New Avenues in Dinitrogen Fixation Research

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Abstract: The present article focuses on a recent finding concerning dinitrogen fixation by using titanium oxide/conducting polymer composite systems and its comparison with an earlier fixation method (Schrauzer process) that makes use of a powdered titanium oxide. Both processes work under the stimulus of light at room temperature and pressure, but dinitrogen is fixed to a solid ammonium salt crystal in the former and to a gaseous ammonia molecule in the latter process. Differences in the physicochemical concepts between the two processes are discussed.

Keywords: conducting materials · nitrogen fixation · semiconductors · solid-state reactions · titanium oxide

Introduction

Our air consists of 78% dinitrogen, and the life of all living organisms relies on the natural dinitrogen fixation by some soil-dwelling bacteria[1] and the artificial fixation by the Haber process.[2] Plants are indebted to these fixations and get nitrogen compounds from the microorganisms and fertilizers in the soil. The fertilizers are mostly derived from ammonia prepared by the Haber process, which is also used for the production of organonitrogen compounds in the chemical industry. According to the report by Smil,[3] about one-third of the protein in a human's diet depends on synthetic nitrogen fertilizers. The Haber process, however, requires high pressures and temperatures in addition to natural gas for the production of hydrogen [Eq. (1)].

$$N_2 + 3H_2 \xrightarrow{\text{catalyst}} 2NH_3 \qquad (1)$$

Hence, it has been an important and long-standing objective of significant international research to find an alternative to the energy-consuming Haber process.[4, 5] Some artificial fixations under mild conditions have been proposed that

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involve physicochemical methods with inorganic semiconductors,[6, 7] chemical reactions with coordinated-dinitrogen species,[8] and electrochemical syntheses.[9] Among these methods, the fixation with semiconductor materials has attracted much attention because it involves the conversion of solar energy to chemical energy (sunpack) as the nitrogen compounds. In 1977, the first fixation route was suggested by Schrauzer and Guth[6] in which N_2 is fixed to ammonia by UV irradiation on moist titanium oxide under ambient conditions of pressure and temperature [Eq. (2), overall reaction].

$$N_2 + 3H_2O \xrightarrow{h\nu} 2NH_3 + 3/2O_2 \qquad (2)$$

Since then a great number of studies has been conducted on material screening and the mechanism for the N_2 fixation. On the other hand, there still exist controversies as to whether the fixation is putative or not, and those who reported unsuccessful N_2 fixation claimed that the apparent N_2 fixation comes from contamination by environmental ammonia.[10]

In this article, the new finding concerning the N_2 fixation to ammonium salt over titanium oxide/conducting polymer hybrid systems[11, 12] is outlined and compared with the Schrauzer's route. This finding should not only validate an earlier Schrauzer process, but establish a more advanced route for converting dinitrogen into a solid explosive compound that can be used as a rocket propellant.

Discussion

The N_2-fixation method proposed by Schrauzer and Guth[6] involves the synthesis of NH_3 from ambient dinitrogen by using TiO_2 powder, water, and light (UV light or sunlight), and hence provides an environmentally sound process. This environmentally sustainable feature distinguishes the method from the other chemical and electrochemical ones that operate under mild conditions which inevitably use organic solvents and/or strong acids or bases during the fixation. In this sense, Schrauzer's process may be regarded as an analogue of the biological N_2-fixation route[1] in the soil for the preparation of NH_3. The general concept of this fixation is to prepare TiO_2 powders doped or loaded with metals, followed by irradiation with UV light. The doping or loading is regarded as a prerequisite for the adsorption and activation of N_2 on the TiO_2 surface.[7] Photogenerated electrons and

holes may reduce N_2 and oxidize adsorbed water, respectively, and these redox reactions are coupled to yield NH_3.

