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# Influence of C<sub>3</sub>N<sub>4</sub> Precursors on Photoelectrochemical Behavior of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> Photoanode for Solar Water Oxidation

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Abstract: Photoelectrochemical water splitting is considered as a long-term solution for the ever-increasing energy demands. Various strategies have been employed to improve the traditional  $TiO_2$  photoanode. In this study,  $TiO_2$  nanorods were decorated by graphitic carbon nitride ( $C_3N_4$ ) derived from different precursors such as thiourea, melamine, and a mixture of thiourea and melamine. Photoelectrochemical activity of  $TiO_2/C_3N_4$  photoanode can be modified by tuning the number of precursors used to synthesize C<sub>3</sub>N<sub>4</sub>. C<sub>3</sub>N<sub>4</sub> derived from the mixture of melamine and thiourea in  $TiO_2/C_3N_4$  photoanode showed photocurrent density as high as 2.74 mA/cm<sup>2</sup> at 1.23 V vs. RHE.  $C_3N_4$  synthesized by thiourea showed particle-like morphology, while melamine and melamine with thiourea derived C3N4 yielded two dimensional (2D) nanosheets. Nanosheet-like C3N4 showed higher photoelectrochemical performance than that of particle-like nanostructures as specific surface area, and the redox ability of nanosheets are believed to be superior to particle-like nanostructures.  $TiO_2/C_3N_4$  displayed excellent photostability up to 20 h under continuous illumination. Thiourea plays an important role in enhancing the photoelectrochemical performance of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>. This study emphasizes the fact that the improved photoelectrochemical performance can be achieved by varying the precursors of  $C_3N_4$  in TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> heterojunction. This is the first report to show the influence of  $C_3N_4$  precursors on photoelectrochemical performance in TiO<sub>2</sub>/ $C_3N_4$  systems. This would pave the way to explore different precursors influence on  $C_3N_4$  with respect to the photoelectrochemical response of  $TiO_2/C_3N_4$  heterojunction photoanode.

**Keywords:** photoelectrochemical;  $TiO_2$ ;  $C_3N_4$ ; heterojunction; water oxidation; photoanode; nanosheets; nanorods

### 1. Introduction

Photoelectrochemical water splitting is one of the ideal methods for solar energy conversion. Enormous efforts have been made to achieve remarkable solar to hydrogen efficiency since the discovery of TiO<sub>2</sub> photoelectrochemical performance. However, development of an efficient photoelectrode with high solar to hydrogen efficiency, which determines how much solar energy is converted to chemical energy, remained as a challenge. TiO<sub>2</sub> remains as one of the benchmark semiconductors for photoelectrochemical performance due to its photostability, chemical stability, nontoxicity and abundance [1–4]. Despite these, TiO<sub>2</sub> suffers from low absorption of visible light due to its wide band gap and high recombination rate of charge carriers. Many strategies have been adopted to overcome these problems such as elemental doping, morphology tuning, and surface modifications—yet, only limited success has been achieved. Fabrication of TiO<sub>2</sub> heterojunction with narrow band gap

semiconductors has shown considerable improvement in the charge carrier separation and hence the photoelectrochemical performances.

Graphitic carbon nitride ( $C_3N_4$ ) 2D material is emerging as the next generation material for photoelectrochemical water splitting owing to its visible light activity and robust chemical stability [5]. Additionally,  $C_3N_4$  can easily be synthesized by simple thermal polymerization of abundantly available nitrogen rich precursors such as thiourea, melamine, urea, and dicyanamide. However, application of this material into photoelectrochemical water splitting only started recently, even though  $C_3N_4$  has desirable band gap and oxidation and reduction potentials [6]. Unlike many promising metal oxides, metal free polymeric  $C_3N_4$  possessing moderate band gap of 2.7 eV is known to be stable in acidic as well as alkaline electrolytes due to the strong covalent bond between carbon and nitrogen in the structure.

Semiconductors with staggered band alignments can be coupled to fabricate the heterojunction, which can improve the solar water oxidation of the photoelectrode due to the increased charge carrier separation [7–11]. Nano structural modification with high surface area is beneficial to further improve the photocurrent density of the heterojunctions [12,13].

