

Deposition of Layered N,C-(TiO₂/ITO) Electrodes for Solar Hydrogen Production via Photoelectrochemical Degradation of Aqueous Pollutant

K.R. Wu^{*}, C.H. Hung^{**}, C.W. Yeh^{***}, C.C. Wang^{*}, T.P. Cho^{****}

^{*} National Kaohsiung Marine University, Kaohsiung, Taiwan, krwu@mail.nkmu.edu.tw

^{**} National Kaohsiung First University of Science and Technology, jeremyh@ccms.nkfust.edu.tw

^{***} Kao Yuan University, alice@cc.kyu.edu.tw

^{****} Metal Industries Research and Development Centre, tpcho@mail.mirdc.org.tw

ABSTRACT

To enhance the visible-light photoelectrochemical (PEC) response, the heterostructured TiO₂/ITO electrodes were codoped with nitrogen (N) and carbon (C) ions grown on ITO glass substrate as a layered N,C-(TiO₂/ITO)ITO (Ti/TO) electrode. Under AM 1.0 simulated solar light irradiation and 1.5 V applied bias, the layered Ti/TO electrode yields simultaneously a hydrogen production rate of 12.0 μmol/cm² h and pollutant degradation rate of 0.0126 l/cm² h, whereas the N,C-ITO electrode shows little activity of pollutant oxidation. One can conclude that the overlaid N,C-TiO₂ layer enhances not only the photocurrent response of the layered Ti/TO electrode at entire applied potentials, but also the flat band potential; a shift of about 0.1 V toward the cathode, which is desperately beneficial in PEC process. The PEC activities are attributable in part to the columnar film surface of the layered Ti/TO electrodes.

Keywords: solar hydrogen, TiO₂, ITO, PEC degradation

1 INTRODUCTION

The photoelectrochemical (PEC) splitting of water using solar energy has attracted substantial attention as a means of producing hydrogen as a clean and renewable resource [1]. Researchers have sought suitable photocatalysts for splitting water since a pioneering work of Honda and Fujishima by employing TiO₂ semiconductor as photoanode in 1972 [2]. 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 [3]. Moreover, photoelectrolytic cleavage of biomass wastes, such as urine, ethanol and glycerol, in water is much more efficient for electricity generation [4] and hydrogen production [5].

For efficient PEC splitting 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 [1]. 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 photogenerated carriers [1]. 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 carriers separation. A heterostructured film, such as TiO₂/ITO, TiO₂/WO₃, CdS/TiO₂ or TiO₂/SnO₂, have been proposed for providing a potential driving force for photogenerated charge carriers separation [6-9]. Dai *et al.* have demonstrated that the superior photocatalytic (PC) reactions of the TiO₂/ITO film are mostly associated with the photogenerated holes, because ITO has a higher work function (~4.7 eV) than TiO₂ and a Schottky barrier can form at the TiO₂/ITO interface, where the ITO thin film accepts electrons [7]. One should note that in heterostructured film not only the proximity of their conduction band to conduction band [10], but also the proper redox positions of heterostructure plays significant roles on charge carriers transfer and thus photocatalysis.

Recently, both N-doped In₂O₃ and ITO (N-ITO) and C-doped In₂O₃ electrodes were demonstrated to be promising photocatalysts with favorable PEC properties, especially under visible light ($\lambda > 378$ nm) [11-13]. However, both ITO and N-ITO films exhibit no PC activity in degradation of methylene blue solution [12], though some PC degradation of azo dyes has been reported [14]. In our previous work, we found that an applied bias could serve as a highly efficient way to suppress hole-electron recombination of the N-doped ITO electrode, where the generated photocurrent density sharply increased with its applied bias potential. This has been ascribed mostly to better electrical conductivity and proper positions of the flat band potentials [11,15] as a result of suppression of InN and SnO₂ phases in the domain-structured N-ITO electrode which is prepared at a low N-doping content [13].

