A Selective Synthesis of TaON Nanoparticles and Their Comparative Study of Photoelectrochemical Properties

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Abstract: A simplified ammonolysis method for synthesizing single phase TaON nanoparticles is presented and the resulting photoelectrochemical properties are compared and contrasted with as-synthesized Ta_2O_5 and Ta_3N_5. The protocol for partial nitridation of Ta_2O_5 (synthesis of TaON) offers a straightforward simplification over existing methods. Moreover, the present protocol offers extreme reproducibility and enhanced chemical safety. The morphological characterization of the as-synthesized photocatalysts indicate spherical nanoparticles with sizes 30, 40, and 30 nm Ta_2O_5, TaON, and Ta_3N_5 with the absorbance onset at ~320 nm, 580 nm, and 630 nm respectively. The photoactivity of the catalysts has been examined for the degradation of a representative cationic dye methylene blue (MB) using xenon light. Subsequent nitridation of Ta_2O_5 yields significant increment in the conversion (ζ: Ta_2O_5 < TaON < Ta_3N_5) mainly attributable to the defect-facilitated adsorption of MB on the catalyst surface and bandgap lowering of catalysts with Ta_3N_5 showing > 95% ζ for a lower (0.1 g) loading and with a lamp with lower Ultraviolet (UV) content. Improved Photoelectrochemical performance is noted after a series of chronoamperometry (J/t), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) measurements. Finally, stability experiments performed using recovered and treated photocatalyst show no loss of photoactivity, suggesting the photocatalysts can be successfully recycled.

Keywords: Ta_2O_5; TaON; Ta_3N_5; methylene blue; photocatalysis; photoelectrochemistry

1. Introduction

Large and small bandgap single metal oxides have traditionally been the class of materials relied upon to assist with photocatalytic environmental remediation [1]. They are typically used (i) as standalone photocatalysts, (ii) with variations in physical dimensions, (iii) with other additives to form heterostructured junctions for enhancing photoactivity [2]. Several studies have indicated that the last of the three approaches is the most effective. Some of the popular strategies included in this approach is using the single metal oxides with co-catalysts such as metals [3], with carbon as additive [4], or with other oxides [5], to either increase optical absorbance or enhance charge separation or both. Such a single metal oxide photocatalyst or their composites have proven their viability in both gas and liquid phase environmental pollutant remediation. The leading examples of single metal oxide photocatalysts

are TiO_2 or ZnO and their combinations with metals [6], an additional (different) oxide [7]. These additives primarily aid in improving photoactivity.

The tantalum-based oxides are less studied although they demonstrate optical and electronic responses, just like TiO_2 and ZnO [8,9]. A leading cause for the limited activity of the tantalum oxide is its inherently large bandgap of 3.9 eV which makes it photoactive only in the far left of the ultraviolet (UV) compared to the popular TiO_2. Besides, tantalum is a more expensive source compared to titanium or zinc. However, as evident from recent research, tantalum–based oxides continue to demonstrate multifunctionality making them worthy of consideration for a systematic investigation [9–12]. Tantalum oxide has a bandgap that straddles the redox potential of water making it a viable candidate, if properly optimized to absorb visible light, that would facilitate production of solar fuels [13]. For example, they can be integrated with the most earth abundant and eco-friendly element—nitrogen—to form oxynitrides: TaO_xN_y (y = 1 − x) [14,15]. This singular option allows for tuning the optical bandgap (E_g) over a wide range of 1.6–4.0 eV solely based on Ta: O: N ratio. Such phases are reported to enhance visible light absorbance with O: N ratio dependent bandgap tunability as shown in Scheme 1. These customizable oxidation potential levels can aid in tuning photo-driven processes triggered using broad spectrum visible absorption. tantalum-based oxides and oxynitrides also demonstrate compatibility with inorganic (metal and other semiconductors) and organic additives [16,17].
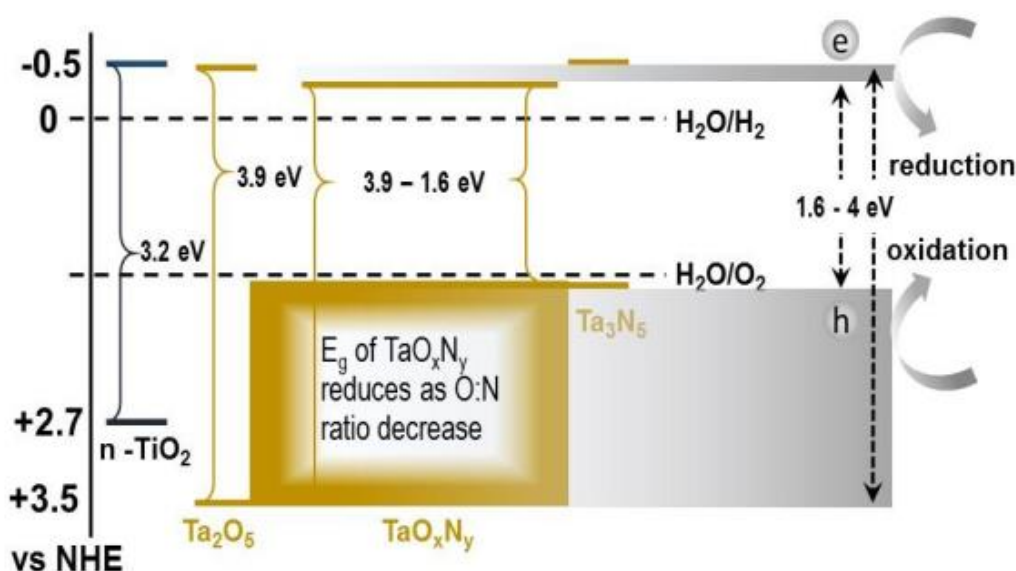
Scheme 1. The bandedge positions of the tantalum-based oxides, oxynitriles (TaO_xN_y), and nitride (Ta_3N_5) relative to the popular TiO_2. As indicated, tantalum-based oxides are amenable to bandgap (Eg) change via tuning the valence band edge by varying O: N ratio to influence photoactivity.

The synthesis and application of tantalum-based oxides, oxynitrides, and their composites have been reported previously in the literature. The catalysts reported here are compared to similar Ta-based catalysts reported elsewhere [18–21]. One of the prominent applications of pure Ta_2O_5 [22] and doped (with alkali) Ta_2O_5 [23] is towards water decomposition/hydrogen evolution [24–26]. Environmental applications such as photocatalytic oxidation of dyes have also been observed [20,27–29]. Following complete nitridation of the Ta_2O_5 results in the formation of Ta_3N_5, which has been reported to aid with water oxidation/oxygen evolution [13,26,30–32]. Further, from a greenhouse gas mitigation standpoint, Ta_2O_5 is also reported to aid with CO_2 reduction [33]. Like other oxides, the photoactivity of tantalum-based oxides is critically influenced by the method used to synthesize them including the additives used in the synthesis and the shape they may evolve [34,35].