 $C_3N_4$  is a metal free semiconductor possesses moderate band gap to harvest visible light. Graphitic-C-<sub>3</sub>N<sub>4</sub> is a very potential layered material due to its ease of synthesis, low production cost, chemical and photostability. As  $C_3N_4$  suffers from low sun light absorption capability and low charge mobility, new synthesis strategies are required to overcome these limitations and improve the photoelectrochemical response [14,15]. Although there have been enormous studies done on the modifications of  $C_3N_4$ , little attention is paid to the influence of precursors on photoelectrochemical performances [16–22]. Morphology of  $C_3N_4$  depends on the precursors used to synthesize, resulting in different photocatalytic activity [19]. Shalom et al. demonstrated the blue shift in the band gap of the  $C_3N_4$  derived from cyanuric acid and melamine precursors compared to that of  $C_3N_4$  synthesized from dicyanamide [23]. It is well recognized that the morphology modifies the electronic structure with the creation of new surface states [23]. Therefore, it is noteworthy that the band gap of  $C_3N_4$ varies depending on the precursor used, as reported in the literature [24,25].

It is also evident from the previous reports that the precursors used for the synthesis of  $C_3N_4$ play a crucial role in altering the photocatalytic behavior [20,22]. For instance, thiourea and urea were considered as precursors for the synthesis of  $C_3N_4$  and found that the photocatalytic performance is enhanced with  $C_3N_4$  obtained by thiourea precursor [26]. Authors claim that the sulphur containing precursor accelerates the thermal polymeric condensation with easy leaving -SH and thereby increases the photocatalytic activity [26]. However, the influence of the precursor on the photoelectrochemical performance has not been investigated. In this work, we have demonstrated the impact of the three different precursors of  $C_3N_4$  such as thiourea, melamine, and mixture of thiourea and melamine with the ratio of 1:1.5 on photoelectrochemical performance of  $TiO_2/C_3N_4$  heterojunction. The choice of precursor plays an important role in deciding the photoelectrochemical performances as it yields various morphological structures. The 1D TiO<sub>2</sub> nanorod arrays were decorated by  $C_3N_4$  with 2D nanosheets and particle such as C<sub>3</sub>N<sub>4</sub> derived from different precursors and their corresponding photoelectrochemical activity was analyzed and discussed in detail. Nanosheets of  $C_{-3}N_4$  exhibit high surface area with high electronic mobility. Our work demonstrates the enhanced photocurrent density for TiO<sub>2</sub> heterojunction with  $C_3N_4$  compared to reported TiO<sub>2</sub> modified  $C_3N_4$  photoanode systems. To the best of our knowledge, this is the first study investigating the influence of  $C_3N_4$  precursors on the photoelectrochemical activity of  $TiO_2/C_3N_4$  photoanodes. This work provides a promising approach to improve solar water oxidation performance of  $TiO_2/C_3N_4$  heterojunction.

#### 2. Experimental

#### 2.1. TiO<sub>2</sub> Nanorods Synthesis

 $TiO_2$  nanorods were synthesized by hydrothermal technique. Titanium butoxide (0.4 mL) was dissolved in hydrochloric acid (26 mL) and water (24 mL). The obtained transparent solution was

transferred to 100 mL Teflon containing fluorine doped tin oxide (FTO) at the bottom and heated in the oven for 3 h at 200 °C. The TiO<sub>2</sub> nanorods grown on FTO was extensively washed with water. TiO<sub>2</sub> nanorods were annealed at 350 °C for 3 h in air.

#### 2.2. Graphitic C<sub>3</sub>N<sub>4</sub> Synthesis

Graphitic  $C_3N_4$  was synthesized by thermal polymeric condensation of different precursors such as thiourea, melamine, and a mixture of melamine and thiourea. Melamine precursor was mixed with a supramolecular complex cyanuric acid. In a typical procedure, 2 g of cyanuric acid (C), 3 g of melamine (M), and 3 g of thiourea (T) were taken for the fabrication of  $C_3N_4$  2D nanosheet and is referred as  $C_3N_4$ -CMT to distinguish the  $C_3N_4$  obtained by different precursors. Two g of cyanuric acid (C) and 3 g of melamine (M) were used for the synthesis of  $C_3N_4$ -CM, while the desired amount of thiourea (T) was considered to obtain  $C_3N_4$ -T. The precursors were grinded in the mortar and transferred to the crucible with the lid. The crucible was placed in a furnace and annealed at 550 °C for 6 h. The obtained yellow powder was dispersed in a solution comprising of isopropyl alcohol and distilled water and ultrasonicated for 48 h. The supernatant solution of  $C_3N_4$  was collected after the centrifugation.

