 32.38° and 40.15° were respectively indexed to (0 -1 9) and (0 -1 13) metastable triclinic crystal planes of H-Ta₂O₅ phase described by space group *P*^{*}₁ [50]. Diffraction peaks corresponding to crystalline TaON at 2θ = 28.2° and 37.2° and TaOF₂ at 2θ = 22.8°, 32.5°, 46.6° and 52.5° were not observed [52-55].

The dependence of crystallization of Ta₂O₅ on temperature, pressure and method of preparation is experimentally well established. Therefore, on the basis of these factors the crystallographic phases of Ta₂O₅ are categorized into three groups: (a) Low-temperature, (b) High-temperature and (c) High pressure phases. Phases *L*, *T*, *TT*, *β*, and *δ* are assigned to Low-temperature category with temperature ranging from 470° to 1360 °C while, at High-temperature (T> 1360 °C) *H*-phase is most stable. The difference in structure for *δ* and *H* phase is exhibited in fig. 2 [56].

For thin films, investigations by Fukomoto et.al have shown [57] that hexagonal structure of δ-Ta₂O₅ described by space group *P*6/*mmm* as most stable. This structure is characterized by value of lattice

constants $a = 7.24 \text{ \AA}$; $b = 7.24 \text{ \AA}$ and $c = 11.61 \text{ \AA}$. In this structure the Ta atoms are located at Wyckoff positions 1a and 3f, while the O atoms are placed at the Wyckoff positions 1b, 3g, and 6l.

According to reports, *H*-phase is formed when Ta_2O_5 is heated to a temperature is greater than 1360°C . When it is cooled to room temperature metastable triclinic crystal structures can be formed. The triclinic symmetry is a distorted tetragonal structure and has a fractional occupancy of 75% in one Wyckoff position corresponding to oxygen [58]. Interestingly, at a temperature of 500°C (Low-temperature range) metastable triclinic crystal structure of *H*- Ta_2O_5 phase described by space group P^*_{-1} was observed in the films. This observation may highlight the dependence of crystallization of Ta_2O_5 on the method of preparation and growth. Therefore, the XRD patterns further substantiates the existence of structure property relationship between the precursor and the final metal oxide film in the sol-gel process. The observed patterns obtained for films **A**, **B** prepared by complexes **1** and **2** respectively, may be attributed to comparatively reduced rate of hydrolysis resulting in the formation of small oligomeric units leading to the elevation of crystallization process to a higher temperature. Moreover, peaks identifying stable hexagonal phase (film **C**) upon modification of $\text{Ta}(\text{OCH}_2\text{CH}_3)_5$ to complex **3** is believed to be the an intermediate state for phase transformation from metastable triclinic phase and may be attributed result of faster rate of hydrolysis as compared to complexes **1**, **2** and $\text{Ta}(\text{OCH}_2\text{CH}_3)_5$. The rate of hydrolysis is key factor in determining the structure of material. In general, tantalum alkoxides undergoes hydrolysis rapidly followed by slower polycondensation, resulting in excessive cross-linking of oligomers. Consequentially, an extensive network is generated which increases the rate of nucleation and growth. This in turn lowers the crystallization temperature for Ta_2O_5 .

However, for films **NA**, **NB** & **NC** the observed diffraction patterns were consistent with the previous reports insinuating that incorporation of non-metals such as C, N or F may inhibit the process of crystallization by reducing the mobility rate of tantalum and oxygen atoms and consequentially, reducing the rate of nucleation [40-43].

The average crystallite sizes of the tantala nanoparticles on films were calculated by Scherrer equation and tabulated in table 4.

3.3 Topographical features

AFM micrographs of the films are illustrated in fig. 3. The images show non-compact morphologies of the deposited Ta_2O_5 thin films and the absence of cracks. RMS surface roughness of the films is tabulated in table 4. The micrographs clearly show that surface roughness of films increases as a function of crystallite size of Ta_2O_5 nanocrystallites. However, the films fabricated from the gels of complexes **1**, **2** and **3** were found to be smoother than the films fabricated from the parent alkoxide. It is believed that nucleophilic substitution of ethoxy group of tantalum (V) ethoxide precursor by substituted 2, 4-pantanedione derivatives, reduced the rate of hydrolysis and thus extent of cross-linking resulting in easier relaxation of polymer strands. Consequentially the films are stable, continuous and smoother. Also

the RMS roughness of ammonia-calcined films was observed to significantly lower than that of oxygen calcined films.

