Dinitrogen Fixation Using Polyfuran-Titanium Oxide and Polycarbazole-Titanium Oxide Hybrid Junction Systems

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Polyfuran-titanium oxide mixed system and polycarbazole/titanium oxide layered system were electrochemically prepared and characterized, and their ability to fix atmospheric dinitrogen was investigated. When white light from a pseudo-solar lamp was exposed to the mixed and layered systems, fixation of N₂ into ammonium perchlorate and ammonia occurred. The fixation yield of the former and the latter systems were respectively comparable to and superior to that of the poly(3-methylthiophene)/titanium oxide system reported previously. The high yields were discussed on the basis of the light-absorption characteristics, physicochemical and morphological properties of the conducting polymers, and the photoactivity of the titanium oxide.

Keywords: nitrogen fixation, polyfuran, polycarbazole, organic/inorganic hybrid materials, titanium oxide

1. Introduction

Recently, we proposed a novel photoinduced N₂-fixation system and process using a junction of poly(3-methylthiophene) (P3MeT) and titanium oxide (TiOₓ) [1-6]. The junction was formed by electrodeposition of ClO₄⁻-doped P3MeT film on the TiOₓ layer prepared by the anodic oxidation of a titanium plate. White-light irradiation of the junction caused the fixation of atmospheric dinitrogen into ammonium perchlorate and ammonia. The fixation reaction proceeded under ordinary pressure and temperature, and the NH₄⁺ClO₄⁻ crystals are formed on the surface and/or in the bulk of the P3MeT film (Fig. 1). Though the fixation mechanism is not conclusive, two-step mechanism has been proposed which involves the photochemical formation of NH₃ at the junction interface and its partial conversion to NH₄⁺ClO₄⁻ in the bulk of P3MeT [7]. The former process of NH₃ formation is known as Schrauzer’s process [8] in which the photo-reduction of adsorbed N₂ is coupled with the photo-oxidation of adsorbed water to give NH₃ and O₂ on the powdered titanium oxide surface under the irradiation of UV-light. However, the fixation has a low reaction rate (fixation rate = 1 ~ 10 µmol m⁻² h⁻¹) and declines in a few to a few tens hours [9, 10]. These drawbacks drove us to find alternative route mentioned above which can fix dinitrogen over a period of ca. ten days at a rate of 19 µmol m⁻² h⁻¹ upon irradiation of white light (486 W m⁻²).

![Fig. 1 Schematic illustration of a P3MeT/TiOₓ junction used to fix atmospheric N₂.](image-url)
However, the conducting polymers used are virtually confined to P3MTe, and thus, feasibility to use other polymers is required in our fixation system. In view of its technological applications in the chemical industries, it is desirable to employ inexpensive raw materials for the synthesis of the polymer films. In this study, we prepare conducting polymers/TiOx systems using lower-cost materials, polyfuran and polycarbazole, and investigate their ability to fix atmospheric dinitrogen under mild conditions.

2. Experimental
2.1. Materials and sample preparation.
Our N2-fixation system is an organic-inorganic composite system consisting of conducting polymer film and TiOx. The TiOx layers were prepared by the controlled-potential anodization of a titanium plate in a dichromethane solution containing tetrabutylammonium perchlorate (TBAP, 0.1 M) or a phosphoric acid solution (0.85 wt%) at 20 °C. The titanium plates (99.5%) were purchased from Sumitomo Metal Industries, Ltd. and contain impurities such as Fe (0.250%), K (0.013%), O (0.200%), and N (0.005%). Prior to the anodization, the Ti plate was degreased by ultrasonic washing with trichloroethylene, acetone, and ethanol (10 min each), and etched by dipping in aq.HF (5%, 5 min) and then in an HF(1%)/HNO3(3%)/H2O2(10%) mixture for 30 min. The etching was followed by washing with distilled-deionized water for 1 min. The electrolyte solutions were introduced to a two-electrode-type cell, and the anodization was conducted at 15 V (for the CH2Cl2 electrolyte solution) or 10 V versus a counter Pt plate (for the phosphoric acid solution). The former and latter TiOx layers will be hereinafter abbreviated as TiOxO and TiOxW, respectively. The distance between the two electrodes was 6 cm, and the area of the An anode exposed to the electrolyte solution was 2.0 cm2 (delimited by an O-ring). The TiOx layers thus obtained were ultrasonically washed in trichloroethylene, acetone, and ethanol (10 min each).

