Research Article

Effect of N,C-ITO on Composite N,C-TiO₂/N,C-ITO/ITO Electrode Used for Photoelectrochemical Degradation of Aqueous Pollutant with Simultaneous Hydrogen Production

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This study reports the effect of N,C-ITO (indium tin oxide) layer on composite N,C-TiO₂/N,C-ITO/ITO (Ti/TO) electrode used for efficient photoelectrocatalytic (PEC) degradation of aqueous pollutant with simultaneous hydrogen production. The structural properties of the composite Ti/TO electrode that determined by X-ray diffraction and Raman scattering, show primarily the crystallized anatase TiO₂ phase and distinct diffraction patterns of polycrystalline In₂O₃ phase. Under solar light illumination, the composite Ti/TO electrode yields simultaneously a hydrogen production rate of 12.0 $\mu\text{mol cm}^{-2} \text{h}^{-1}$ and degradation rate constant of $12.6 \times 10^{-3} \text{ cm}^{-2} \text{h}^{-1}$ in organic pollutant. It implies that the overlaid N,C-TiO₂ layer enhances not only the photocurrent response of the composite Ti/TO electrode at entire applied potentials, but also the flat band potential; a shift of about 0.1 V toward cathode, which is desperately beneficial in the PEC process. In light of the X-ray photoelectron spectroscopy findings, these results are attributable partly to the synergetic effect of N,C-codoping into the TiO₂ and ITO lattices on their band gap narrowing and photosensitizing as well. Thus, the Ti/TO electrode can potentially serve an efficient PEC electrode for simultaneous pollutant degradation and hydrogen production.

1. Introduction

The photoelectrocatalytic (PEC) splitting of water using solar energy has attracted substantial attention as a means of producing hydrogen as a clean and renewable resource [1–3]. Researchers have sought suitable photocatalysts of the splitting of water since a pioneering work of Fujishima and Honda by employing titanium dioxide (TiO₂) semiconductor as photoanode in 1972 [4]. As an anatase TiO₂ photoanode is excited by incident light with wavelengths shorter than 387 nm, electrons and holes can be generated. In short, the photogenerated holes oxidize and decompose water, even some organic or inorganic substances in aqueous solution, at the photoanode while the electrons can interact with hydrogen ions into hydrogen at the counter platinum

(Pt) electrode. It has been shown that hydrogen production can be enhanced by irradiating Pt/TiO₂ suspensions with simultaneous degradation of azo dyes [5]. Moreover, photoelectrolytic cleavage of biomass wastes, such as urine, ethanol and glycerol, in water is much more efficient for electricity generation [6] and hydrogen production [7–9].

For efficient PEC splitting of water, the n-type photoanode is required to have narrow band gap around 2.0 eV, suitable negative flat band potential, good stability and high quantum efficiency [10]. Among various semiconductor photocatalysts, TiO₂ is one of the most popular catalysts because it is environmentally friendly and chemically stable in electrolyte solution with high quantum efficiency. However, the use of TiO₂ is limited by its wide band gap (~3.2 eV). Alternatively, semiconductors with smaller

band gaps, such as CdS (2.4 eV), Fe₂O₃ (2.3 eV), and Cu₂O (2.2 eV), commonly suffer from photocorrosion in electrolyte solution and fast recombination of the photo-generated carriers [10–13]. It is well known that metal or semiconductor with a high work function coupled with other semiconductor can significantly enhance the oxidation ability of photogenerated holes in the semiconductor, due to efficient carrier separation. A heterostructured film, such as TiO₂/ITO (indium tin oxide), TiO₂/WO₃, CdS/TiO₂ or TiO₂/SnO₂, has been proposed for providing a potential driving force for photogenerated charge carrier separation [14–18]. Dai et al. have demonstrated that the superior photocatalytic reactions of the TiO₂/ITO film are mostly associated with the photogenerated holes because ITO has a higher work function (~4.7 eV) [19] than TiO₂ and a Schottky barrier can form at the TiO₂/ITO interface, where the ITO thin film accepts electrons [16]. One should note that both the proximity of their conduction band to conduction band [20] and the proper redox positions of heterostructure play significant roles on charge carrier transfer and thus photocatalysis in the heterostructured film.