#### 2.3. $TiO_2/C_3N_4$ Fabrication

The heterojunction  $TiO_2/C_3N_4$  was fabricated by dip coating method.  $TiO_2$  on FTO substrate was dipped in 3 mL of milky white  $C_3N_4$  (CMT, CM, and T) suspension for 3 h at room temperature. The substrate was dried using nitrogen gun and annealed for 3 h at 300 °C to obtain the maximum adhesion of  $C_3N_4$  on  $TiO_2$ .

#### 3. Materials Characterization

The phase identification was carried out by Bruker D8 advance diffractometer equipped with Cu K $\alpha$  source. The morphology of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, and TiO<sub>2</sub> photoanodes was characterized by using a field-emission scanning electron microscopy (FE-SEM) with an acceleration voltage of 5 kV and working distance of 8 mm (SU-Hitachi). The transmission electron microscope (TEM) (Technai G2 F20, FEI Company, Hillsboro, OR, USA) analysis were carried out at voltage of 200 kV, which was equipped with high-angle annular dark-field image (HADDF), scanning TEM (STEM), and energy dispersive spectroscopy (EDS). UV-Visible absorbance spectra were measured by JASCO UV-vis spectrometer.

#### 4. Photoelectrochemical Characterization

Photoelectrochemical performances of  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM,  $TiO_2/C_3N_4$ -CMT, and  $TiO_2$  photoelectrochemical with a typical three electrode configuration using an Ivium potentiostat with Ag/AgCl as a reference electrode and Pt plate as a counter electrode. All the photoelectrochemical measurements were carried out at room temperature in sodium hydroxide electrolyte with pH 14. Using a reference cell, solar simulator's light intensity with an AM 1.5 G filter was calibrated to 1 sun (100 mW/cm<sup>2</sup>). Linear sweep voltammetry (LSV) measurements were carried out with scan rate of 20 mV/s in the anodic direction. Photostability was measured under standard solar illumination condition in sodium hydroxide electrolyte at 1.23 V vs. RHE. Incident to photon current conversion efficiency (IPCE) values were measured at 1.23 V vs. RHE using light source with monochromator. Electronic impedance spectroscopic measurement (EIS) was recorded at 1.23 V vs. RHE with the frequency range from 10 mHz to 100 kHz [27].

#### 5. Results and Discussion

TiO<sub>2</sub> nanorod arrays on FTO were synthesized by facile hydrothermal technique. Decoration of obtained  $C_3N_4$ - was carried out using dip coating method. TiO<sub>2</sub> nanorods were dipped in  $C_3N_4$  suspension obtained by different precursors for 3 h followed by annealing at 300 °C for 3 h. SEM reveals

the morphological difference of  $C_3N_4$ - derived from thiourea, melamine, and mixture of thiourea and melamine. When only thiourea is used for the synthesis of the  $C_3N_4$  particle-like morphology was obtained, as shown in the Figure 1b. However, sheet-like 2D morphology was achieved by the melamine and melamine mixed thiourea precursors (Figure 1c,d). Schematic of the synthesis is provided in the Figure 2. It can be noticed from the SEM images that the  $C_3N_4$  sheets have covered the TiO<sub>2</sub> nanorods. XRD of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> shows only the TiO<sub>2</sub> peak, as  $C_3N_4$  has low crystallinity and thin layers (Figure 3a). For the comparison, XRD of the  $C_3N_4$  powder sample has also been presented in Figure 3a. HRTEM measurements have been carried out to further confirm the distribution of  $C_3N_4$  sheets on TiO<sub>2</sub> nanorods in TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> heterojunction.  $C_3N_4$  sheets have uniformly covered the TiO<sub>2</sub> nanorods, which is evident by the Figure 1. Elemental mapping of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> demonstrates the presence of C, N, Ti, and O.



Figure 1. FE-SEM of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T (c) TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and (d) TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT.



**Figure 2.** Schematic diagram of the synthesis of TiO<sub>2</sub>, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT.



**Figure 3.** (a) X-ray diffraction patterns (XRD) of TiO<sub>2</sub>, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT. (b) Transmission electron microscope (TEM) image of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>. (c) HAADF-STEM elemental mapping of sample TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> showing the distribution of Ti, O, C, and N.

While it is hard to distinguish the carbon present on the  $TiO_2$  nanorod from the copper grid, the EDAX confirms the presence of the nitrogen surrounding the  $TiO_2$  nanorod.