Immediately after the preparation of the TiOx, potentiostatic electropolymerization of furan (Tokyo Kasei Kogyo Co., >99%) or carbazole (Tokyo Kasei Kogyo Co., >96%) on the TiOx layer was carried out by varying the polymerization potential (E). Polyfuran (PF) and polycarbazole (PCz) films were prepared at 13 °C by using dichromethane solutions of furan (0.1 M) + TBAP (0.1 M) and carbazole (5 mM) + tetraethylammonium perchlorate (65 mM), respectively. The amount of electricity (Q) for the polymerization of the PF and PCz films were 400 and 250 mC cm2, respectively. Prior to the electropolymerization, furan was purified by distillation.

2.2. N2-fixation procedures.
White-light irradiation from a fluorescent lamp (Hitachi Co., Model FL20SSN, 30 W) or pseudo-solar lamps (Wacom I-SUNSUN (75 W) or Seric XC-100AF (100 W)) equipped with an IR-cut filter was performed through a quartz window having a 220 mm diameter in a acrylic container (500×500×750 mm3) which contains the samples, digital thermo- hygrometer, and air. The relative humidity inside the container was not specifically controlled; however, the container was placed in an air-conditioned room, keeping the atmosphere in it at ca. 20 °C and 40 %RH throughout the illumination. Light intensity was measured by a pyranometer (EKO MS-601).

The amount of the N2-fixation products was determined by the indo-naphthol method [11] which can be used for the quantification of NH4+ and NH3.

2.3. Characterization of the samples.
The junction samples were characterized by the Fourier transform infrared spectroscopy (FT-IR, JASCO FT/IR-410), X-ray photoelectron spectroscopy (XPS, ULVAC phi ESCA5400 spectrometer with AlKα radiation), and scanning electron microscopic observations (SEM, Topcon ABT-32). For the XPS measurements, the absolute binding energy scale was obtained by setting the C1s peak to 284.6 eV.

3. Results and Discussion
3.1. Electropolymerization behaviors of PF and PCz films.
The electropolymerization in this study competes with the growth of the TiOx layers. When the oxidation potential of the monomeric precursor is relatively low, the former electrode reaction precedes the latter, and therefore, the electro-polymerized film is formed on the TiOx layer (i.e., formation of a layered structure). This is the case for the use of 3-methylthiophene [1,2,4,5] and carbazole [12]. Indeed, green-colored PCz films were deposited on the TiOxW in the potential range of 20 to 70 V to form the PCz/TiOxW layered structure.

On the other hand, when the oxidation potential of the monomer is rather high, the rate of the
electropolymerization is comparable to that of the growth of the TiOₓ and hence the formation of the mixed film is expected. Such mixed structure is intriguing since the area of the photo-active region, junction interface between the conducting polymer and the TiOₓ, may be larger than that of the layered structure. In accordance with our expectation, use of furan with higher oxidation potential [13,14] led to the formation of the mixed films in the potential region of 100 to 200 V. PF films were previously electrodeposited on a Pt plate [15,16], and the authors reported that brown and black films were formed at lower and higher oxidation potentials, respectively. In our electrosyntheses also, the PF films exhibited color change from grayish brown to grayish black at ca. 170 V.

3.2. Characterization of junction systems.

The PF-TiOₓ composite layer prepared at 180 V was peeled off the substrate by scratching and mixed with KBr, and its FT-IR spectrum was recorded (Fig. 2a). Included in this figure for comparison is the PF film prepared on an indium-tin-oxide coated glass (ITO, Geomatech Co.) under the same solution and electrolysis conditions (Fig. 2b). This spectrum agrees well in shape and peak positions with the black PF film deposited on a Pt plate [15,16]. Spectra a and b show bands at 3200 – 3600 and 1620 cm⁻¹, attributed to adsorbed water [15,17,18]. The hygroscopic character of TiOₓ [19] and PF [15] may be responsible for the bands. The strong absorptions centered at 1100 and 627 cm⁻¹ are due to the ClO₄⁻ ion doped in the PF films [13]. The former absorption is superposed on polyfuran C-O stretching vibration [15]. The signal at 1400 cm⁻¹ can be assigned to polyfuran C=O stretching vibration and ring deformation, and C-H ring deformation was observed at 800 cm⁻¹. In the spectrum a, a broad absorption band located between 500 and 1000 cm⁻¹ was observed and are assignable to Ti-O stretching vibration of titanium oxide [20,21]. In the spectrum b, a C=O stretching band at 1700 cm⁻¹ and aliphatic C-H stretching band in the region of 2800-3000 cm⁻¹ were observed, indicating furan ring opening [15,16] upon the electropolymerization of furan on the Pt substrate. The absence of these bands in the spectrum a demonstrates the formation of high-quality PF film without furan ring rupture on the TiOₓ layer. These results of the FT-IR measurements show the composite is a mixture of PF and TiOₓ.