This work presents partial and complete nitridation of Ta_2O_5 using two different approaches. The approach to partial nitridation of Ta_2O_5 reported herein is first of its kind is a simple one that

guarantees synthesis of a single phase of TaON. A comparison of the Ta_2O_5, TaON, and Ta_3N_5 activity as photocatalysts for the remediation of a representative environmental pollutant methylene blue (MB) is discussed and compared. The practical viability of TaON is tested by recycling the catalyst multiple times and the results of photoelectrochemical measurements are used to obtain mechanistic insights into the improved performance by the in-house catalysts.

2. Results

2.1. Characterization of the Photocatalyst

2.1.1. Analysis of Nanoparticle Morphology Using Scanning Electron Microscopy (SEM)

The physical features of the commercial and the in-house synthesized samples were examined using the SEM. The commercial samples (Figure S2) are non-spherical with large nanoparticle clusters, with some as big as 300 nm. For the most part these clusters tend to be ~100 nm average diameter. In comparison, the in-house oxide samples are more spherical, with an order of magnitude smaller diameter clusters of 20–30 nm. Further, the size distribution among the in-house nanoparticles is narrow and well controlled, as shown in Figure 1a. The SEM image of the sample obtained after partial and complete nitridation is shown in Figure 1b,c respectively. The nitridation process slightly alters the physical morphology of the clusters, notably introducing the atomic defects. It is to be noted that such defects contribute to the adsorption of pollutant molecules and electron-paramagnetic resonance (EPR) studies are suggested for further exploration of the nature of such defects [36]. The post nitridation particle sizes for the partially and completely nitrided samples is observed to be ~40–50 nm (Figure 1b) and ~30–40 nm (Figure 1c) respectively. To understand further if these clusters contain smaller particles, a transmission electron microscopy (TEM) analysis was performed. TEM analysis is important because a smaller size of the in-house synthesized samples can indicate the availability of more surface, which is consistent with a surfactant—assisted method used for synthesis. It is also important to mention that the availability of more surface is a pre-requisite for ensuring better contact between the photocatalyst and the pollutant molecules leading to enhancement in the dye adsorption and facilitate interfacial redox processes such as catalysis.
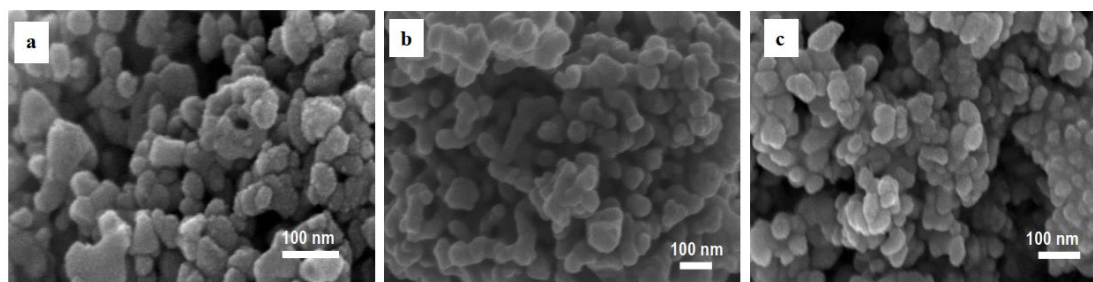

Figure 1. The scanning electron microscope (SEM) image of the (**a**) as-synthesized oxide from Ta-precursor after annealing in air, (**b**) partial nitridation of the annealed oxide, and (**c**) complete nitridation of the oxide. Inherent crystal-defects developed during each synthesis step are noted to add on the altered morphology of the catalyst samples.

2.1.2. HRTEM Analysis of the Photocatalysts Samples before and after Nitridation

The High Resolution Transmission Electron Microscopy (HRTEM) analysis of the in-house synthesized thermally annealed samples before and after nitridation is shown in Figure 2. The particle sizes of the thermally annealed samples in the air (Figure 2a) are ~6–7 nm. The particle sizes of the partially annealed samples in humidified NH_4OH vapor (Figure 2b) are ~10 nm. Finally, the samples prepared by treatment in dry NH_3 are larger at ~20–30 nm. The high-resolution images of all the samples show distinct evidence of crystallinity after annealing. These images indicate that the annealing leads to crystallization, as observed with other oxides [37]. The figures also show the

respective selected area electron diffraction (SAED) pattern of the samples. The presence of the geometric diffraction pattern confirms thermally induced crystallization. The characteristic d-spacings are marked in the image and suggest that the samples shown in Figure 2a–c are respectively Ta_2O_5, TaON, and Ta_3N_5. Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) analysis was performed using N_2 physisorption and the surface area was estimated to be 1.6 m^2/g for commercial Ta_2O_5, 41.08 m^2/g for Ta_2O_5 (in-house), and 17.44 m^2/g for the Ta_3N_5.
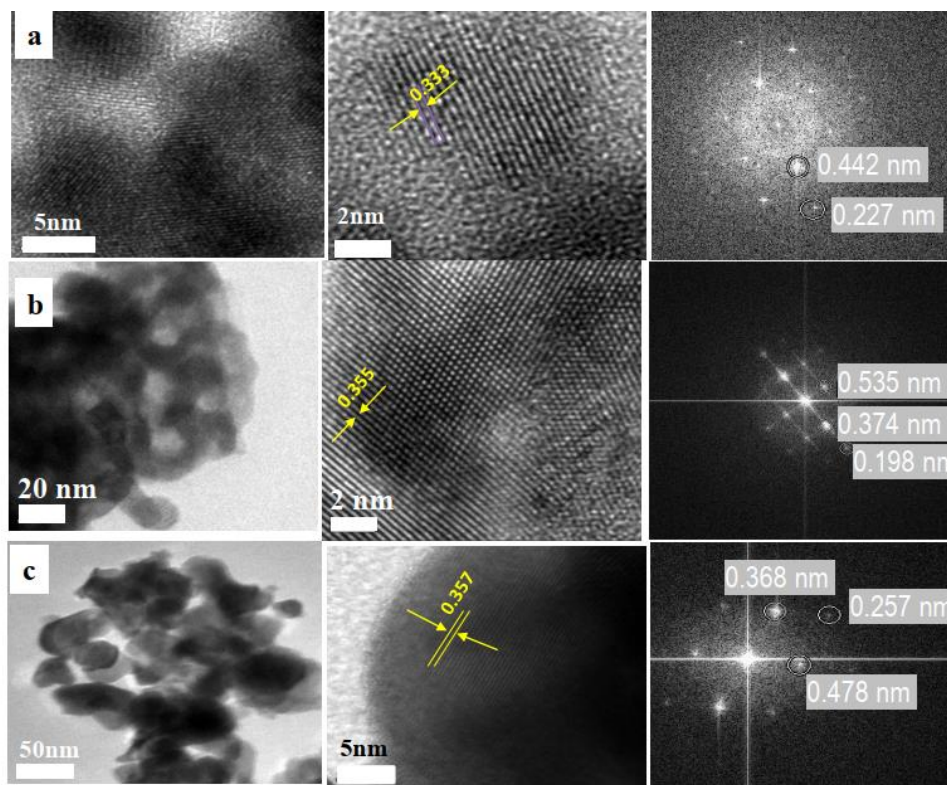