Photocatalysis is well known to be a very useful technique in various environmental applications for degrading a wide range of contaminants in air or water. TiO₂ is one of the most suitable semiconductors for several environmental applications, including air purification, water disinfection and hazardous waste remediation [21–23]. TiO₂ codoped with anionic species, such as carbon (C) and nitrogen (N), appears to have very promising visible-light photocatalytic properties in NO oxidation, methylene blue (MB) degradation, and *Escherichia coli* disinfection [24–27]. Yin et al. have shown that substitution of the O sites by N and C is responsible for visible-light photocatalytic activities [27]. It has been found that the N,C-TiO₂ films prepared at low doping concentrations of N (1.3%) and C (1.8%) have exhibited superior photocatalytic degradation of MB solution [28]. Moreover, TiO_{2-x}N_x catalyst with a low doping concentration ($x = 0.021$) has shown the highest activity for the 4-chlorophenol decomposition under the visible-light irradiation [29, 30]. On the other hand, both N-doped In₂O₃ [31] and ITO (N-ITO) [32] and C-doped In₂O₃ [33] electrodes were demonstrated to be promising photocatalysts with favorable PEC properties, especially under visible light ($\lambda > 378$ nm). However, both ITO and N-ITO films exhibit no photocatalytic activity in degradation of MB solution [32], though photocatalytic degradation of azo dyes has been reported active [34]. We previously found that an applied potential could serve as a highly efficient way to suppress hole-electron recombination of the N-ITO electrode, where the generated photocurrent density sharply increased with its applied potential. This was ascribed mostly to better electrical conductivity [31] and proper positions of the flat band potentials [35] as a result of suppression of InN and SnO₂ phases in the domain-structured N-ITO electrode which was prepared at a low N-doping content [32]. However, the origin of visible-light ability of the N-ITO films has not been exploited yet. To enhance the visible-light PEC response, the heterostructured TiO₂/ITO electrodes were codoped with N and C ions grown on ITO glass

substrate, as a layered composite N,C-TiO₂/N,C-ITO/ITO electrode (Ti/TO), for better durability and charge carriers transfer and thus PEC capability [36].

Dimethyl sulfoxide (DMSO) is one of the most common phenol-free organic solvents applied in semiconductor manufacturing industries due to its superior solvent property and water miscibility. However, DMSO is unable to be removed effectively by most typical biological wastewater treatment units [37]. The biodegradation of DMSO might cause the formation of some volatile and noxious compounds such as dimethylsulfide, methylmercaptan and hydrogen sulfide, causing another pollution problem [38]. Since that DMSO is also an effective radical scavenger for hydroxyl radicals ($\bullet$ OH), the wastewater treatment processes that can produce high-concentration $\bullet$ OH radicals will be candidate processes for DMSO removal. Accordingly, some advanced oxidation processes (AOPs) such as H₂O₂/UV [39], O₃/UV [40], corona discharge [41], or UV/TiO₂-based photocatalysts [42] are being developed for the particular purpose of reducing the DMSO concentration in the wastewater. In this study, we aim at the characterization of N,C-TiO₂/ITO electrode with emphasis on the role of the intercalated N,C-ITO layer for PEC degradation of DMSO aqueous pollutant with simultaneous hydrogen production.