The XPS analyses on C, Cl, and Ti for the PF-TiOₓ composite film revealed that the doping level (= the number of ClO₄⁻ ions associated with one furan unit) and the mixed ratio of TiOₓ to furan ring unit are 29% and 2.9, respectively. The doping level is nearly equal to the reported value for the PF film, 26% [13]. Similarly the doping level of the PCz film was determined to be 32%.

3.3. N₂-fixation experiments using PF-TiOₓ and PCz/TiOₓ junctions.

White light from a fluorescent lamp (4 W m⁻²) was irradiated to the PF-TiOₓ composite film (Eₑ = 180 V). Fig. 3 shows the SEM images of the film surfaces taken after 2 (a, b) and 5 weeks of white-light illumination (c). The NH₄⁺ClO₄ crystals grew in a cylindrical fashion, and increased in size and abundance with the irradiation time – very similar in morphology to the N₂-fixation product for the P3Met/TiOₓ junction system [4,5]. These results present possible use of PF in our fixation reaction.

Fig. 4 shows the SEM images of the PCz/TiOₓ junctions exposed to white light (pseudo-solar lamp, 260 W m⁻²) for 7 days: The PCz films were prepared at 20 (a), 40 (b), 50 (c), and 70 (V). Their thicknesses, determined by the SEM observations, were 3.0 (a), 2.5 (b), 2.3 (c), and 2.2 μm (d). Also in this case, NH₄⁺ClO₄ needle crystals were generated by the illumination, showing again the successful use of PCz in the N₂-fixation reaction. Note that the shape of the crystals are dependent on Eₑ: granular-type crystals at 20 V and needle crystals in the potential range of 40 to 70 V, and that the numerical density of the granular crystallites is much higher than that of the needle crystallites. Though not shown here, the SEM
images of the PCz films taken before the illumination revealed that compact and porous films were formed at 20 V and in the region of 40 – 70 V, respectively. If we assume that the ClO₄⁻ ions (the dopant to offer an anionic part of the N₂-fixation product, NH₄ClO₄) are distributed homogeneously in the compact PCz film, but are not so in the porous film, the above-mentioned differences in morphology and numerical density of the crystallites may be explained.

3.4. N₂-fixation yield.

The yield of N₂ fixation for the PF-TiOₓ/O and PCz/TiOₓ/W junctions were measured by the indo-naphthol method, and investigated as a function of the electro-polymerization potential, E_c.

Fig. 5 shows the plot of N₂-fixation yield, η, versus E_c for the PF-TiOₓ/O junctions which were exposed to white light (pseudo-solar lamp, 54 W m⁻²) for 7 days. The plot shows the rise of η to a maximum and its subsequent fall; η was maximum of 1.5 mmol m⁻² when E_c = 180 V. This yield was comparable to that obtained under the same irradiation conditions for the P3MeT/TiOₓ junction, 1.8 mmol m⁻² [7]. In our previous study, the effect of anodic oxidation potential (E_a) of TiOₓ on η was investigated and demonstrated constant high reactivity of TiOₓ below E_a = ca. 10 V and its monotonic decrease with increasing E_a above ca.
10 V: For example, $\eta = 1.8$ and 0.6 mmol m$^{-2}$ at $E_a = 10$ and 30 V, respectively, for the P3MeT/TiO$_x$ junction system [7]. This result may be accounted for by assuming that the TiO$_x$ layers prepared at lower potentials (0 V < $E_a$ < 10 V) have more defects (oxygen vacancies) than those prepared at higher potentials ($E_a$ > ca. 10 V), since such defects are expected to show activity for the adsorption, activation, and reduction of N$_2$ [2, 9, 22-24]. In the PF-TiO$_x^0$ junction, it exhibited higher activity for the N$_2$-fixation though the TiO$_x^0$ was prepared at as high as 180 V. One possible explanation for this is the effect of the hybridization of PF and TiO$_x^0$. In the P3MeT/TiO$_x$ layered structure, the P3MeT film causes a reduction in the number of photons reaching the photoactive junction interface (see Fig. 1), while the photoactive region involves the film surface in the PF-TiO$_x^0$ hybrid system, and its efficient photo absorption characteristics make up for the low activity of the TiO$_x^0$ to give a high N$_2$-fixation yield comparable to the P3MeT/TiO$_x$ system.