The lowering of surface roughness of films on treatment with ammonia at 500 °C may once again be attributed to the incorporation of nitrogen leading to the elevation of crystallization process to a higher temperature and hence smoother surface.

3.4 Optical Characterisation

The optical transmittance obtained for all the films is shown in fig.4. The spectra show strong transmission features at 360 nm and 390 nm with transmittance extending in the visible region in the range of 60% -80% for all the films. Films **A, B, C** and **D** exhibited higher transmittance (75%-80%) than ammonolyzed films **NA, NB** and **NC** (50%-65%). Notably, red shift in the wavelength of transmission edge was observed on incorporation of nitrogen and fluorine.

Moreover, the decrease in transmittance and red shift was greater upon fluorine incorporation. Since fluorine doping has not been extensively studied in tantala films, thus the observed transmittance can be due to several possibilities. The most relevant possibility is that a minimum energy state is achieved when the fluorine atom replaces the Oxygen atom and forms a bond with a tantalum atom. Thus, the O atom is displaced to an interstitial site generating a defect state in the mid-gap region near to the conduction band. This may be attributed to the fact that F atom accepts one electron which is originally localized at the O site, while the remaining electron stays in the Ta region with the state just below the conduction band minimum. The remaining electrons can easily be transferred away due to its high energy state and leave a positively charged F doped center leading to significant decrease in transmittance and shift of $\lambda_{\max}$ and most importantly decrease in the band gap of F-doped Ta₂O₅ film from reported value of 3.9 eV to 3.05 eV [59, 60].

Investigations focused on the band gap engineering have shown that the conduction band of pure Ta₂O₅ is composed of Ta 5d orbital with a negative potential of -7.3 eV and the valance band is made up of O 2p orbital having a negative potential of -3.4 eV, hence resulting in a wide band gap of 3.9 eV [44]. In general, when an oxygen vacant site is generated in the lattice of Ta₂O₅ due to removal of oxygen atom, two electrons localize on the two adjacent Ta atoms leading to the reduction of Ta⁺⁵ to Ta⁺⁴. Consequentially, donor states are formed which are 0.75 – 1.18 eV below the conduction band thereby, reducing the overall band gap energy of Ta₂O₅ nanocrystallites [61].

However, the replacement of oxygen atom with an anion in the lattice site may affect the electronic edges or introduce impurity states between the valance band and conduction band of Ta₂O₅. When oxygen is replaced with lighter elements such as nitrogen, carbon or boron, the valance band of Ta₂O₅ will possibly be depopulated by one, two or three electrons (depending on dopant respectively). At the same time, there is generation of intra band gap states which results in the increase of negative potential of valance band of Ta₂O₅ and absorption in near UV or visible region. However, if we keep the irradiation at 365 nm as the

case in this report, the population of electrons will increase significantly in the conduction band and simultaneously the number of holes generated will also increase leading to an enhanced photocatalytic performance.

The band gap energy of all films was quantitatively determined from Tauc equation corresponding to direct gap n-type semiconductors via plotting $(\alpha h\nu)^2$ versus photon energy (E_g) (fig. 5) [62]. The band gap of Ta₂O₅ on film D was calculated to be 3.55 eV, which was 0.35 eV less than the reported band gap of pure Ta₂O₅ nanoparticles in powder form, showing the efficiency of films over powdered nanomaterials as photocatalysts [30]. Moreover, lowering of band gap was observed upon substituting one ethoxide ligand with substituted-2,4-pentanedione. The observed band gap values of film **A**, **B** and **C** are 3.48 eV, 3.47 eV and 3.52 eV respectively. This lowering of band gap may be attributed to the fact that substitution of ethoxide ligands with different β -diketones increased the steric hindrance offered to the substitution of hydroxyl group leading to reduced rate of hydrolysis to an extent that only small oligomeric units are formed. It is reasonable to conceptualize that this will lead to elimination of defects in Ta₂O₅ upon calcination at 500 °C [36, 54]. From the observed band gap values, it is believed that the rate of hydrolysis in complex **3** is faster than that of **1** and **2** resulting in the formation of small oligomeric units, forming short cross-linked matrix in the gel of precursor **3** during polycondensation reaction. As a result Ta₂O₅ nanocrystallites on film **C** fabricated from complex **3** is more crystalline leading to high band gap as compared to films **A** and **B**.