2. Experimental Procedure

An in-house closed-field unbalanced magnetron sputtering system (MIRDC, Taiwan) was used to prepare the samples. This system has four vertical magnetron targets each of dimensions 300 × 110 × 10 mm. TiO₂/ITO film electrodes were codoped with N and C ions on as-received ITO (17 Ω/sq. and 100 ± 10 nm thick) glass substrates. In short, a N,C-ITO film was initially deposited onto an unheated rotating substrate using ITO and graphite targets, on one side of the chamber. After the intercalated N,C-ITO film was completed, the substrate holder was rotated toward a pair of titanium targets (99.5% purity) without opening the chamber for the successive deposition of N,C-TiO₂ layer. This heterostructured composite N,C-TiO₂/N,C-ITO/ITO electrode was denoted as Ti/TO. Meanwhile, two other types of N,C-TiO₂/ITO and N,C-ITO/ITO film electrodes, denoted as N,C-TiO₂ and N,C-ITO, respectively, were prepared for comparison. All other sputtering parameters were held constant where the O₂ and N₂ gas proportion was kept at a low rate of 9% in an Ar/O₂/N₂ gas mixture, which had a total flow rate of 55 sccm. Details of the N,C-TiO₂ films, which were prepared at low doping concentrations of N and C were presented elsewhere [28, 32]. An as-received ITO electrode with a thickness of 300 nm was used for comparison. Table 1 presents the physical, morphological, and microstructural properties of the samples.

The crystal structures of the samples were analyzed using a high-resolution X-ray diffractometer (XRD, Rigaku ATX-E) and Micro-PL/Raman spectroscopy (Jobin-Yvon T64000). The surface topography of each sample was analyzed using an atomic force microscope (AFM, SPI 3800N, Seiko) with a scan resolution of 512 × 512 pixels. The microstructure and

TABLE 1: Physical and microstructural properties of samples along with their H_2 yield rates in 4.0 N Na_2CO_3 solution under irradiation of AM 1.0 simulated solar light and 1.5 V applied bias.

Sample	Thickness of TiO_2 : ITO, nm	XRD intensity ratio		RMS, nm	H_2 yield rate, $\mu mol\ cm^{-2}\ h^{-1}$
		(400)/(222)	(440)/(222)		
N,C-ITO	— : 1.4	12.15	4.51	16.3	24.6
N,C- TiO_2	2.1 : —	0.97	0.77	18.5	25.0
Ti/TO	0.4 : 1.4	38.53	5.93	33.6	28.8
ITO	— : 0.3	0.99	0.65	<2.0	—

thickness of the films were investigated by a scanning electron microscope (SEM, JEOL JSM-6700F). The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a high-resolution X-ray photoelectron spectrometer (ULVAC-PHI Quantera SXM/Auger AES 650). Optical absorption of the samples was measured with respect to air using a UV spectrophotometer (Hitachi UV-2900).

PEC oxidation tests were performed using a standard PEC three-cell system that included a sample anode, a saturated calomel electrode (SCE) as a reference electrode and a Pt wire counter electrode 2.0 M Na_2CO_3 solution, (pH $\sim$ 11). The initial concentration of DMSO was 0.03 M. The DMSO residual concentration was monitored by a gas chromatography (GC, HP4890) with flame ionization detection (FID) as its detector. The analytic conditions of the GC/FID for DMSO quantification were capillary separation column (60-m long $\times$ 0.53 mm, 5 μ m, VOCOL, Supelco Co.), temperature ramping from 100°C up to 220°C, and detector temperature was set at 250°C. The system was controlled by a potentiostat (CHI 610C). The samples were illuminated by artificial sunlight (Newport 96000 150 W solar simulator) with a light intensity of Air Mass (AM) 1.0 (75 mW cm^{-2}).

3. Results and Discussion

3.1. Microstructural, Morphological, and Optical Properties. Figure 1 presents the XRD patterns of all three samples along with ITO substrate, which shows distinct diffraction patterns of polycrystalline In_2O_3 phase [36]. All ITO preferred planes revealed in the N,C- TiO_2 are about the same characteristics as in the ITO electrode. However, N,C-ITO and Ti/TO samples exhibit a significantly different pattern against the ITO substrate; the former two exhibit relatively large intensity ratios of (400)/(222) and (440)/(222) planes, as listed in Table 1, which are associated with the increase in resistivity of the host ITO. The increase in resistance of conducting ITO substrate has been correlated to the decrease in fill factor of dye-sensitized TiO_2 solar cells [43]. The intensity ratio that is mostly ascribed to the N dopant increases with its concentration in the ITO lattice [32]. This implies that the intensity ratio, namely, resistivity, can be suppressed by doping fewer amount of N with C ions into the host ITO. In addition, a phase separation of small SnO_2 particles in the host crystalline ITO lattice may occur, since tin is liable to be segregated close to the surface of the lattice or along its grain boundaries under elevated deposition or posttreatment

FIGURE 1: XRD patterns of the composite Ti/TO electrode along with N,C- TiO_2 , N,C-ITO, and ITO film electrodes, where A, R, and I stand for anatase, rutile, and ITO phase, respectively.

conditions [44, 45]. This can cause the increase in resistivity of the N,C-ITO films. The segregation of SnO_2 particles can be further examined by Raman scattering spectra in the following section.