Figure 2. The figure shows the HRTEM images of the in-house synthesized thermally annealed samples (**a**) before nitridation, and (**b**) after partial nitridation (NH_4OH) and (**c**) after complete nitridation (dry NH_3). From left to right the images in (**a–c**) also indicate the characteristic d-spacing, and the SAED pattern confirming that the nanoparticles are crystalline Ta_2O_5, TaON, and Ta_3N_5 respectively.

2.1.3. Phase Identification Using X-ray Diffraction (XRD)

The phase of the oxide and the nitride samples was determined using XRD analysis. The in-house un-annealed sample did not show any distinguishable Bragg peaks indicating that they are amorphous. However, post thermal treatment, the in-house synthesized samples showed distinct Bragg peaks (Figure 3a) indicating that annealing transforms the amorphous samples to polycrystalline aggregates. These characteristic peaks in both samples matched with the standard JCPDS (Joint Committee on Powder Diffraction Systems) database. The commercial and in-house samples indicated a match with file # 00-018-1304 identifying as Ta_2O_5. The XRD of the sample after partial nitridation is shown in Figure 3b and is identified as TaON (JCPDS # 01-071-0178 40). Miller indices as identified in the XRD patterns of the newly synthesized single phase TaON also are shown. The XRD pattern of the fully reduced phase of $Ta_2O_5 - Ta_3N_5$ obtained after conventional high temperature dry ammonia treatment can be indexed to the Ta_3N_5 phase (JCPDS # 00-019-1291) as shown in Figure 3c. The formation of crystalline phases is an essential pre-requisite to any photocatalytic activity [38,39]. Scherer analysis was performed by applying the expression: crystallite size $= \frac{0.9\lambda}{\beta cos\theta}$, where β is the full width at half maximum (FWHM) of characteristic peaks in the sample, θ is the Bragg angle. The particle sizes estimated for Ta_2O_5, TaON, and Ta_3N_5 were ~26 nm, 27 nm, and 29 nm, respectively.
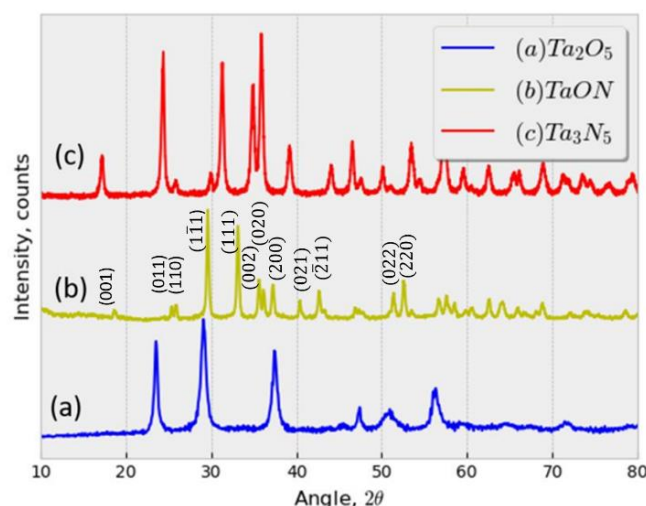
Figure 3. X-Ray diffractograms of the as-synthesized (**a**) Ta_2O_5 (JCPDS # 00-018-1304), (**b**) TaON (JCPDS # 01-071-0178 40), and (**c**) Ta_3N_5 (JCPDS # 00-019-1291).

2.1.4. Optical Analysis Using Spectroscopy

The absorbance spectra of the Ta_2O_5 and the Ta_3N_5 prepared as films on Indium-Tin-Oxide (ITO) coated glass are shown in Figure 4 and the inset shows pictures of the powder of the three samples. The Ta_2O_5 is white (the onset absorbance of the in-house sample extrapolates to 320 nm). Both TaON and Ta_3N_5 are colored and this coloration is indicative of the incorporation of nitrogen. The Ta_2O_5 has a bandgap in the range of 3.6–3.9 eV and the onset noted in this range is consistent with the observations reported on oxides synthesized using wet chemical approaches [40]. This onset is also evidence that photoactivity is driven predominantly by UV light. Unlike Ta_2O_5, the TaON and Ta_3N_5 show a significant red shift into the visible region. The absorbance of TaON (~580 nm) and Ta_3N_5 (~630 nm) are indicative of smaller bandgaps. The experimental determination of the bandgap was performed using the Tauc plot analysis [41,42]. A bandgap of 3.66 eV, 2.1 eV and 1.71 eV for Ta_2O_5, TaON, and Ta_3N_5, respectively was estimated from this analysis as indicated in the inset of Figure 4.
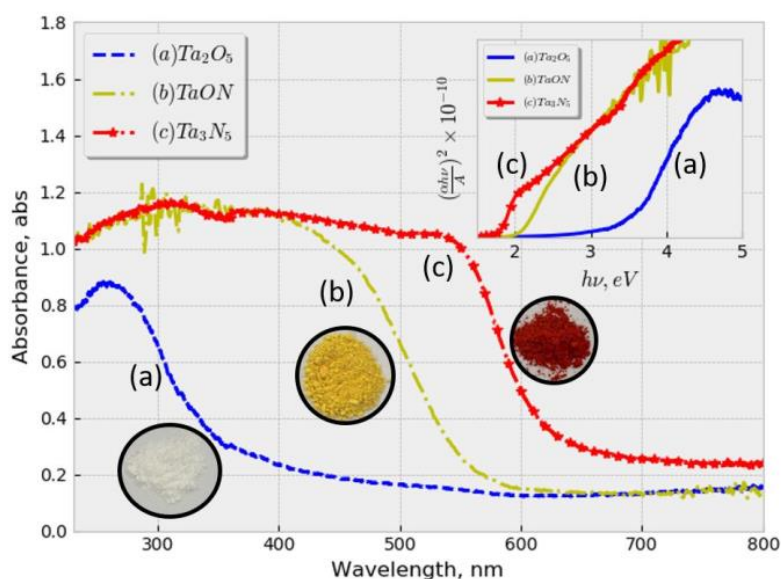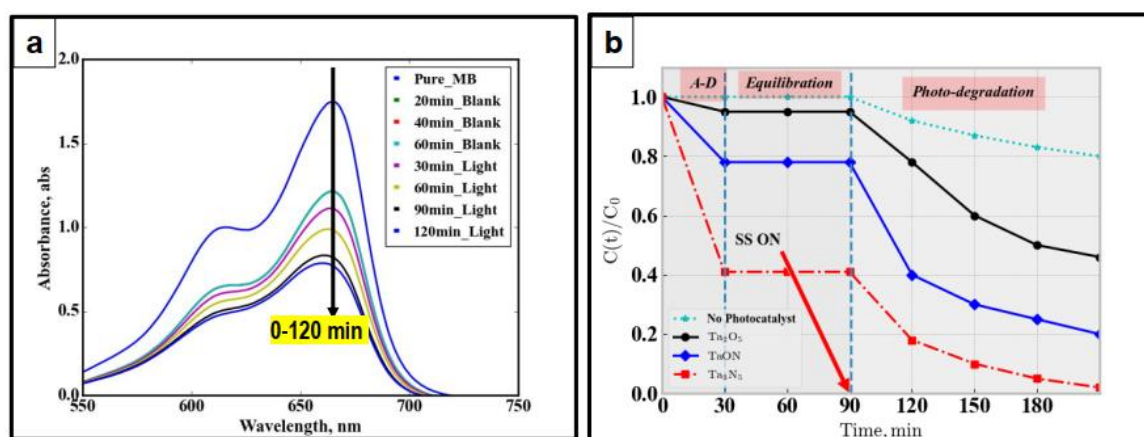