Titania codoping with anionic species, such as C and N, appears to have very promising visible-light PC properties

on pollutant oxidation [16,17]. Yin *et al.* have shown that substitution of the O sites by N and C is responsible for visible-light PC activities [17]. To enhance the visible-light PEC response, the heterostructured TiO₂/ITO electrode was codoped with nitrogen and carbon ions grown on ITO glass substrate, as a layered N,C-(TiO₂/ITO)ITO film electrode (Ti/TO), for better durability and charged carriers transfer and thus PEC capability. We aimed to investigate the Ti/TO electrodes for solar hydrogen production with simultaneous degradation of aqueous pollutant.

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 removed effectively by most typical biological wastewater treatment units [18]. Thus, some advanced oxidation processes, e.g. O₃/UV, or UV/TiO₂-based photocatalysts are being developed for the particular purpose of reducing the DMSO concentration in the wastewater [19,20]. In this study, DMSO was chosen as the target pollutant for PEC degradation with simultaneous hydrogen production.

2 EXPERIMENTAL PROCEDURE

A closed-field unbalanced magnetron sputtering system (MIRDC, Taiwan) was used to prepare the samples. Layered TiO₂/ITO films were codoped with N and C ions on as-received ITO (17 Ω/sq. and 100±10 nm thick) glass substrates. In addition to the heterostructured Ti/TO film, N,C codoped TiO₂ (N,C-TiO₂, 2.2 μm) and ITO (N,C-ITO, 1.8 μm) samples were prepared under the same sputtering conditions as each counterparts of the Ti/TO were, denoted as N,C-TiO₂ and N,C-ITO, respectively. An as-received ITO electrode (e-ITO) with a thickness of 300 nm was used for comparison. Details were described elsewhere [12,21].

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 samples was analyzed using an atomic force microscope (AFM, SPI 3800N, Seiko). The microstructure and thickness of the films were investigated by a scanning electron microscope (SEM, JEOL JSM-6700F).

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 in DMSO or 4.0 N Na₂CO₃ solution (pH~11). The initial concentration of DMSO was 0.03 mole/L. The DMSO residual concentration was monitored by a GC (HP4890) with FID as its detector. The analytic conditions of the GC/FID for DMSO quantification were: VOCOL separation column (60-m long×0.53 mm, 5 μm, 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 AM

1.0 (75 mW/cm²). An applied bias of 0.5 V and 1.5 V vs. SCE was used in all PEC and electrolysis tests, since a total of applied bias of higher than 2.0 V has been reported to be supplied to drive electrolysis in a practical PEC system [22].

3 RESULTS AND DISCUSSION

3.1 Microstructural and Morphological Properties

Fig. 1 presents the XRD patterns of all three samples along with e-ITO electrode, which shows distinct diffraction patterns of polycrystalline cubic bixbyite In₂O₃ phase. All ITO preferred planes revealed in N,C-TiO₂ sample are about the same characteristics in the e-ITO electrode. However, N,C-ITO and Ti/TO samples exhibit a significantly different pattern against the e-ITO, exhibiting 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 [12]. The increase in resistance of conducting ITO substrate has been correlated to the decrease in fill factor of dye sensitized TiO₂ solar cells [1]. The intensity ratio that is mostly ascribed to the N dopant increases with its concentration in the ITO lattice [12]. 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 SnO₂ 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 post treatment conditions [23]. This can cause the increase in resistivity of the N,C-ITO films. The segregation of SnO₂ particles can be further examined by Raman scattering spectra in the following section.

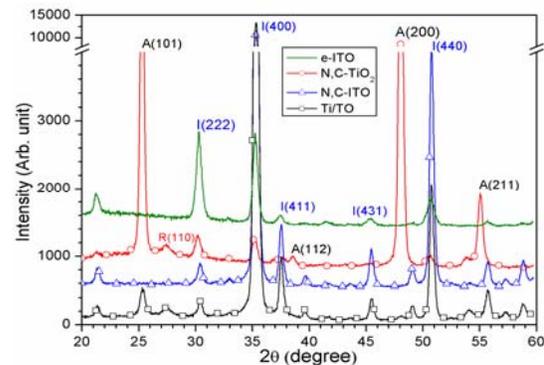


Fig. 1: XRD patterns of all three samples and e-ITO electrode; A: anatase, I: In₂O₃