Raman spectra are known to be very sensitive to local crystallinity and microstructures near the film surface. The Raman spectra shown in Figure 2 reveal a typical pattern of the anatase TiO_2 phase for both N,C- TiO_2 and Ti/TO samples [36]. The most intense Raman peaks of the two samples are in the range of $144 \pm 0.5\ cm^{-1}$, which implies well-crystallized nature of the anatase TiO_2 phase [46]. A broad peak around $235\ cm^{-1}$ of SnO_2 phase is observed in sample N,C-ITO. The same broad peak with very weak intensity is also observed in Ti/TO sample, as shown in the inset of Figure 2. This confirms the finding that a little SnO_2 phase is segregated from the host ITO lattice, as discussed in the XRD patterns in Figure 1.

Figure 3 displays representative SEM surface morphologies of the N,C-ITO, Ti/TO and N,C- TiO_2 along with ITO substrate. The N,C-ITO film reveals various shapes and sizes of prismatic grains (50–200 nm) with few small

FIGURE 2: Raman spectra of the composite Ti/TO electrode along with N,C-TiO₂, N,C-ITO, and ITO film electrodes.

subgrains oriented in the same direction on the surface of the film, as shown in Figure 3(a). This grain-subgrain structure is commonly found in typical DC-sputtered ITO film in Figure 3(b) [44] and on N-ITO films prepared at an optimal N content [32]. This implies that the N,C-ITO film still preserves a relatively low resistance. As presented in Figure 3(c), the columnar film morphology observed on the Ti/TO is more distinct in comparison with that on the N,C-TiO₂ in Figure 3(d). The AFM measurements also indicate that the N,C-ITO has the RMS roughness of 16.3 nm, where the N,C-TiO₂ has the value of 18.5 nm. The composite Ti/TO electrode is of the highest RMS of 33.6 nm, as shown in Table 1. One can expect that a significant increase in surface morphology renders more reactive surface area of the sample.

Figure 4 shows the absorption spectra of four samples. Both the UV light absorbing absorption and absorption edge are enhanced for the Ti/TO as a result of the synergetic effect of two film components, as compared to that of the N,C-ITO or N,C-TiO₂ alone. The band gap energy of the Ti/TO electrode is estimated to be about 2.75 eV while the ITO substrate is reportedly of a large band gap energy of ~3.8 eV. Notably, the N,C-ITO and N,C-TiO₂ have barely the same value of 2.98 eV, but the UV absorption of the former is stronger than that of the latter. This implies that the Ti/TO electrode benefits an enhanced absorbing capability in the UV regions from being supported on the N,C-ITO instead of pure ITO substrate.

3.2. XPS Spectra Analysis. After *in situ* Ar⁺ etching for a depth of 5 nm, the C1s, In3d, Sn3d, N1s, and O1s core levels on the ITO and N,C-ITO film electrode were measured by high-resolution XPS (step size = 0.01 eV) in order to examine the effect of carbon and nitrogen dopants on the Ti/TO electrode. The binding energies were calibrated using the C1s energy of 284.6 eV. As shown in Figure 5(a), an