Figure 4. The absorbance spectra of the (**a**) as-synthesized Ta_2O_5, (**b**) TaON, and (**c**) Ta_3N_5. As indicated in the photographs of the samples, the coloration, shown alongside, conforms to the corresponding absorbance spectra. Tauc's plots for bandgap (E_g) estimation are shown in the inset. E_g for Ta_2O_5, TaON, and Ta_3N_5 were estimated to be 3.66, 2.21, and 1.71 eV respectively. (This figure is best viewed in color).

2.2. Evaluation of the Photocatalytic Activity towards Methylene Blue Degradation

2.2.1. Methylene Blue Absorbance and Photolytic Conversion

Methylene blue (MB) is a multi-purpose organic colored dye and a representative model pollutant whose photodegradation is of immense interest [43,44]. The optical spectra of a pure aqueous MB solution demonstrate visible light absorbance with a starting characteristic peak absorbance at 670 nm [45,46]. Therefore, its degradation can be probed using spectrometry by tracking the change at 670 nm. Figure 5a shows the representative dye absorbance before illumination and the effects of photoillumination using UV–vis light. The dye demonstrates notable photolytic conversion with the Xe lamp as the excitation source. The conversion observed was 25%.

Figure 5. (**a**) A set of representative absorbance spectra of the dye, methylene blue, 28.6 mM MB, in the presence of 0.1 g in-house synthesized Ta_2O_5 photocatalyst indicating a gradual decrease under Xe lamp solar simulator (SS). (**b**) A comparison of the adsorption, equilibration, and photocatalytic conversion of MB in the presence of 0.1 g Ta_2O_5, TaON, and Ta_3N_5 each is presented.

2.2.2. Comparing Photoactivity of In-House Ta_2O_5, TaON, and Ta_3N_5

The activity of in-house Ta_2O_5 was compared with TaON (synthesized by using our aforementioned novel approach) and Ta_3N_5 (produced by conventional thermally reduced processes) for MB degradation. As can be seen, the dark absorbance phase during equilibration is remarkably different for the two photocatalysts. Interestingly, a significant drop in absorbance of the dye is noted during dark equilibration with TaON and Ta_3N_5. It is also to be noted that the adsorption of MB increases significantly as the nitrogen content in the nitrogen-derivatives of Ta_2O_5 is increased. The results in Figure 5b highlight the observation that TaON and Ta_3N_5 contribute significantly more towards MB conversion. A conversion of 64%, 80%, and 98% are noted for the Ta_2O_5, TaON, and Ta_3N_5 respectively using Xe lamp illumination. The higher conversion with Ta_3N_5 compared to TaON is attributed to the greater absorbance of the MB on the former.

3. Discussion

The physical/surface, optical, and photocatalytic studies discussed thus far point to the viability of the (i) use of the surfactant–based method to produce well controlled tantalum-based oxide photocatalysts, (ii) their conversion by nitridation to $TaON/Ta_3N_5$, and (iii) their application towards pollutant remediation. Some of the immediate and obvious questions that arise from the preceding analyses are: What is the reason for improved photocatalysis? How stable is the photocatalyst upon repeated use? How does nitridation lead to enhancement in the photocatalytic activity beyond the parent Ta_2O_5 performance? This discussion addresses each of these questions and also highlights some of the limits of the nitridation process.

3.1. Chronoamperometry (j/t) and Linear Sweep Voltammetry (j/V) Measurements

The analysis of photoelectrochemical (PEC) data offer valuable information into the separation and transport mechanisms of charges photogenerated in the catalysts upon illumination. This approach allows for tracking both hole and electrons generated in the catalysts and can be correlated with the photocatalytic activity [47,48]. The chronoamperometry or j/t responses of the commercial and in-house synthesized Ta_2O_5 obtained with a Pt wire as the counter electrode in a 3-electrode PEC cell are shown in the Figure S3A. The multiple on-off chop light cycles show that the response in both films are light triggered and the reproducible nature of these responses indicate that the films formed on the conducting glass slides are reproducible (Figure 6A). Further, the photocurrent after complete nitration to Ta_3N_5 is significantly higher. The bar graph in Figure 6B provides a summary of the average photocurrent from Ta_2O_5, TaON, and Ta_3N_5. The inserts of Figure 6B shows the photographs of the films after the PEC measurements, indicating they are stable (do not delaminate). The in-house Ta_2O_5 shows a photocurrent of 0.42 μA/cm^2 while the commercial Ta_2O_5 response is approximately 0.41 μA/cm^2. The slightly higher photocurrent with the in-house Ta_2O_5 could be attributed to the difference in the physical dimensions of the nanoparticles and/or the improved photoactivity of this film but has to be verified using alternative approaches (discussed below). At the same time, the corresponding photocurrent using TaON and Ta_3N_5 are observed to be ~2 ± 0.5 μA/cm^2 and 2.2 ± 0.2 μA/cm^2 respectively—an almost 9–10-fold increase in the photoresponse. This shows that the photoelectrons generated in the nitrided samples are significantly higher compared to the oxide and can be attributed to the effective visible light utilization resulting from the lowered bandgap.