Interestingly, significant narrowing of band gap as observed for ammonolyzed films **NA**, **NB** and **NC** (3.31 eV, 3.05 eV and 3.37 eV respectively). This substantiates the increase of negative potential of valence band in Ta₂O₅ due to the mixing of O 2p orbitals with the 2p orbitals of interstitial nitrogen in films **NA**, **NC** and fluorine in film **NB**. As already discussed earlier, upon fluorine doping the band gap value of Ta₂O₅ depreciates from 3.55 eV to 3.05 eV, which implies a change from inactive to active in the near UV and visible region thereby making it lucrative for solar energy conversion applications.

3.5 Photocatalytic performance under UV irradiation

The photocatalytic activity of the fabricated films was assessed by the degradation of methylene blue dye (MB) under UV light irradiation. Fig. 6 shows the percent degradation $[(C/C_0) \times 100]$, where $C = (C_0 - C_t)$ and C_0 is the initial pollutant concentration after equilibrium while, C_t is the pollutant concentration after t minutes of irradiation [63-65]. After UV irradiation on all films dipped in MB dye solution for 480 minutes (8 hrs.), film **NB** degraded methylene blue up to 87.27% followed by **NA** and **NC** (77.28% and 74.21% respectively). However, films (**A**, **B**, **C** and **D**) calcined under oxygen flux degraded only 67.83%, 69.76%, 58.87% and 62.01% respectively.

The pioneering work of Asahi et.al [64] lead to the development of new generation of non-metals doped semiconductor photocatalysts. It is well established that for a material to be an efficient photocatalyst, it is required to have large surface area and/or high crystallinity so that increased number of active sites and accelerated charge separation can be achieved. Moreover, reduction ability of the excited

photoelectrons is also an important factor which affects the photocatalytic performance of the material [66-69]. Although investigation of Ta_2O_5 as photocatalyst is still in its early stages but recent investigations show that since tantalum based oxides have relatively negative conduction band which enables them to have strong reduction ability. This unique property makes these tantalum based oxides a promising candidate for efficient photocatalysis.

However, as it is obvious from the band gap studies discussed in section 3.4 that large band gap can mitigate the photocatalytic performance of Ta_2O_5 as it causes inactivity in near UV-visible region. Nevertheless, nitrogen and fluorine doping have been successful in narrowing the band gap of these materials. The higher photocatalytic activities of N-doped films **NA** and **NC** may be attributed to smaller band gaps and existence of increased defects as well as oxygen vacancies. In these films substitutional as well as interstitial nitrogen is present as confirmed by XPS analysis in section 3.2. This interstitial nitrogen atom relatively has higher electronegativity and thus binds to only one lattice oxygen, thereby, shifting the oxygen atom out of that plane and towards the interstitial cavity forming a NO fragment which binds to Ta through its π electrons. Consequentially, two defect bands for π bonding system of NO is generated i.e. π bonding and π^* antibonding NO state. While, the π NO lies below the valance band minimum but the π^* NO is 0.64 eV above the valance band maximum which could be responsible of reduction in the band gap leading to an increased photocatalytic efficiency [70].

On the other hand, in case of F-doped film **NB** the exceptional photocatalytic performance may be possibly attributed to the increased charge separation efficiencies. Although the 2p state of fluorine has one unpaired electron as compared to oxygen which ideally should be transferred to the empty tantalum state but this electron is found trapped at one of the 5d states which is about 0.75 eV to 1.18 eV below the conduction band, leading to the generation of defect band state upon chemical reduction of Ta^{+5} to Ta^{+4} [39, 69].