PEC performance was investigated for  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM,  $TiO_2/C_3N_4$ -CMT and  $TiO_2$  to understand the influence of the precursor influence. Linear sweep voltammetry under chopped illumination has been performed and compared in Figure 4a. The pristine  $TiO_2$  nanorod exhibits the photocurrent density of 0.76 mA/cm<sup>2</sup> while  $TiO_2/C_3N_4$ -T and  $TiO_2/C_3N_4$ -CM show 1.28 and 1.71 mA/cm<sup>2</sup>, respectively, under 100 mW/cm<sup>2</sup> solar simulated radiation in the presence of sodium hydroxide electrolyte (pH = 14). When the thiourea mixed with melamine was used as a precursor for  $C_3N_4$ ,  $TiO_2/C_3N_4$ -CMT exhibited 2.74 mA/cm<sup>2</sup>, which is the highest photocurrent density reported to the best our knowledge for  $TiO_2/C_3N_4$  photoelectrode.

IPCE was measured with three electrode configurations in sodium hydroxide electrolyte at 1.23 V vs. RHE. As expected TiO<sub>2</sub> shows IPCE (Figure 4b) only under short wavelength region, which ranges from 300 nm to 400 nm. TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT photoanode showed higher photoconversion response (80%) compared to TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and TiO<sub>2</sub>. TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T exhibits 42% of IPCE in 400 nm wavelength while melamine with cyanuric acid derived C<sub>3</sub>N<sub>4</sub> in TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>- CM showed enhancement in the IPCE, which is about 69% at 400 nm. The pristine TiO<sub>2</sub> photo-response was limited to the UV region, the C<sub>3</sub>N<sub>4</sub> decorated TiO<sub>2</sub> photoconversion efficiency was slightly extended to visible region.



**Figure 4.** (a) LSV, and (b) IPCE of  $TiO_2$ ,  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM, and  $TiO_2/C_3N_4$ -CMT. (c) Stability of  $TiO_2/C_3N_4$ -CMT in sodium hydroxide electrolyte with pH 14 at room temperature.

The investigation by Yang et al. shows IPCE extended to visible region as in the absorption edge of  $C_3N_4$  decorated TiO<sub>2</sub> red shifted compared to that of TiO<sub>2</sub> [28]. Similar trends were noticed with several TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> systems [29,30].

The obtained IPCE spectra are in consistent with the absorption spectra of  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM,  $TiO_2/C_3N_4$ -CMT and  $TiO_2$  where  $TiO_2/C_3N_4$  photoanodes exhibit slight decrease in the band gap (Figure 5b). The enhanced IPCE for  $TiO_2/C_3N_4$ -CMT could be due to improved charge separation at the interface as  $TiO_2$  forms staggered band alignment with  $C_3N_4$  [29–31].



**Figure 5.** (a) Electronic impedance spectra measured in the presence of sodium hydroxide electrolyte (pH 14) at 1.23 V vs. RHE and (b) Tauc plot of TiO<sub>2</sub>, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT.

To evaluate the stability of the  $TiO_2/C_3N_4$ -CMT photoanode, the photoresponse for 19 h was measured in sodium hydroxide electrolyte at 1.23 V vs. RHE, as shown in Figure 4c. Slight increase in the photocurrent was noticed for the initial hours which could be due to the photocharging. Negligible decrease in the photocurrent density was noticed after the prolonged light irradiation.

The LSV plots for  $TiO_2/C_3N_4$ -CMT before and after the photostability measurement are shown in Figure S2a. The fresh electrode shows 2.74 mA/cm<sup>2</sup> of photocurrent density, whereas the aged electrode exhibits 2.10 mA/cm<sup>2</sup>. The FE-SEM image is presented in Figure S2b. The post-mortem analysis of the aged electrode confirms that the morphology of  $C_3N_4$  nanosheets on the  $TiO_2$  was similar to that of the fresh electrode (Figure 1d).

The slight decrease in the photocurrent density could be due to slow etching of  $C_3N_4$  nanosheets with prolonged time. The remarkable stability and photocurrent density of  $TiO_2/C_3N_4$  reveals the high photostability of the heterjunction.

EIS is a powerful tool to study the kinetic charge transfer at the electrode/electrolyte interface. The Nyquist plots for  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM,  $TiO_2/C_3N_4$ -CMT, and  $TiO_2$  are depicted in the Figure 5a.  $TiO_2/C_3N_4$ -CMT shows the depressed arc, implying that the charge transfer rate is enhanced in the heterojunction, whereas the largest arc shown by the pristine  $TiO_2$  implies the large charge transfer resistance. The abo-ve results suggest that the coating of  $C_3N_4$  obtained by thiourea with melamine on  $TiO_2$  nanorod decreases the charge transfer resistance, which indicates that the facile charge transport at the interface. This observation is in consistent with the LSV in Figure 4a.