(**A**)

Figure 6. *Cont.*

(B)
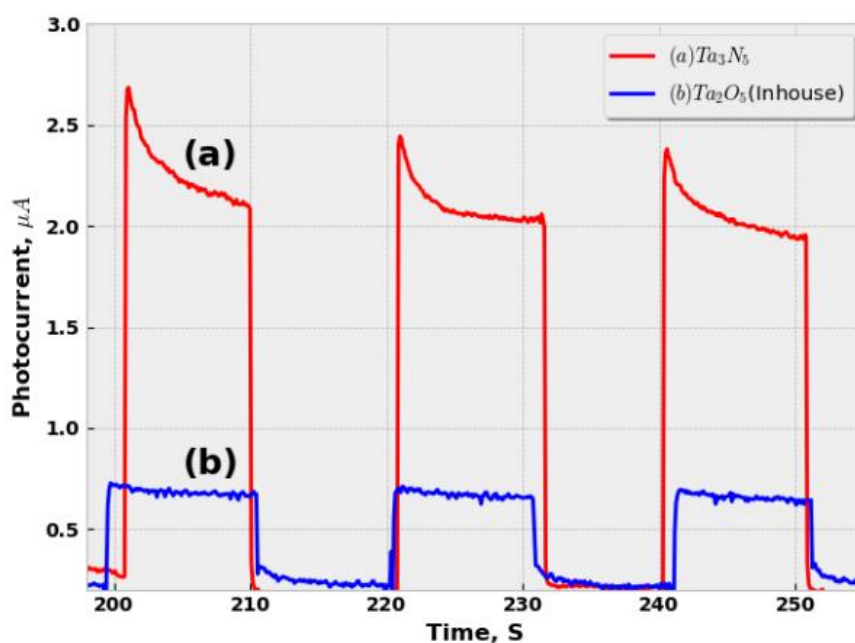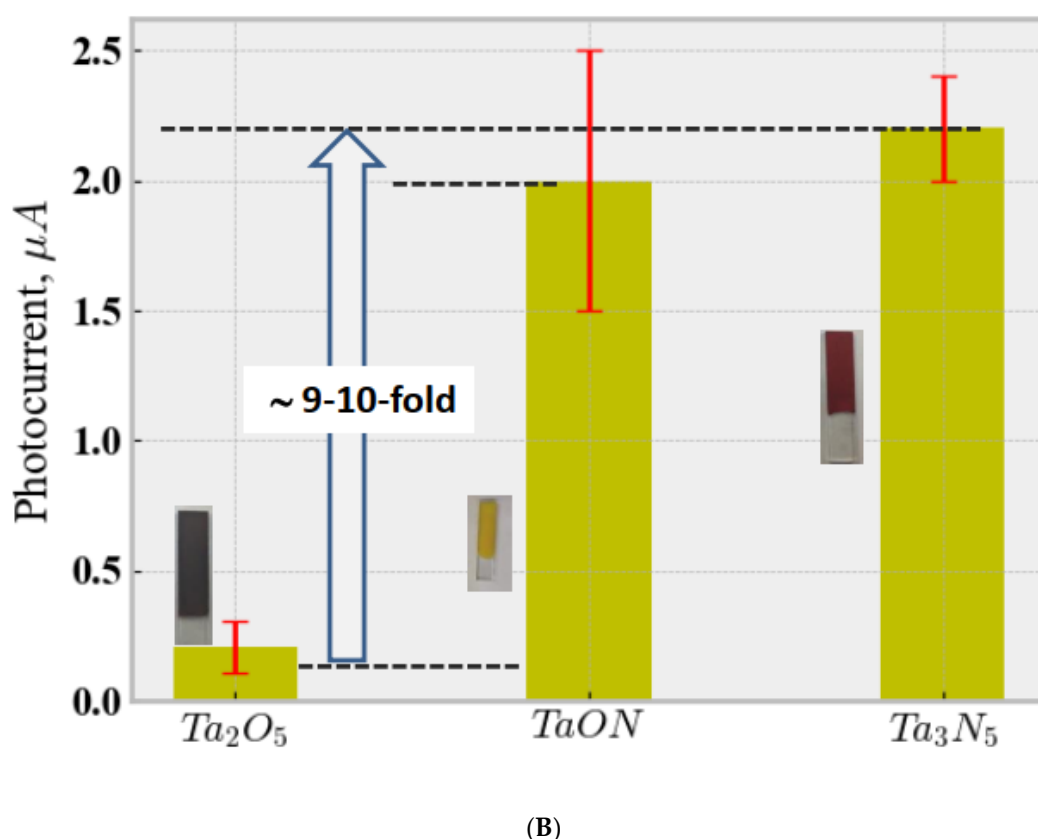
Figure 6. (**A**) The chronoamperometry (i/t) responses for the as-synthesized Ta_2O_5 and Ta_3N_5 samples. (Operating conditions: Pt counter electrode, leak-free Ag/AgCl (in 0.2M NaOH) as the reference electrode and sample coated ITO slide as a working electrode. Light intensity: 80 mW/cm^2, applied potential μM). (**B**) Photocurrent responses from Ta_2O_5 and its subsequent nitrogen derivatives. The error bars represent the range obtained with different films. (Operating conditions: Pt counter electrode, leak-free Ag/AgCl (in 0.2M NaOH) as the reference electrode and sample coated ITO slide as a working electrode. Light intensity: 80 mW/cm^2, no external bias applied).

### 3.2. Electrochemical Impedance Spectroscopy (EIS)

The basis for performing the EIS analysis on the tantalum-based photocatalysts is to gain insights into film properties such as the n-/p-characteristics and a qualitative estimate of the extent of charge separation [49,50]. The plot of the impedance response for the Ta_2O_5 and Ta_3N_5 photocatalyst films is shown in Figure S4. Firstly, the positive slope evident from all of the samples indicates that the Ta_2O_5, TaON, and Ta_3N_5 demonstrate n-type characteristics. Secondly, the Ta_2O_5 in-house sample shows a low radius of curvature compared to the commercial sample indicating that charge separation is better with the in-house samples. Finally, the application of the nitridation process to Ta_2O_5 to form TaON and Ta_3N_5 is beneficial as it shows the lowest radius of curvature indicating the most effective transport among the three photoactive films. Thus, the series of PEC measurements indicate that (i) the in-house Ta_2O_5 and Ta_3N_5 demonstrate photocurrent generation, (ii) reproducible and stable response, and (iii) the Ta_3N_5 demonstrates a distinguishable enhancement in the photocurrent response compared to the Ta_2O_5 films which can be attributed to the better charge separation, transport across the film thickness, and collection at the underlying ITO plate.