intensive C1s peak is observed in the N,C-ITO, but a very weak peak is noticed in the ITO. The former is mostly attributed to free graphitic nature (C–C) and is regarded as a photosensitizer [47], whereas the latter is the result of Ar⁺ etching off the adventitious carbon on the air-exposed ITO surface. No other noticeable XPS peak can be found in the N,C-ITO within the narrow scan range (i.e., 280–292 eV). This implies that the sputtered carbons did not substitute the lattice oxygen atoms to form the In–C or Sn–C bond. This is because a relatively low carbon concentration is used during the film deposition. Moreover, the O1s XPS spectra of the ITO film in Figure 5(b) were resolved into two peaks; one, at 530.6 eV, is probably due to oxygen in hydroxyl (OH) groups; the other, at 529.8 eV, is assigned to the In–O and Sn–O bonds in crystalline In₂O₃ and SnO₂, respectively [31]. The N,C-ITO shows a shift to lower binding energy (529.65 eV) for the O1s peak of the crystalline In₂O₃ and SnO₂. This shift is in good agreement with the results found for substitutional N-doped TiO₂ and In₂O₃ and C-doped In₂O₃ [31, 33].

The N1s XPS spectra show only a weakened peak at around 396 eV in the N,C-ITO and no such peak is found in the ITO film (see Figure 5(c)). The best fitting of the N1s XPS spectra was obtained at a binding energy of 395.9 eV. No such peaks at 398 eV and 400 eV were found due to a relatively low nitrogen concentration used the electrode deposition [48]. Thus, the N1s XPS peak at 395.9 eV that results from the substitution of the oxygen sites by nitrogen ions is highly responsible for the visible-light photocatalytic activity [49], whereas the C1s peak at 284.6 eV of the graphite source is regarded as a photosensitizer.

As seen in Figure 5(d), the core level of In3d of the N,C-ITO sample shows a small shift to a lower binding energy, as compared with that of the ITO film. After curve fitting using Gaussian distribution functions, the In3d XPS peak appears only at 444.1 eV with a full width at half maximum (FWHM) of 1.4 eV, which is very close to a value of 444.4 eV of the ITO sample and the reported value of 444.2 eV of crystalline In₂O₃ in the literature [50]. The formation of InN phase can be ruled out since no other In3d XPS peak at 442.4 eV can be rationally deconvoluted from the spectra of the N,C-ITO. A little lower binding energy shift suggests that N-substitution could hardly modify the electronic interaction of indium with the oxygen anions under our sputtering conditions.

Alternatively, two peaks, 8.5 eV apart, due to Sn3d_{3/2} and Sn3d_{5/2} XPS peaks, are observed in Figure 5(e). The best fitting for the ITO sample was achieved with two components at binding energies of 486.1 and 487.1 eV (figure not shown). The first peak is assigned to SnO and the second to SnO₂ [50]. However, these two components shifted to lower binding energies of 485.8 and 486.7 eV for the N,C-ITO. A shift to a lower binding energy implies that the creation of SnN (486.2 eV) may not occur in the N,C-ITO [51]. Thus, the formation of SnN phase can be ruled out. Instead, this binding energy shift suggests a reduction of the Sn cation valence state due to a substitutional cationic doping. When N replaces O, the valence state of Sn⁴⁺ is reduced to Sn²⁺, causing the binding energy of the Sn3d_{5/2}

FIGURE 3: Plain view of SEM images of: (a) N,C-ITO, (b) ITO, (c) Ti/TO, and (d) N,C-TiO₂ films.

peak to shift to lower energy. Meanwhile, the atomic ratio of SnO₂/SnO phase of the N,C-ITO is higher than that of the ITO indicating the formation of an SnO₂-rich surface which confirms the results revealed by the XRD and Raman measurements. One can conclude that the observed red shifts in absorption and the band gap narrowing can be mostly attributed to the N-doping, but be a little to the C-doping of the N,C-ITO layer.