Fig.7 exhibits the changes in concentration of MB as a function of irradiation time for the all films. The slope of obtained from straight lines of the plot $\ln C_0/C$ vs irradiation time represents the rate of reaction (k) and high value of R^2 insinuate that the degradation reaction follow pseudo- first order kinetics according to Langmuir– Hinshelwood model [71]. The rate constants (k) and R^2 values are tabulated in table 5.

Thus, reduction of the rate of recombination can be done by using electron-hole scavengers. In the reductive degradation process, the rate of the oxidative half reaction concerning positively charge hole in the valance band is closely related to the effective removal of the partner species, i.e. photoelectrons present in the conduction band, by suitable electron scavengers. This electron scavenger should be present in the solution and available at the Ta_2O_5 films and solution interface [72]. Whereas, in the oxidative destruction of a target organic substrate, a hole scavenger should be present in the same environment so as to consume the generated hole in the valance band [73, 74]. The most frequently used electron scavenger is molecular oxygen which leads to formation selective oxygen species and thus participates in the process of oxo-functionalization of hydrocarbons. On combining with photoelectrons

on the surface of Ta₂O₅ the O₂ molecules gives exceptionally reacting species such as the superoxide radical O₂[•] and the singlet oxygen ¹O₂ leading to the generation of strong oxidants like H₂O₂ and O₃ [72-74].

Since h⁺, •OH and •O²⁻ radicals are highly reactive oxidizing species which effect the degradation of methylene blue in the order h⁺ > •OH > •O²⁻ [75]. Therefore, photo-induced reactions in presence of a catalyst occur via absorption of a photon (having energy equal to or greater than E_g of the catalyst) leading to a charge separation due to the promotion of an electron from the VB to CB of semiconductor catalyst. This results in generation of a hole (h⁺) in VB. This activated electron combine with an oxidant producing a reduced product and also h⁺ combine with a reductant producing an oxidized product. The oxidant may be a dye molecule or electron acceptors such as O₂ absorbed on the catalyst surface or dissolved in water generating a superoxide radical anion •O²⁻ and similarly, h⁺ can combine with dye molecule to form R⁺ or react with OH⁻ or H₂O oxidizing them into •OH radicals. The resulting •O²⁻ and •OH radicals can oxidize most azo dyes to the mineral end-products. Accordingly, the reactions occurring at semiconductor surface causing degradation of dyes can be expressed as:

The enhanced performances of the films calcined under ammonia environment is believed to be a consequence of band gap narrowing upon incorporation of nitrogen and fluorine in Ta₂O₅ lattice leading to increased number photogenerated electrons and holes created by the excitation of electrons and decreased rate of e⁻/h⁺ pair recombination leading to enhanced degradation of MB at the surface of Ta₂O₅ nanostructures film [73-75]. Thus the observed photodegradation of MB establishes that photocatalytic activity of tantalum films strongly depends on the band gap of the catalyst, which in this case had been engineered via chelating the parent alkoxide with nucleophilic β-diketone ligands to

control the rate of hydrolysis and importantly the formation of tantalum oxyfluoride and oxynitride nanocrystallites upon ammonolysis.

Although the investigation of Ta₂O₅ as photocatalyst for degradation of organic pollutants present in water is in its early stages but recent reports [76-80] indicate that with proper band gap engineering it has the potential to be an alternative to TiO₂. E. Mendoza-Mendoza et.al [76] prepared Ta₂O₅ nanoparticles via mechanical milling of TaCl₅ and LiOH/KOH reagents followed by a subsequent **calcination** step. It exhibited the in-situ generation of LiCl/KCl and the partial **crystallization** of Ta₂O₅ at low-temperature. These nanoparticles showed enhanced degradation rate of MB attaining a degradation percentage of about 81% within 180 min under UV-vis irradiation. A.A. Ismail et.al [77] synthesized **mesoporous** sulfur (S)-doped Ta₂O₅ **nanocomposites** via **sol-gel** reaction of **tantalum chloride** and **thiourea** in the presence of a F127 **triblock copolymer** as **structure directing agent**. These hybrids gels were calcined at 700 °C for 4 h to obtain mesoporous S-Ta₂O₅ nanocomposites. They found an excellent **photocatalytic activity** of about 92% for the **photodegradation** of **methylene blue**, after three hours **illumination** under visible light. Similarly, Xiaomin Shi et.al [78] reported the synthesis of novel 3D N-doping Ta₂O₅ **nanoflowers** (NFs) at different annealing temperatures ranging from 700 °C to 850 °C under a NH₃ flux. The nanoflowers prepared at 750 °C were reported to demonstrate high surface adsorption and enhanced **photocatalytic** performance via degradation of **Methylene Blue** (MB). Moreover, Jing Li et.al [79] reported an improved photocatalytic performance of microspherical Ta₂O₅ powders prepared by flame assisted hydrolysis of tantalum ethoxide. Recently, G. Nagaraju et.al [80] reported the preparation of Ta₂O₅ nanoparticles by the ultrasonic-assisted method and 96 % degradation of MB after 2 h under visible **light irradiation**.