3.3. Evaluation of the Reusability of the Photocatalysts

MB is a complex molecule with multiple benzene rings and functional groups that results in its photodegradation through several intermediates [44]. Therefore, it is reasonable to evaluate the re-use

of the photocatalysts since the parent dye or intermediate could be adsorbed on the photocatalyst sites effectively preventing the site from further participating in degradation. Therefore, after the first use, the Ta_2O_5 photocatalyst was removed, washed, centrifuged, and dried in the presence of a positive draft of enriched oxygen at a temperature of 400 °C. This oxidative approach has been shown earlier to aid in recovering most of the photoactivity of oxide catalysts [51]. The results of such a treatment followed by a second and a third use are shown in Figure 7 along with the performance of the pristine catalyst as a comparison. It may be noted that the re-used catalyst shows the same activity as the pristine indicating that the photoactive surfaces are available intact after the oxidative treatment. This analysis indicates that it is possible to reuse the photocatalyst making it an effective and viable option for photo-assisted environmental remediation.
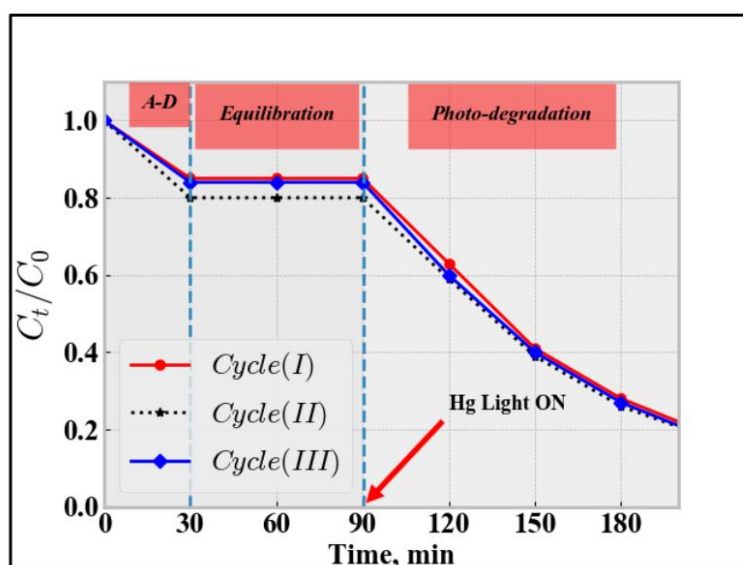
Figure 7. A comparison of the activity of the photocatalyst TaON toward the degradation of MB after multiple reuse cycles. Following the first time use the catalyst was recovered by oxidative treatment and repeated. as shown. (28.6 μM MB, air equilibrated UV-vis illumination).

3.4. Methylene Blue Oxidation Routes

Although it has been reported that tantalum based photocatalysts (Ta_2O_5, [52,53] and its nitrogen substituted compounds [54,55]) can degrade MB, the mechanism of the photocatalytic activity on Ta_3N_5 or comparing it with Ta_2O_5 is not yet reported. A preliminary analysis of the possible mechanism of photodegradation based on reports using these and other photocatalysts used in MB photodegradation is therefore presented here first. The direct photolytic degradation of methylene blue is possible using UV-vis light because of its ionic characteristics [56] but negligible photoactivity towards MB conversion is noted under visible light, specifically in the range between 400 and 500 nm where MB does not absorb as much as it does further into the red [57,58]. Elsewhere, it is also reported that both single metal large bandgap oxide such as Ta_2O_5 [52] or a composite photocatalysts such as $InVO_4$–$BiVO_4$ [59], produce e/h pairs simultaneously that individually lead to hydroxyl radical formation which cause MB degradation. Even in a non-oxide based material, such as a sulfide-based visible light driven photocatalyst, a mechanism involving both e/h driven hydroxyl radical formation (e.g., CdS) for MB degradation and CB electrons-driven formation of superoxide which in turn can produce hydroxyl radicals for MB degradation is reported [60].

The observed enhancement in overall MB conversion by as-synthesized Ta_2O_5, TaON and Ta_3N_5 ($\zeta_{Ta_2O_5}$: 64% < ζ_{TaON} : 80% < $\zeta_{Ta_3N_5}$: 98%; Figure 5b) can be attributed to two clearly elucidated processes:

(i) **Adsorption of MB molecules on catalyst surface:** The intrinsic atomic defects introduced on the surface of the crystal lattices during their synthesis as inferred from SEM analysis in this study are proposed to provide better anchorage to the MB molecules. Electrostatic interaction between MB and defect-generated charge centers in the catalyst surface is a possibility behind improved adsorption.

Therefore, we hypothesize that any additional synthesis step carried out in obtaining the nitrogen derivatives of Ta_2O_5: TaON and Ta_3N_5 introduces additional crystal defects on the catalyst surface, thereby introducing a larger number of intrinsic charge centers that act as effective anchors to the cationic MB molecules. Accordingly, the significant improvement in the adsorption of MB molecules on Ta_3N_5 catalyst surface as inferred from Figure 5b and Table 1 can be attributed to the highest number of surface defects introduced during longer nitridation period (15 h) as compared to that for TaON (1.5 h).

Table 1. Contribution of adsorption and photocatalysis toward the overall conversion of MB by Ta_2O_5, TaON, and Ta_3N_5. Significant improvement in adsorption-contribution toward MB removal can be attributed to the better anchorage provided to MB molecules by nitrided catalysts due to the increased atomic defects.

Catalyst	Adsorption Contribution (%)	Photocatalysis Contribution (%)
Ta_2O_5	~5	~60
TaON	20	60
Ta_3N_5	40	58

Electron paramagnetic resonance (EPR) analysis of each of the catalysts is undergoing for a thorough understanding of the physico-chemical nature of the defects.

(ii) **Valence band edge position and reduced bandgap:** The contribution from adsorption-desorption (A-D) equilibration toward overall MB conversion under dark conditions significantly differs in cases of Ta_2O_5, TaON and Ta_3N_5 while the contribution from photocatalytic removal (after the SS is turned on) does not significantly differ (Figure 5b). This can be explained by the lowered optical bandgap complimenting with the shallower valence band edge of TaON and Ta_3N_5. It is well known from experimental as well as first principle calculations that the conduction band edge positions of Ta_2O_5, TaON, and Ta_3N_5 are largely similar while the valence band edges get shallower as the nitrogen content increases in the catalysts [15,61,62]. As-synthesized Ta_2O_5, TaON and Ta_3N_5 photocatalysts in this work clearly demonstrate similar responses such as the shift of apparent flatband potential (E_{fb}) toward negative potential (Table 2, Figure S3B) and the reduction in bandgap (Figure 4).