Raman spectra are known to be very sensitive to local crystallinity and microstructures near the film surface. The Raman spectra shown in Fig. 2 reveal typical patterns of the anatase TiO₂ phase for both N,C-TiO₂ and Ti/TO samples. The most intense Raman peaks of the two

samples are in the range of $144 \pm 0.5 \text{ cm}^{-1}$, which implies well-crystallized nature of the anatase TiO_2 phase [24]. A broad peak around 235 cm^{-1} of SnO_2 phase is observed in N,C-ITO sample. The same broad peak with very weak intensity is also observed in Ti/TO sample, as shown in the inset of Fig. 2. This confirms the finding of the XRD patterns discussed in Fig. 1.

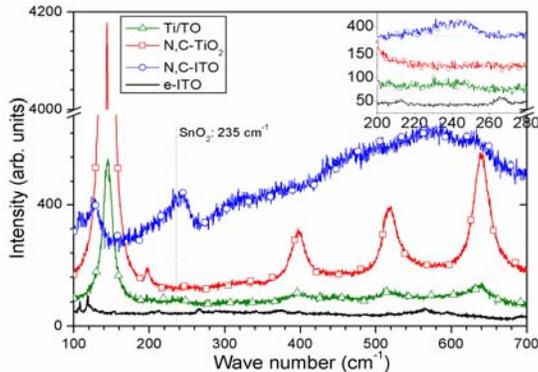


Fig. 2: Raman spectra of all three samples and e-ITO electrode

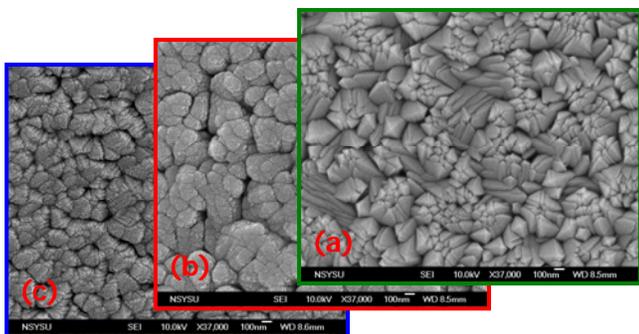


Fig. 3: Plain view of SEM images: (a) N,C-ITO, (b) Ti/TO and (c) N,C-TiO₂ samples

Fig. 3 displays plain SEM images of N,C-ITO, Ti/TO and N,C-TiO₂ samples. The N,C-ITO film reveals various shapes and sizes of prismatic grains (50-200 nm) with few small sub-grains oriented in the same direction on the surface of the film, as shown in Fig. 3(a). This grain-subgrain structure is commonly found in typical DC-sputtered ITO films [23] and on N-doped ITO films prepared at an optimal N content [12]. This implies that the N,C-ITO film still preserve a relative low resistance. As presented in Fig. 3(b), the columnar film morphology observed on Ti/TO sample is more distinct in comparison with that on N,C-TiO₂, as shown in Fig. 3(b) and 3(c), respectively. The AFM measurements indicate that the N,C-ITO has a RMS roughness and specific surface area ratio of 16.3 nm and 1.21, where N,C-TiO₂ has the corresponding values of 18.5 nm and 1.25, respectively. The Ti/TO film which consisted of a N,C-ITO film overlaid by a DC-sputtered TiO₂ film with a thickness of 300 nm has the values of 33.6 nm and 1.35, respectively, as shown in Table 1. One can expect that a significant increase in

surface morphology renders more reactive surface area of the sample.

Table 1: General structural properties of samples

sample	In ₂ O ₃ intensity ratio		RMS (nm)
	(400)/(222)	(440)/(222)	
N,C-ITO	12.15	4.51	16.3
N,C-TiO ₂	0.97	0.77	18.5
Ti/TO	38.53	5.93	33.6
e-ITO	0.99	0.65	<2.0