The value of $E_c$ (180 V) showing the maximum of $\eta$ coincides with the potential at which the composite film shows color change of grayish brown to grayish black. González-Tejera et al. prepared polyfuran films on a Pt plate and found that the electric conductivity of the brown film is lower than that of the black film, i.e., the lower doping level of the former film compared with the latter [25]. As described in section 1, the expected reaction scheme of our N$_2$-fixation involves the photochemical formation of NH$_3$ at the polymer/TiO$_x$ interface and its partial conversion to NH$_3$·ClO$_4^-$ by the action of dedoping of the conducting polymer [7]. Additionally, recent our results revealed that the NH$_3$-formation process is also dependent on the doping level since use of the undoped polymer film gave rise to the formation of trace amounts of NH$_3$ and NH$_4^+$·ClO$_4^-$ [26]. Based on this scheme, the lower the doping level of the PF (the smaller the ClO$_4^-$ content in the PF), the lower is the N$_2$-fixation yield. In view of these considerations, the decrease in $\eta$ with decreasing $E_c$ (105 V < $E_c$ < 180 V) in Fig. 4 may be accounted for by a decrease in the doping level with decreasing $E_c$. Above the potential of 180 V, the anodization precedes the electropolymerization of PF, resulting in the composite film enriched with TiO$_x^0$. This enrichment should cause decreases in the contact (or junction) area between the PF and TiO$_x^0$ (the site for the NH$_3$ formation) and in the volume of a PF bulk (acting as a site for the conversion of NH$_3$ to NH$_4^+$·ClO$_4^-$), leading to a lowering in $\eta$ with $E_c$.

Fig. 6 shows the dependence of $\eta$ on $E_c$ for the PCz/TiO$_x^w$ junction cells exposed to white light from the pseudosolar lamp (260 W m$^{-2}$, 7 days). A maximal $\eta$, 3.6 mmol m$^{-2}$, was exhibited by the compact film prepared at $E_c = 20$ V (see section 3.3). This value is higher than that for the P3MeT/TiO$_x$ junction treated under the same illumination conditions, 2.2 mmol m$^{-2}$; and hence, it was found that the compact PCz film is more efficient and promising than the PF and P3MeT films in our N$_2$-fixation system. The values of $\eta$ in the potential region of $E_c = 40 \sim 70$ V are nearly
equal to that for the P3MeT/TiOₓ junction. As described in section 3.3, the PCz films in this potential range are characterized by their porous structure and are similar in morphology to the P3MeT film. Hence, these results may be an indication that the more compact the film structure, the higher is the N₂-fixation yield: Use of the compact film leads to the formation of granular crystallites of NH₄ClO₄ with higher numerical density, while needle crystallites with lower numerical density are formed in the porous film, the total yield of the N₂-fixation products in the former case being higher than that in the latter. A clear account for the cause of these findings may be far from simple since it would be closely related to the N₂-fixation mechanism; however, further materials screening should give answers to this issue and help us to understand the mechanism.

4. Concluding Remarks
Since the findings of the N₂-fixation reaction using a conducting polymer/anodic titanium oxide, poly(3-methylthiophene) has been used as the conducting polymer layer [1-6]. The present study addressed the alternate use of lower-cost conductive polymer materials, polyfurans and polycarbazoles, instead of poly(3-methylthiophene). Specifically, the fixation yield of the polycarbazole/titanium oxide system is larger by a factor of 1.6 than that of the poly(3-methylthiophene)/titanium oxide junction cell reported previously. This result is of technological importance since it presents feasibility to increase the fixation yield by further materials screening.

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References