4. Conclusion

Tantalum pentoxide, oxynitride and oxyfluorides thin films were fabricated using tetraethoxo (β-diketonato) tantalum (V) complexes synthesized in the present work. All the films were prepared in duplicate, one set of films was calcined at 500 °C under oxygen flow for 1 hr while the other set of films was subjected to ammonolysis at the same temperature for same duration. Notably, upon comparative evaluation of all the films a structure-property relationship was discerned. It was observed that substituted 2, 4-pentanedione derivatives, reduced the rate of hydrolysis and thus extent of cross-linking leading to easier relaxation of polymer strands in sol-gel process. Consequentially, small oligomeric units are generated due to which phase transformation as well as elevation of crystallization temperature is observed for Ta₂O₅ crystallites.

Interestingly, the X-ray photoelectron spectroscopy results exhibited the presence of fluorine as tantalum oxyfluoride in ammonolyzed film fabricated from [Ta(OEt)₄(CF₃COCH₂COCH₃)]_m precursor, whereas, nitrogen was incorporated into the films fabricated from [Ta(OCH₂CH₃)₄(CH₃COCHClCOCH₃)]_m and [Ta(OCH₂CH₃)₄(CH₃COC(CH₃)₂COCH₃)]_m precursors which were ammonolyzed. Moreover, chemical environment of the films prepared from same precursors but calcined under oxygen flow at 500 °C for 1hr insinuated the formation of tantalum pentoxide only. Significant narrowing of band gap energy was

observed from 3.55 eV for film D prepared from unmodified tantalum (V) ethoxide to 3.05 eV for film **NB** (tantalum oxyfluoride) prepared from $[\text{Ta}(\text{OEt})_4(\text{CF}_3\text{COCH}_2\text{COCH}_3)]_m$. Consequentially, film NB exhibited enhanced photocatalytic performance and photodecomposed 87.27 % of methylene blue under UV irradiation for a period of 480 minutes. The enhanced photocatalytic performance of $\text{Ta}_2\text{O}_x\text{F}_y$ is attributed mainly to the incorporation of fluorine which facilitated lowering of band gap energy and reduction in the rate of recombination of the photogenerated electrons and holes. Compared to their counterpart films **A** and **C** calcined under oxygen flow which degraded 67.83% and 58.87% of methylene blue dye, the ammonolyzed films **NA** and **NC** demonstrated enhanced photocatalytic performance by degrading 77.28% and 74.21% methylene blue respectively under UV irradiation for a period of 480 minutes.

This study establishes the generation of Tantalum oxyfluoride and oxynitride nanocrystallites upon ammonolysis of the films fabricated from the gels of synthesized tetraethoxo (β -diketonato) tantalum (V) precursors. Moreover, the findings reveal lowering of band gap energy of Ta_2O_5 via formations of $\text{Ta}_2\text{O}_x\text{F}_y$ and $\text{Ta}_2\text{O}_x\text{N}_y$ rendering it activity in visible light. Hence, these films can become potential candidates for possible applications in industrial effluent treatment and as photo-electrodes in photo-electrochemical studies.

Declarations

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Conflict of Interest

The authors report no conflict of interest.

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Tables

Table 1: Atomic percentage of doped nitrogen and fluorine for Ta₂O₅ thin films.