3.2 Photoelectrochemical Properties

Fig. 4 shows a set of current-voltage (IV) characteristics recorded on three samples and e-ITO electrode in dark and under illumination of simulated solar light. Under illumination, the photocurrent increases sharply as the applied potential reaches 0.5 V and 0.3 V vs. SCE on N,C-ITO and Ti/TO electrodes, respectively. 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 N,C-TiO₂ sample. Under illumination, however, the e-ITO electrode exhibits no gain on photocurrent with a breakdown point at about 0.9 V vs. 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 potential from -0.70 to -0.82 V vs. SCE is achieved on N,C-ITO sample, which was estimated from the I-V measurements in Fig. 4 [25]. The 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 and photosensitizing [16,21]. Moreover, the overlaid N,C-TiO₂ layer (300 nm thick) enhances not only the photocurrent response of the layered electrode at the entire applied potentials, but also the flat band potential from -0.82 to -0.91 V vs. SCE; a shift of negative flat band potential is desired for facilitating the PEC process [1,25].

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 0.42 mA/cm² and hydrogen yield rate of 28.8 μmol/cm² h in 4.0 N Na₂CO₃ solution (pH~11). Comparatively, the N,C-ITO electrode has a photocurrent density of 0.35 mA/cm² and a hydrogen yield rate of 24.6 μmol/cm² h, respectively. However, the N,C-TiO₂ electrode exhibits a photocurrent density of 0.09 mA/cm² and a relatively high hydrogen yield rate of 25.0 μmol/cm² h, respectively.

The PEC and PC activities of the layered Ti/TO film were further evaluated by studying the degradation of DMSO aqueous solution with simultaneous hydrogen production under illumination of simulated solar light. Hydrogen evolution by electrolysis was undetectable at an applied bias of even higher than 2.0 V vs. SCE, which is in good agreement with the report by Mishra et al. [22]. The PEC activities of Ti/TO electrode at 1.5 V show a

significant increase in the hydrogen evolution with simultaneous DMSO degradation activity, as summarized in Table 2. The hydrogen yield rate obtained at 1.5 V was $12.0 \mu\text{mol}/\text{cm}^2$; about 40 times higher than that at 0.5 V ($0.3 \mu\text{mol}/\text{cm}^2 \text{ h}$) vs. SCE, which is correlated well with the sharp increase of photocurrent density of $0.61 \text{ mA}/\text{cm}^2$ at 1.5 V vs. SCE (figure not shown). The degradation rate is found to fit approximately a pseudo-first-order kinetic model as a function of applied bias; the degrading rate constant of DMSO was equal to $0.0108 \text{ l}/\text{cm}^2 \text{ h}$ and $0.0126 \text{ l}/\text{cm}^2 \text{ h}$ at an applied bias of 0.5 V and 1.5 V, respectively. In other words, only a 17% increase in degradation rate was gained as the applied bias was raised from 0.5 V to 1.5 V, but a 50% increase in degradation rate was obtained from the PC ($0.072 \text{ l}/\text{cm}^2 \text{ h}$) to PEC reaction at 0.5 V.

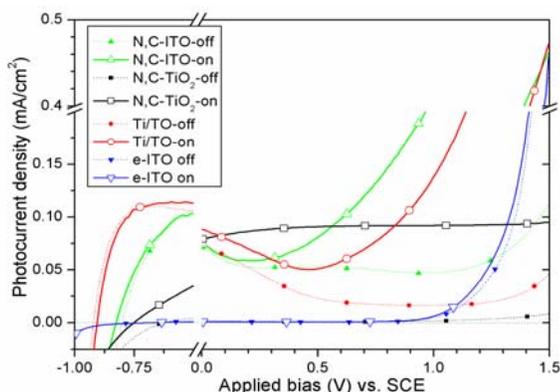


Fig. 4: Photocurrent response of three samples and e-ITO electrode

Table 2: The degradation rate and hydrogen yield rates obtained from the PEC reaction in DMSO solution

sample	degradation rate, $\text{l}/\text{cm}^2 \text{ h}$		hydrogen yield rate, $\mu\text{mol}/\text{cm}^2 \text{ h}$	
	0.5 V	1.5 V	0.5 V	1.5 V
Ti/TO	0.0108	0.0126	0.3	12.0

4 CONCLUSION

In summary, the layered Ti/TO electrode that combined a versatile N,C-TiO₂ top layer and novel bias-driven N,C-ITO intercalated layer is expectedly to perform the synergetic PEC capability for simultaneous DMSO degradation and hydrogen production under solar light illumination. In addition to a distinct columnar morphological feature, the overlaid N,C-TiO₂ layer enhances both the photocurrent response and the negative flat band potential of the layered Ti/TO electrode as well.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan, ROC, for financial support this research under Contract No. NSC 98-2221-E-022 -004 -MY2.