Table 2. Apparent flat–band potential (E_{fb}) for Ta_2O_5 and its subsequent nitrogen derivatives. (Refer to Figure S4 for the J/V response).

Sample	E_{fb}, V
Ta_2O_5 (As-synthesized)	−0.63 ± 0.3
TaON	−0.95 ± 0.3
Ta_3N_5	−0.96 ± 0.3

Consequently, Ta_2O_5 (E_g = 3.66 eV) offers the highest capability toward MB oxidation owing to its deepest valence band edge. TaON (E_g = 2.21 eV) and Ta_3N_5 (E_g = 1.71 eV) have shallower band edges that offer lesser oxidation capability of MB molecules as compared to Ta_2O_5. On the other hand, TaON and Ta_3N_5 absorb a larger fraction of the solar spectrum (light source is Xe light solar simulator, AM = 1.5) owing to their reduced bandgaps. This fact is verified by the 9–10-fold larger improvement in J/t response by TaON and Ta_3N_5 as compared to Ta_2O_5 (Figure 6B). Consequently, the availability of e/h pairs under solar simulator illumination follows the order Ta_2O_5 < TaON < Ta_3N_5, and the depth of the valence band edge follows the order Ta_2O_5 > TaON > Ta_3N_5 under simulated solar irradiation. Thus, the abundance of e/h pairs and depth of valence band edge position in the catalysts produce a complimenting redox process that results in the observed constancy of photocatalytic MB removal.

Therefore, a hole driven oxidation of hydroxyl ions to form hydroxyl radicals and electron driven formation of superoxide ion, which eventually leads to the formation of hydroxyl radicals, is suggested.

4. Experimental

Methylene Blue (M9140-25G, Sigma Aldrich, St. Louis, MO, USA), Ammonia (Anhydrous UN1005, Air gas, Reno, NV, USA), Ammonium Hydroxide (Fisher Chemical, Lot# 174361, Hampton, NH, USA) were purchased from commercial vendors as indicated in the brackets. Ultra-high purity water for making the solution was obtained using the Millipore water purification system (resistivity = 18.2 MΩ·cm). The chemicals were used "as is" without any alteration or purification for synthesis, as described in the protocol detailed in Figure 8a,b. A suspension of the synthesized material is prepared with the dye in water. A steadily increasing loading of 0.05 g, 0.075 g, 0.1 g, and 0.15 g of the photocatalyst Ta_2O_5, TaON, or Ta_3N_5 and 200 mL volume of 28.6 μM Methylene Blue solution was ultrasonicated for three minutes and then stirred magnetically. It was later transferred to a borosilicate photocatalytic reactor for experimental analysis.
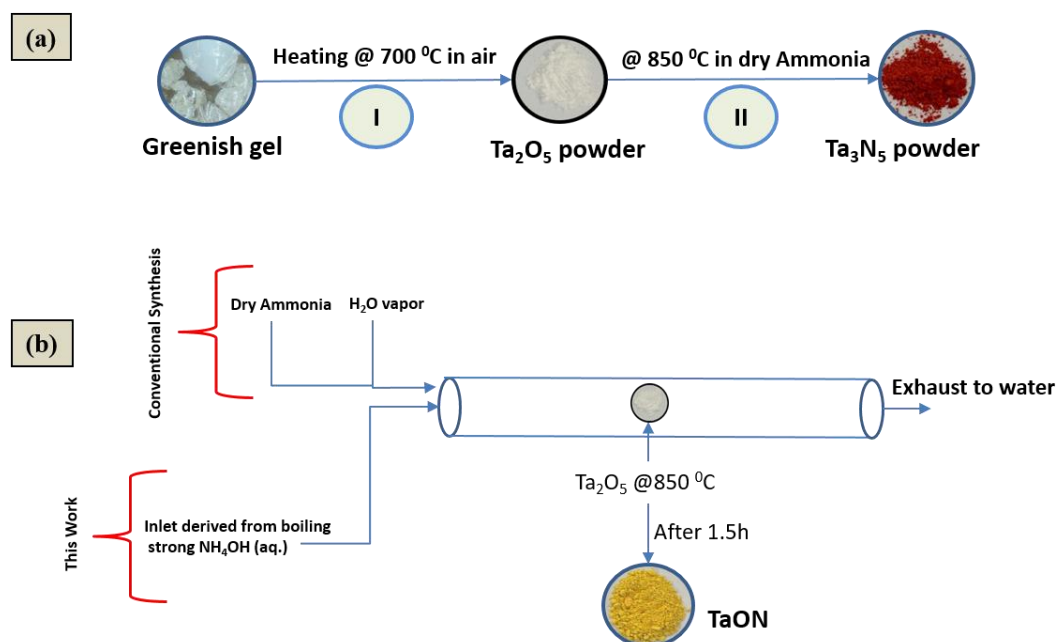
Figure 8. (**a**) The step-by-step process to synthesize (I) the oxide phase (Ta_2O_5) from Ta-Precursor, and (II) the subsequent thermal treatment step for its complete nitridation (Ta_3N_5) [63]. (**b**) The simplified method of nitridation for synthesizing TaON using NH_4OH solution (NH_4OH: H_2O (*v/v*) = 150:100, temperature of the heating bath (ethylene glycol): 300 °C).

4.1. Synthesis Approach

The popular method used in the synthesis of Ta_2O_5 involves tantalum chloride as a precursor [52]. Further, from our previous studies, the use of glacial acetic acid has indicated the formation of oxides with a high surface area that maintain stability [64]. Besides, ethoxide precursors have reportedly been known for interactions resulting in stable complexes with metal cations in acidic media [63,65]. Based on these references, in our previous work, we investigated the use of an ethoxide precursor with glacial acetic acid implementing the sol-gel process [63]. We studied the complete nitridation of as-synthesized Ta_2O_5 crystals in the same work to achieve single phase Ta_3N_5, and herein we present a novel partial nitridation technique to achieve single phase TaON. Partial nitridation can lead to TaO_XN_Y, where $x \neq y$. In particular, the strict requirement of finding an optimal ratio of oxygen to nitrogen as demanded by the most stable phase of TaON imposes challenges during its synthesis [15]. Traditionally, the common route of synthesizing TaON has been the gas phase nitridation of corresponding oxides

at high temperature. Ammonia, the most common nitrogen source used in such synthesis routes, is shown to produce the fully reduced form of Ta_2O_5 (i.e., Ta_3N_5) [63,66–68] while moist ammonia is reported to thermodynamically support the yield of TaON [69–71]. Challenge of controlling the precise flowrate of multiple fluids in such approaches often leads to the formation of various mixed (oxy)nitrides. On the other hand, the use of gaseous ammonia is not always a first choice—neither in research facilities nor in commercial plants due to the associated hazards [72]. Additional challenges are encountered due to the requirement of a precise flow of water vapor (together with the flow of dry ammonia) to produce single phase TaON [73]. Therefore, the traditionally popular methods of synthesizing TaON are prone to restrict absolute reproducibility of TaON [71,73,74].