The optical absorption of the photoelectrodes were measured by the UV-visible diffused reflectance spectra. The Tauc plot can be used to determine the optical band gap of the semiconductors. It is observed from the Tauc plot (Figure 5b) that there is only slight variation in the band gap of  $TiO_2$  and  $TiO_2/C_3N_4$  heterojunctions, which is quite obvious when bulk  $C_3N_4$  is reduced to nanoscale the band gap of the  $C_3N_4$  increases.

The chemical states of the TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> photoelectrode have been analysed by XPS (Figure 6 and Figure S1). The high-resolution spectra of XPS confirm the presence of Ti, C, N, and O (Figure S1). Figure 6a compares the N s peak arising from TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T, TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM, and TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT. It is noticed that a broad peak, which can be deconvoluted to two overlapping peaks, appear at 400.33 eV and 399.36 eV for N1s, which indicates the formation of C<sub>3</sub>N<sub>4</sub> and this peak corresponds to N-(C)<sub>3</sub> [32]. The high-resolution C 1s XPS spectra exhibit two signals peaked at 284.6 eV and 288.5 eV, suggesting the presence of two chemical states of carbon. The peak at 284.6 eV originates from sp<sup>2</sup> carbon adsorbed on the surface of C<sub>3</sub>N<sub>4</sub>, while the second peak centered at 288.5 eV indicates the presence of N-C=N bonding. XPS spectra of Ti for TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT show two distinct peaks corresponding to Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> at 463.91 eV and 458.13 eV, which can be ascribed to the presence of Ti<sup>4+</sup>.

Based on the aforementioned discussion and the previous reports, plausible mechanism has been depicted in Figure 7 [29–31,33]. The band diagram of TiO<sub>2</sub> and C<sub>3</sub>N<sub>4</sub> heterojunction can be envisaged as displayed in Figure 7. The heterojunction exhibits type II heterojunction once the Fermi level reaches the equilibrium, the conduction band minimum is more negative than that of TiO<sub>2</sub> and valance band maximum position is suitable for hole transport from TiO<sub>2</sub> to C<sub>3</sub>N<sub>4</sub>. Therefore, it forms a favourable interface for the transfer of the charge carriers. The holes are collected on the surface of the C<sub>3</sub>N<sub>4</sub>, while electrons are collected on TiO<sub>2</sub> nanorod.

It is well recognised that 2D nanosheets exhibit superior photoelectrochemical activity compared to the particle-like nanostructures [34]. Nanosheets-like morphology facilitates an easier flow of photocharge carriers towards the surface than particle-like nanostructures. Therefore, 2D nanosheets of  $C_3N_4$  in TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CM and TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT outperform the particle-like  $C_3N_4$  of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-T. This study emphasizes the fact that the thiourea modified  $C_3N_4$  shows enhanced performance than that of the  $C_3N_4$  synthesized from only thiourea or melamine. Cyanuric acid is known to form supramolecular complexes with melamine which yields sheet-like 2D structure [23,35]. This offers the ability to synthesize the 2D sheet-like  $C_3N_4$  simply by forming the supramolecular complexes and altering the precursors. However,  $C_3N_4$  prepared from only thiourea yielded particle-like morphology, which showed enhanced photoelectrochemical performance than the pristine TiO<sub>2</sub>. It is noteworthy that the thiourea modified  $C_3N_4$  has a profound influence in altering the morphology and thereby the photoelectrochemical performance of the TiO<sub>2</sub>. Cyanuric acid and melamine form hydrogen bonding, which prohibits the immediate sublimation of melamine, cyanuric acid, and thiourea, thus promoting polycondensation reaction. From the previous reports it is evident that thiourea influences the level of the polymerization during the growth of  $C_3N_4$  [36]. The conventional  $C_3N_4$  was prepared by bulk condensation of the nitrogen rich monomers such as melamine, urea, and dicyanamides, where  $-NH_2$ is the leaving group during the polycondensation [32]. However, the polycondensation suffers incomplete polymerization due to kinetic limitations [14]. Previous reports have claimed that the sulphur mediated polycondensation, where the -SH group serves as a leaving group. Sulphur atom is expected to influence the polymeric network of g-C<sub>3</sub>N<sub>4</sub> such as conformation and connectivity of the polymer, which in turn tunes the texture and electronic properties [14,36,37]. Density functional theory simulations have confirmed that the polymerization has a remarkable influence on H<sub>2</sub> evolution rate as it brings slight change in the potential of the conduction band. In the present case, the  $TiO_2/C_3N_4$ -CMT outperforms the individual precursor melamine and thiourea derived C<sub>3</sub>N<sub>4</sub> heterojunction counterparts. The enhanced photoelectrochemical performance is presumably due to the presence of the thiourea with melamine and cyanuric complexes. Photocurrent density value of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT was compared with various reported photoanodes of  $TiO_2/C_3N_4$  heterojunctions (Table 1). Wang et al. reported the fabrication of  $TiO_2/C_3N_4$  where  $C_3N_4$  was synthesized by expensive arc ion plating technique. The photocurrent density achieved by this photoanode was ~0.7 mA/cm<sup>2</sup> [38].