REFERENCES

- [1] J. Nowotny, T. Bak, M.K. Nowotny and L.R. Sheppard, *Int. J. Hydrog. Energy* 32, 2609, 2007.
- [2] A. Fujishima and K. Honda K. *Nature* 238, 37, 1972.
- [3] A. Patsoura, D.I. Kondarides and X.E. Verykios, *Appl Catal B* 64, 171, 2006.
- [4] D.I. Kondarides, V.M. Daskalaki, A. Patsoura and X.E. Verykios, *Catal. Lett.* 122, 26, 2008.
- [5] M. Antoniadou, P. Bouras, N. Strataki and P. Lianos, *Int. J. Hydrog. Energy* 33, 5045, 2008.
- [6] H. Irie, H. Mori, K. and Hashimoto, *Vacuum* 74, 625, 2004.
- [7] W. Dai, X. Wang, P. Liu, Y. Xu, G. Li and X. Fu, *J. Phys. Chem. B* 110, 13470, 2006.
- [8] H. Chen, S. Chen, X. Quan, H. Yu, H. Zhao and Y. Zhang, *J. Phys. Chem. C* 112, 9285, 2008.
- [9] J. Bai, J. Li, Y. Liu, B. Zhou and W. Cai, *Appl. Catal. B* 95, 408, 2010.
- [10] A.J. Nozik and R. Memming, *J. Phys. Chem.* 100, 13061, 1996.
- [11] K.R. Reyes-Gil, EA. Reyes-Garcia and D. Raftery, *J. Phys. Chem. C* 111, 14579, 2007.
- [12] K.R. Wu, C.W. Yeh, C.H. Hung, L.H. Cheng and C.Y. Chung, *Thin Solid Films* 518, 1581, 2009.
- [13] Y. Sun, C.J. Murphy, K.R. Reyes-Gil, EA. Reyes-Garcia, J.P. Lilly and D. Raftery, *Int. J. Hydrog. Energy* 33, 5967, 2008.
- [14] M.H. Habibi and N. Talebian, *Dyes Pigment* 73, 186, 2007.
- [15] Y. Bessekhoad, D. Robert and J.-V. Weber, *Catal. Today* 101, 315, 2005.
- [16] D. Noguchi, Y. Kawamata, and T. Nagatomo, *J. Electrochem. Soc.* 152, D124, 2005.
- [17] S. Yin, M. Komatsu, Q. Zhang, F. Saito and T. Sato, *J. Mater. Sci.* 42, 2399, 2007.
- [18] S. Matsui, Y. Okawa and R. Ota, *Water Sci. Technol.* 20, 201, 1998.
- [19] J.J. Wu, M. Muruganandham and S.H. Chen, *J. Hazard. Mater.* 149, 218, 2007.
- [20] A.M. Cojocariu, P.H. Mutin, E. Dumitriu, A. Vioux, F. Fajula and V. Hulea, *Chemosphere* 77, 1065, 2009.
- [21] K.R. Wu and C.H. Hung, *Appl. Surf. Sci.* 256, 1595, 2009.
- [22] P.R. Mishra, P.K. Shukla, A.K. Singh and O.N. Srivastava, *Int. J. Hydrog. Energy* 28, 1089, 2003.
- [23] M. Kamei, Y. Shigesato and S. Takaki, *Thin Solid Films* 259, 38, 1995.
- [24] V. Swamy, A. Kuznetsov, L.S. Dubrovinsky, R.A. Caruso, D.G. Shchukin and B.C. Muddle, *Phys. Rev.* 71, 184302, 2005.
- [25] M. Radecka, M. Rekas, A. Tenczek-Zajac and K. Zakrzewska, *J. Power Sources* 181, 46, 2008.