A detailed experimental setup for the simplified method for synthesizing single phase TaON reported in this discussion is presented in Figure 8b, Figure S1. The primary idea presented here is to replace the complex inlet of multiple phases in traditional synthesis protocols. Inspired from the fact that the gaseous phase of ammonia (NH_3) reacts reproducibly with water (H_2O) to give liquid phase ammonium hydroxide (NH_4OH), we hypothesized and successfully verified that a simpler-to-handle liquid phase of NH_4OH can replace the complex nitrogen source used in traditional methods (dry ammonia together with water vapor). In such an approach, the nitridation rate can be controlled as a function of two easily controllable parameters: pH of NH_4OH solution and the heating bath temperature. Tuning of these parameters offers an easier option for selective nitridation of Ta_2O_5 nanocrystals and hence single phase TaON. As the reaction between NH_3 and H_2O is reversible, the liquid phase NH_4OH gives off a mixture of ammonia gas and water vapor when heated, and it serves as the reliable source of humidified nitrogen as required in the conventional synthesis of TaON.

4.2. Material Characterization

The characterization of the photocatalysts was performed using several complementary tools. A Hitachi® S-4700 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan) was used to examine the physical features of the powder. An attached electron dispersive spectrometer (EDS) (Hitachi, Tokyo, Japan) was used to determine the photocatalyst composition. Crystalline features of the photocatalysts were examined using an XRD (Cu-Kα, λ = 1.5418 Å) instrument from Bruker (D2 Phaser) (Bruker, Madison, WI, USA) and the Scherer equation was performed in order to determine the crystalline size of nanoparticles. High resolution transmission electron microscopy ((HR)TEM) (Hitachi, Tokyo, Japan) analysis was performed using a JEOL 2100F instrument equipped with a selected area electron diffraction (SAED) analyzer (Hitachi, Tokyo, Japan). The optical properties of the powder were examined using a UV–vis diffuse absorbance measurement with a Shimadzu UV 2501PC spectrophotometer (Shimadzu, Columbia, MD, USA). The BET surface area of the synthesized materials were determined using a micromeritics system (model flow sorb II—2300) (Micromeritics, Hannover, Germany).

4.3. Determination of Photocatalytic Properties

The photocatalytic reactions were performed using two light sources (details in Table S1). First, a slurry reactor comprising a tubular borosilicate vessel of 500 mL volume with a lamp (450 W Hg vapor source) introduced in the annulus of the vessel was used along with jacketed temperature control achieved using a stream of cooling water. The details of the reactor assembly are presented elsewhere. The photocatalysts in quantities of 0.05 g, 0.75 g, 0.1 g, and 0.15 g were used in subsequent experiments by making as suspensions in 200 mL of an aqueous methylene blue (28.6 μM). Second, an open configuration comprising of a batch type reactor with top down illumination using a 580 W Xenon lamp as the light source was used. The latter reactor allowed for facilitating visible light illumination experiments. Since Hg lamp is not a good source to compare the performance of photocatalysts with varying bandgaps, Xe lamp with lower UV content than Hg lamp was used as a solar simulator (AM = 1.5) in the photocatalytic degradation studies. In both cases, the photocatalyst was kept

suspended by continuous stirring to ensure homogeneous distribution in the MB solution. The lamp was turned on only after the dye equilibrated on the catalysts surface, i.e., a saturation plateau for the dye concentration was achieved (~1.5 h). The 5 mL slurry aliquots were sampled every 30 min in a plastic vial and centrifuged (~20 min) to remove the suspended particles. Several successive samples were probed at regular intervals using a Shimadzu UV-vis-2501PC spectrophotometer (Shimadzu, Columbia, MD, USA). For reusability tests, part of the sample (0.1 g) was recovered after centrifuging the 0.3 g sample-slurry, extracting the maximum possible precipitate. The adsorbed residue was burned off from the dried sample under oxidative conditions at 400 °C over a gradual stream of air.

4.4. Determination of Photoelectrochemical Properties

The photoelectrochemical measurements were performed using a potentiostat/galvanostat (Autolab PGStat series, Metrohm, Riverview, FL, USA). The measurements were recorded for films of the photocatalyst prepared by depositing an aqueous suspension of the photocatalyst slurry on conducting (FTO) glass slide followed by N_2 annealing at 350 °C. Chronoamperometry, Linear sweep voltammetry, and measurements for bandgap estimation (Tauc plots) were obtained using 0.2 M aqueous NaOH. A Xe lamp was used as a light source with a $CuSO_4$ filter for high UV cut off. A Pt mesh was used as the counter electrode and Ag/AgCl was used as a reference.

5. Conclusions

A simplified and extremely reproducible approach to partial nitridation of Ta_2O_5 resulting in single phase TaON is successfully demonstrated. The physical features, phase evolution, and optical properties are systematically analyzed. Particles ranging from ϕ = 30–40 nm, 40–50 nm, and 30–40 nm for Ta_2O_5, TaON, and Ta_3N_5 respectively is reported. The photodegradation of a representative cationic dye, methylene blue, was effectively carried out with ~95% conversion of the dye at various loading amounts under solar simulator. The photoactivity of the novel catalyst was further examined after subjecting to mild oxidative thermal treatment. The catalyst activity matches that of non-used catalyst, post thermal treatment. The main features of the photocatalysts identified include: (i) synthesis of well–faceted oxides, oxynitrides and nitrides, (ii) increased adsorption of dye and visible light activity noted with the increase of nitrogen content in the nitrogen derivatives of the oxide catalyst, and (iii) enhanced separation of photogenerated charges contributes to better photoactivity as evidenced from a series of complementary photoelectrochemical measurements (primarily a ~9–10 fold increase in photocurrent as a function of increased nitridation). Salient features of the novel TaON synthesis approach include (i) a robustly reproducible single phase TaON synthesis method that is least associated with gaseous hazards, (ii) a simplified protocol suitable for laboratory as well as largely scalable synthesis of single phase TaON, and (iii) a cost-effective miniaturized method that replaces flowmeters with a constant temperature bath, and costly anhydrous ammonia gas with cost-friendly ammonium hydroxide.

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