SAMPLE	Nitrogen content (%)	Fluorine Content (%)
NA	0.45	0.00
NB	0.00	1.00
NC	0.25	0.00

Table 2: Average crystallite sizes, RMS roughness, band gap energies (E_g) and percent degradation of MB dye for Ta₂O₅ thin films.

Sample	Average crystallite size (nm)	RMS Roughness (nm)	Band gap energy [E _g] (eV)	Degradation of MB (%)
A	—	3.12	3.47	67.83
B	—	2.89	3.46	69.76
C	20.4	3.75	3.52	58.87
D	8.2	3.21	3.55	62.01
NA	—	1.89	3.26	77.28
NB	—	1.14	2.94	87.27
NC	—	2.68	3.32	74.41

Table 3 Rate constants for degradation reactions of methylene blue in presence of undoped Ta₂O₅, N-doped Ta₂O₅ and F-doped Ta₂O₅ thin films as photocatalyst.

Sample	Rate constant [<i>k</i>] (<i>min</i> ⁻¹)	R ²
A	0.001963	0.988312
B	0.002416	0.996184
C	0.002486	0.996785
D	0.002063	0.986968
NA	0.003055	0.996812
NB	0.002819	0.997577
NC	0.003839	0.972856

Table 4: Average crystallite sizes, RMS roughness, band gap energies (E_g) and percent degradation of MB dye for Ta₂O₅ thin films.

Sample	Average crystallite size (nm)	RMS Roughness (nm)	Band gap energy [E _g] (eV)	Degradation of MB (%)
A	—	3.12	3.48	67.83
B	—	2.89	3.47	69.76
C	20.4	3.75	3.52	58.87
D	8.2	3.21	3.55	62.01
NA	—	1.89	3.31	77.28
NB	—	1.14	3.05	87.27
NC	—	2.68	3.37	74.41

Table 5: Rate constants for degradation reactions of methylene blue in presence of undoped Ta₂O₅, N-doped Ta₂O₅ and F-doped Ta₂O₅ thin films as photocatalyst.

Sample	Rate constant [<i>k</i>] (<i>min</i> ⁻¹)	R ²
A	0.001963	0.988312
B	0.002416	0.996184
C	0.002486	0.996785
D	0.002063	0.986968
NA	0.003055	0.996812
NB	0.002819	0.997577
NC	0.003839	0.972856

Figures

Figure 1

(a) XPS survey spectra of Ta₂O₅ thin films NA fabricated from complex 1; B, NB from complex 2 and calcined under oxygen/ammonia gas flow for 500 °C for 1h. (b) XPS profile of Ta 4f. (c) XPS profile of F 1s and (d) XPS profile of N 1s.

Figure 2

XRD patterns of Ta₂O₅ thin films A, NA fabricated from complex 1; B, NB from complex 2; C, NC from complex 3 and D from unmodified Ta(OEt)₅ and calcined under oxygen/ammonia gas flow for 500 °C for 1h.

Figure 3

2D AFM surface images of Ta₂O₅ thin films A, NA fabricated from complex 1; B, NB from complex 2; C, NC from complex 3 and calcined under oxygen/ammonia gas flow for 500 °C for 1h.

Figure 4

The optical transmittance of Ta₂O₅ thin films A, NA fabricated from complex 1; B, NB from complex 2; C, NC from complex 3 and D from unmodified tantalum (V) ethoxide and calcined under oxygen/ammonia gas flow for 500 °C for 1h.

Figure 5

Plot of $(\alpha h\nu)^2$ v/s photon energy (E_g) for Ta₂O₅ thin films A, NA fabricated from complex 1; B, NB from complex 2; C, NC from complex 3 and D from unmodified tantalum (V) ethoxide and calcined under oxygen/ammonia gas flow for 500 °C for 1h.

Figure 6

Photocatalytic degradation of methylene blue by Ta₂O₅ thin films under UV light over a time period of 480 minutes.

Figure 7

Graphical determination of pseudo-first order reaction rate for the degradation of methylene blue by Ta₂O₅ thin films A, NA fabricated from complex 1; B, NB from complex 2; C, NC from complex 3 and D from unmodified tantalum (V) ethoxide under UV light over a time period of 480 minutes.