3.3. Photoelectrochemical Properties. Figure 6 shows a set of current-voltage (*I-V*) characteristics recorded on the composite Ti/TO electrode along with N,C-TiO₂, N,C-ITO, and ITO film electrodes in Na₂CO₃ solution under illumination of AM 1.0 simulated solar light. The illuminated photocurrent increases sharply as the applied potential reaches 0.5 V and 0.3 V versus SCE on the Ti/TO and N,C-ITO, respectively. Note that there is no saturation of photocurrent observed in both two samples, which indicates efficient charge separation under illumination, while the saturation of photocurrent can be seen on the N,C-TiO₂ electrode at a typical applied potential of 0.3 V versus SCE. Under illumination, however, the ITO substrate exhibits no

gain of photocurrent with a breakdown point at about 0.9 V versus SCE. This indicates that the N and C dopants can enhance the PEC properties of pristine ITO film. That is, a shift of the flat band (onset) potential from -0.7 to -0.82 V versus SCE is achieved by using the intercalated N,C-ITO layer, which can be estimated from the *I-V* measurements in the PEC test [52]. Under solar light illumination, a relatively high photoactive response of the Ti/TO electrode is attributable to, at least in part, the synergetic effect of N,C-codoping on band gap narrowing [25] and photosensitizing [47]. Moreover, the N,C-TiO₂ layer (400 nm thick) enhances not only the photocurrent response of the layered Ti/TO electrode at the entire applied potentials, but also the flat band (onset) potential from -0.82 to -0.91 V versus SCE; a shift of negative flat band potential is desired for facilitating the PEC process [10, 52].

Under irradiation of AM 1.0 simulated solar light and 1.5 V applied bias, the layered Ti/TO film electrode has the highest photocurrent density of 0.47 mA cm^{-2} , that is, a gain of 0.42 mA cm^{-2} , and a hydrogen yield rate of $28.8 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ in 4.0 N Na₂CO₃ solution (pH ~ 11), as shown in Figure 6 and Table 1. Comparatively, the N,C-ITO electrode has a photocurrent density of 0.46 mA cm^{-2} ,

FIGURE 4: Absorption spectra of the composite Ti/TO electrode along with N,C-TiO₂, N,C-ITO and ITO film electrodes.

TABLE 2: Hydrogen yield rates and degradation rate constants of the Ti/TO and N,C-TiO₂ electrodes under illumination of AM 1.0 stimulated solar light.

sample	H ₂ yield rate, $\mu\text{mol cm}^{-2} \text{h}^{-1}$		DMSO rate constant, $\text{cm}^{-2} \text{h}^{-1}$	
	0.5 V	1.5 V	0.5 V	1.5 V
N,C-TiO ₂	10.2	11.8	12.5×10^{-3}	12.8×10^{-3}
Ti/TO	0.3	12.0	10.8×10^{-3}	12.6×10^{-3}

that is, a gain of only 0.35 mA cm^{-2} , and a hydrogen yield rate of $24.6 \mu\text{mol cm}^{-2} \text{h}^{-1}$, respectively. However, the N,C-TiO₂ electrode exhibits a photocurrent density of 0.09 mA cm^{-2} and a relatively high hydrogen yield rate of $25.0 \mu\text{mol cm}^{-2} \text{h}^{-1}$, respectively.

The PEC activity of the Ti/TO and N,C-TiO₂ electrodes was further evaluated by degrading DMSO pollutant maxed in Na₂CO₃ aqueous solution with simultaneous hydrogen production under irradiation of AM 1.0 simulated solar light. As shown in Figure 7 and Table 2, the hydrogen yield rate obtained at 1.5 V is $12.0 \mu\text{mol cm}^{-2} \text{h}^{-1}$, about 40 times higher than that ($0.3 \mu\text{mol cm}^{-2} \text{h}^{-1}$) at 0.5 V versus SCE, which is correlated well with a sharp increase in a photocurrent density of 0.65 mA cm^{-2} , that is, a gain of 0.61 mA cm^{-2} , at 1.5 V versus SCE. Under illumination of AM 1.0 simulated solar light, the degrading rate constant of DMSO is equal to $10.8 \times 10^{-3} \text{ cm}^{-2} \text{h}^{-1}$ and $12.6 \times 10^{-3} \text{ cm}^{-2} \text{h}^{-1}$ at an applied bias of 0.5 V and 1.5 V versus SCE, respectively. In other words, only a 17% increase in degradation rate constant is gained as the applied bias was raised from 0.5 V to 1.5 V, but a 50% increase in degradation rate constant was obtained from photocatalytic ($7.2 \times 10^{-3} \text{ cm}^{-2} \text{h}^{-1}$) to PEC reaction at 0.5 V. The N,C-TiO₂ electrode yields about the same hydrogen evolution of $11.8 \mu\text{mol cm}^{-2} \text{h}^{-1}$ at 1.5 V versus SCE as the Ti/TO, whereas it evolves a hydrogen yield rate of $10.2 \mu\text{mol cm}^{-2} \text{h}^{-1}$ at 0.5 V versus SCE which is much