Quite recently, a more advanced concept was proposed by us.[11, 12] It involves the preparation of titanium oxides (TiO_x) by anodic oxidation, electrosynthesis of conducting polymer films on the TiO_x, and white-light irradiation of the resulting TiO_x/conducting polymer composites. Several important differences should be noted in the preparation of titanium oxides and the energetics of dinitrogen reduction between Schrauzer's and our fixation methods. In the course of our previous studies on the surface chemistry of semiconductors,[13, 14] it was revealed that TiO_2 (rutile) prepared by firing has a more intimate interaction with its surroundings than silicon and gallium arsenide; this was demonstrated by specific cases in which it was brought into contact with air or conducting polymer materials. Further, our recent investigation showed a greater chemical activity of the TiO_x than the TiO_2.[15] These findings provided the underlying principle of our N_2-fixation research: The surface reactivity of TiO_x should not only enhance the adsorption and activation of N_2, but allow intimate interactions through electron exchange with conducting polymers if the TiO_x is coupled with them. The interactions allow the formation of a high-quality junction interface that can be treated as a band-like structure (Figure 1). This in turn leads to the formation of a depletion layer
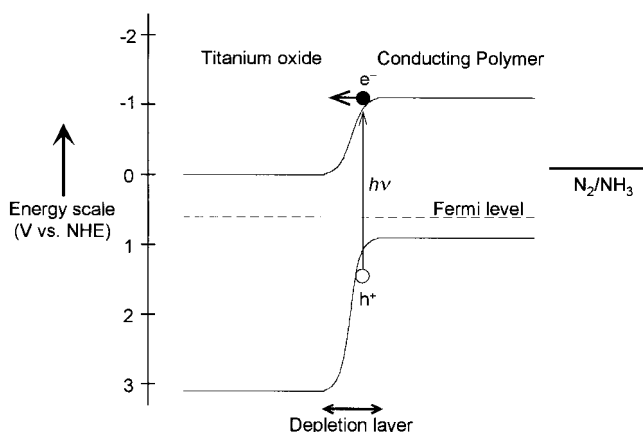
at the interface, since the TiO_x and conducting polymer have n-type and p-type electric conductivity, respectively, and high-energy electrons are available by the absorption of light in this layer of the conducting polymer. If we assume that the photogenerated electrons are transferred to the N_2-adsorption and activation sites at the interface before intraband relaxation in the depletion layer (hot-electron injection[18]), the electron energy as high as -1.1 V against NHE (normal hydrogen electrode) makes it energetically possible to reduce N_2 in the presence of water, E^0 (standard redox potential for N_2/NH_3) $= -0.0922$ V against NHE[19] [see Figure 1 and Eq. (3), the cathodic half-reaction of Eq. (2)].

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \qquad E^0(N_2/NH_3) = -0.0922 \text{ V against NHE} \quad (3)$$

This is in contrast to the situation with Schrauzer's route in which conduction-band electrons in the TiO_2, about $+0.1$ V for rutile and about -0.2 V for anatase,[17] are used for the reduction; the electron energy is comparable to E^0, and this is one of the major drawbacks of the route. Also notable is the additional nature of the TiO_x/conducting polymer interface. The interface exhibited high-quality rectifying (diode) characteristics.[15] Thus it should favor the efficiency of hole–electron separation and then the photoreactivity.

Table 1 lists the typical reaction systems, light source, reaction conditions, and ammonia production rate for the Schrauzer's process.[6] Dinitrogen is reduced to NH_3 (major) and N_2H_4 (trace) when moist TiO_2 powder is exposed to UV light from a 360 W Hg-Arc lamp (or sunlight) at 30–180 °C (or 25–35 °C) in air or in an N_2 atmosphere. Also included in Table 1 are the features of the current fixation route proposed by the authors.[11, 12] A double-layered type of reaction system, a composite of titanium oxide (TiO_x) and poly(3-methylthiophene) (P3MeT), is employed in lieu of the powdered TiO_2 (Figure 2). The former is a native oxide (NTO) or an
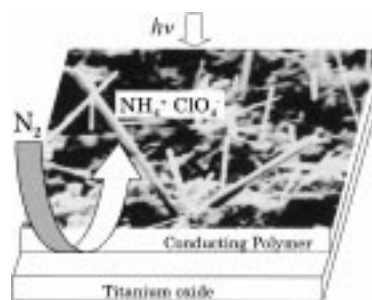

Figure 1. Energy band diagram for titanium oxide (TiO_x)/conducting polymer junctions shown for the case in which poly(3-methylthiophene) (P3MeT) is used as the conducting polymer layer. The values of electron affinity and band gap energy of the P3MeT and titanium oxide were taken from refs. [16] and [17], respectively.

Figure 2. Schematic representation of a P3MeT/TiO_x composite system used to fix N_2 into the $NH_4^+ClO_4^-$ needle crystals.