Table 1. Comparison of photocurrent density of various  $TiO_2/C_3N_4$  photoanodes for water oxidation.

Photoanode	Photocurrent Density (mA/cm <sup>2</sup> )	Reference
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> core shell array	0.045	[31]
CuNi@g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> nanorods	0.89	[33]
TiO <sub>2</sub> /P-g-C <sub>3</sub> N <sub>4</sub>	0.20	[15]
$0D 1D g-C_3N_4/TiO_2$ nanotube arrays	0.12	[30]
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> nanorod	0.29	[29]
$C_3N_4/TiO_2$ nanotube	1.5	[28]
C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> nanorod	2.74	This Work



**Figure 6.** X-ray photoelectron spectra (XPS) of (**a**) C 1s and (**b**) N 1s of  $TiO_2/C_3N_4$ -T,  $TiO_2/C_3N_4$ -CM, and  $TiO_2/C_3N_4$ -CMT photoanode.



Figure 7. Schematic diagram illustrating the possible mechanism of water oxidation by TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-CMT.

Wie et al. have demonstrated that melamine derived  $C_3N_4$  with TiO<sub>2</sub> heterojunction, which exhibited the photocurrent density of 1.5 mA/cm<sup>2</sup> [39].  $C_3N_4$  sensitized TiO<sub>2</sub> nanotube showed 1.5 mA/cm<sup>2</sup> [28]. Yang et al. reported red  $C_3N_4$ , which exhibited 2.2 mA/cm<sup>2</sup> in a higher voltage range, whereas in the lower voltage region it only showed 0.5 mA/cm<sup>2</sup> [40]. The current work demonstrates the role of thiourea on the photoelectrochemical performance and it is noteworthy that the photoelectrode TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>–CMT achieved 2.74 mA/cm<sup>2</sup>, which is highest photocurrent density reported for C<sub>3</sub>N<sub>4</sub> sensitized TiO<sub>2</sub> till date.

#### 6. Conclusions

We fabricated  $TiO_2/C_3N_4$  heterojunction using different precursors of  $C_3N_4$  such as thiourea, melamine and mixture of thiourea and melamine. It was found that the  $C_3N_4$  derived from the mixture of thiourea and melamine in  $TiO_2/C_3N_4$  heterojunction exhibited significantly enhanced photoelectrochemical activity. The photocurrent density of 2.74 mA/cm<sup>2</sup> at 1.23 V vs. RHE was achieved for  $TiO_2/C_3N_4$  photoanode, which is the highest photocurrent density compared to previous reports, to the best of our knowledge. Melamine and the mixture of thiourea and melamine precursors yielded  $C_3N_4$  nanosheets while particle-like morphology was obtained by thiourea precursor, which could be due to the difference in degree of polymerization during the growth of  $C_3N_4$ . The formed  $C_3N_4$ D nanosheet from the mixture of thiourea and melamine precursors in  $TiO_2/C_3N_4$  heterojunction improves the charge separation resulting in enhanced photoelectrochemical performance for water oxidation. The IPCE value was 80% for  $TiO_2/C_3N_4$  photoanode while the pristine  $TiO_2$  showed only -31%. This study shows the precursor influence of  $C_3N_4$  on photoelectrochemical performance of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> heterojunction. This study sheds light on optimizing the photoelectrochemical activity by modifying the precursors of  $C_3N_4$  and thereby improving the water oxidation performance of TiO<sub>2</sub>. The present work revisits the strategies for the fabrication of heterojunction as well as achieving high photoelectrochemical performance of TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> photoanode.

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