greater—34 times—than the Ti/TO. This is in accordance with the photocurrent density of the N,C-TiO₂ electrode displayed in Figure 7. These imply that the Ti/TO electrode is preferably suitable for PEC applications with a higher applied bias and the N,C-TiO₂ electrode is generally applicable to a wide range of applied bias.

It is known that an applied bias is used to facilitate the electron transport across the TiO₂/ITO interface and the external circuit [53]. When the applied bias is sufficiently high to pull all of the excited electrons, the concentration of photogenerated holes can be the rate-determining step at the catalyst/electrolyte interface. The saturated photocurrent depends not only upon the types of catalysts and their morphology, crystal phase, and crystallinity, but also upon the types of electrolyte, organic compound, and their concentrations [53–56]. For instance, the TiO₂ nanopore arrays that revealed a saturated photocurrent of 5.8 times as high as that for coated TiO₂ nanofilm electrode has had 2 times as high as the coated TiO₂ nanofilm electrode at an applied bias of 0.5 V versus SCE in PEC process for degradation of aqueous tetracycline solution [56]. This indicates that upon an applied bias on the high photocurrent-saturated electrode, the separation and transport efficiency of photogenerated electron/hole pairs is much higher than that for the conventional coated TiO₂ electrode. This implies that the higher the saturated photocurrent is, the greater the photocatalytic oxidation and the better the efficiency can be rationally expected [54]. However, the reasons for this unexpected low increase in the DMSO rate constant of the Ti/TO electrode are not clear yet and further investigation is being undertaken in our lab.

4. Conclusion

The Ti/TO film electrode that combines a versatile layer of N,C-TiO₂ and a novel intercalated layer of N,C-ITO reveals a synergetic photocatalytic capability for simultaneous DMSO degradation and hydrogen production. The structural properties of the sample electrodes, determined by X-ray diffraction (XRD) and Raman scattering, show that the overlaid N,C-TiO₂ film exhibits primarily the crystallized anatase TiO₂ phase and the intercalated N,C-ITO film shows distinct diffraction patterns of polycrystalline In₂O₃ phase. Under AM 1.0 simulated solar light irradiation and 1.5 V applied potential, the photocurrent density of the Ti/TO film electrode is 20% and 4.7 times higher than that of the N,C-ITO and N,C-TiO₂ electrodes, respectively. Moreover, the Ti/TO electrode yields simultaneously a hydrogen production rate of $12.0 \mu\text{mol cm}^{-2} \text{h}^{-1}$ and degradation rate constant of $12.6 \times 10^{-3} \text{ cm}^{-2} \text{h}^{-1}$, whereas the N,C-ITO electrode shows no pollutant oxidation. In view of the synergetic effect of N,C-codoping on the composite Ti/TO electrode, not only the N,C-TiO₂ layer enhances the photocurrent response and a cathode shift of the flat band potential, but also the intercalated N,C-ITO layer can significantly increase photocurrent response at a high applied potential. These are desperately beneficial in the PEC process of pollutant degradation and hydrogen production as well.

FIGURE 5: XPS high-resolution spectra of: (a) C1s, (b) O1s, (c) N1s, (d) In3d, and (e) Sn3d core levels for the N,C-ITO and ITO film electrodes.

FIGURE 6: Photocurrent response of the Ti/TO and N,C-TiO₂ electrodes along with N,C-ITO and ITO substrates in Na₂CO₃ solution.

FIGURE 7: Photocurrent response of the Ti/TO and N,C-TiO₂ electrodes in Na₂CO₃ mixed with DMSO aqueous solution.

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