Abstract in Japanese: 酸化チタン/導電性ポリマー複合系を用いた最新の空中窒素固定法に焦点を当て、酸化チタン粉体を利用する方法（シュラウザー法）との比較検討を行った。双方のシステムとも、常温常圧下での光照射により作動するが、前者において窒素は固体アンモニウム塩結晶として、後者においてはアンモニアガスとして固定される。本稿では、上記２つのプロセスの物理化学的コンセプトの相違について言及する。

electrochemically-prepared oxide layer (ETO) on a titanium plate, and the latter layer is electropolymerized on the oxides in a CH_2Cl_2 electrolyte solution. Simultaneously with the electropolymerization, radical cationic (polaron) and dicationic (bipolaron) species are generated in the P3MeT film, and a supporting electrolyte anion (ClO_4^-) is loaded in it to maintain the electroneutrality conditions.[20] Upon exposure to white light from an 18 W fluorescent lamp (300–1300 lx) (or pseudo-solar lamp) in air [(ca. 20 °C, ca. 40 % relative humidity (RH)] or in a moist N_2 atmosphere, the compo-

Table 1. A comparison of our N_2-fixation process with that of Schrauzer and Guth.

	Schrauzer's process[a]	Current process[b]
system	gas–solid reactor containing wet TiO_2 powder packed bed type	gas–solid reactor with TiO_x/P3MeT layered systems P3MeT is doped with ClO_4^-
titanium oxide	powdered TiO_2 with a particle size of 0.2 μm mixture of rutile and anatase doped with 0.2% of Fe_2O_3	native oxide or electro-oxidized layer contains 0.25% Fe purplish blue appearance
fixation products	NH_3 (major) and N_2H_4 (trace)	$NH_4^+ClO_4^-$ needle crystal
fixation rate	$3–6$ mmol $h^{-1}g^{-1}$ of TiO_2 or $4–8$ μmol $h^{-1}m^{-2}$ of TiO_2	3.6 μmol $h^{-1}m^{-2}$ of TiO_x (fluorescent lamp, 1200 lx) 8.3 μmol $h^{-1}m^{-2}$ of TiO_x (pseudosolar lamp, 1200 lx)[c]
light source	360 W Hg-Arc lamp sunlight	18 W fluorescent lamp pseudosolar lamp[c]
ambient conditions	$25–180\,°C$, atmospheric pressure	ca. $20\,°C$, atmospheric pressure, $40\pm5\%$ RH
reaction time	several hours	several to scores of days

[a] Data taken from ref. [6]. [b] Data taken from refs. [11] and [12]. [c] T. Ogawa, T. Kitamura, K. Hoshino, unpublished results.

site functions as a novel fixation system and dinitrogen is fixed into $NH_4^+ClO_4^-$. Interestingly the ammonium salt crystals grow in a cylindrical fashion and increase in size and abundance with the illumination time and intensity. Figures 3 to 5 show some typical scanning electron micrograph (SEM) images of the needles. Several important features are noted in the low-magnification SEM images of these figures:

Figure 3. Scanning electron micrograph (SEM) images of a P3MeT deposit exposed to white light (1300 lx, 7 days) in a moist N_2 atmosphere. The deposit (bright region composed of a film and irregular-shaped conglomerates) was peeled off the ETO layer and then mounted on a carbon adhesive tape (dark background). The $NH_4^+ClO_4^-$ needles with high aspect ratios are observed, some of which are curved by the electron-beam irradiation. Scale bar: 100 μm.

1) The needles come off the granular particles of the P3MeT indicating that they have been synthesized from the particles.
2) The needles appear straight, some of which extend up to 200 μm. The formation of such very long needles occurs most readily in a moist nitrogen atmosphere (Figure 3).
3) The needles are capped in the shapes of a cone, semi-spherical, and flattened toroid structures (images a–c in Figure 4)—very similar in morphology to carbon nanotubes.[20] The formation of a solid pipette-like structure (image d) is also a commonly observed event.
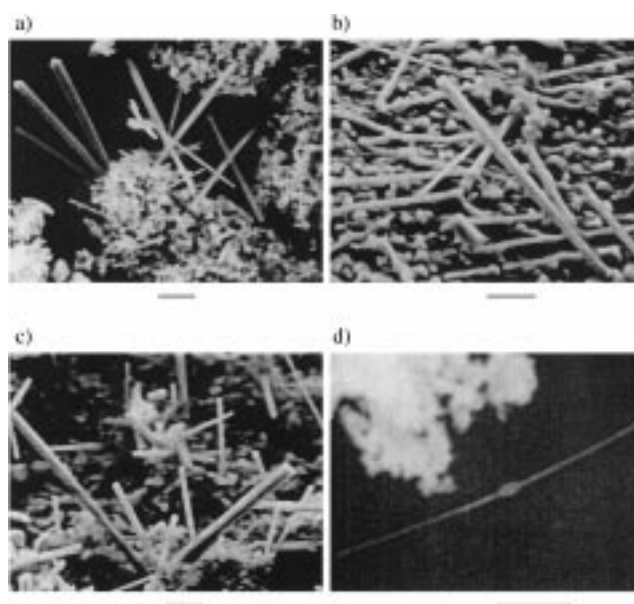

Figure 4. SEM images (a–c) of the $NH_4^+ClO_4^-$ needles with various caps. The needles were grown on the P3MeT/ETO system in air under the following illumination conditions: a) 1300 lx and 9 days; b) 300 lx and 180 days; c) 1300 lx and 180 days. Image d) shows the growth of a needle with a solid pipette-like structure (1300 lx, 5 days). Scale bar: 10 μm.

4) Needle structures are also observed on the back surface of the P3MeT film, that is, at the interface between the TiO_x and the P3MeT (image a in Figure 5), but they are much smaller in size and number than those on the free surface of the P3MeT (image b).

These intriguing features may help the elucidation of the needle formation mechanism and in turn the N_2-fixation mechanism; further information should be available from the high magnification SEM images, but when electron-beam irradiation (15 kV) was focused on the needle surface under high magnification, bending of the needles (see Figure 3) or their explosion (due to the explosive property of $NH_4^+ClO_4^-$)[22] occurs, thus making it difficult to determine their fine structures.

The rate of NH_3 production in the Schrauzer's process is typically $4–8$ μmol $h^{-1}m^{-2}$ TiO_2; this is comparable to that of the $NH_4^+ClO_4^-$ formation in the current process under the action of a fluorescent lamp (1200 lx), 3.6 μmol $h^{-1}m^{-2}$ TiO_x.
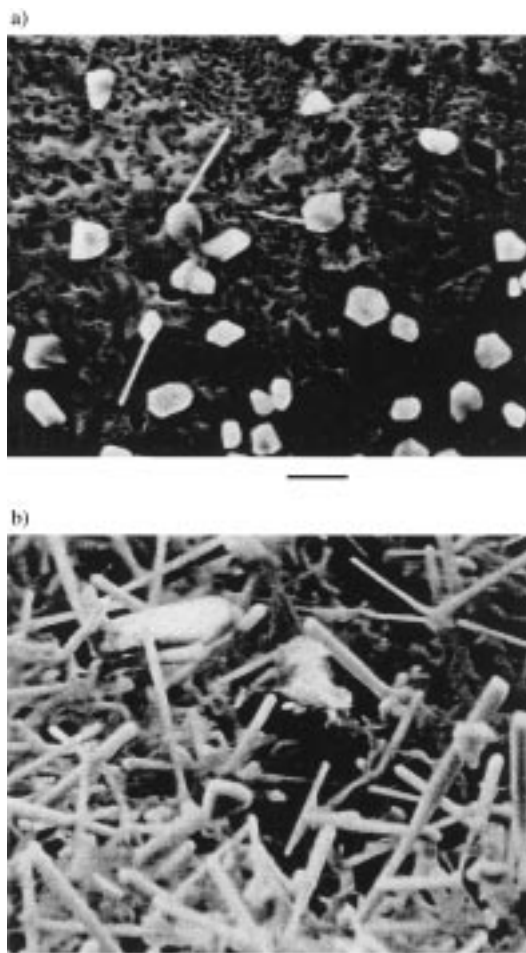
Figure 5. SEM images of the $NH_4^+ClO_4^-$ needles grown on a) the back and b) the free surfaces of the P3MeT deposit formed on the NTO layer. The P3MeT/NTO system was exposed to white light (300 lx) for 170 days in air. Scale bar: 10 μm.

The alternate use of a pseudosolar lamp (1200 lx) enhances the latter rate by a factor of about two (8.3 μmol h^{-1} m^{-2} TiO$_x$).[23] The absorption of light by titanium oxides is a prerequisite for the N_2 fixation in both of the routes, but they suffer some drawbacks to light absorption. In the former case, light cannot penetrate into the TiO$_2$ powder bed, while the TiO$_x$ layer is shielded from light by the P3MeT overlayer in the latter case; the UV/Vis absorption spectrum of the film exhibited its panchromatic characteristics over the wavelength range of 200 to 900 nm and its transmittance of only a few percent. In view of these drawbacks, a simple comparison of the N_2 fixation rate cannot be made. However, considering the low power and poor emission characteristics of the fluorescent lamp in the UV region in addition to the shielding effect of the P3MeT, the TiO$_x$ may be expected to have a high activity for N_2 adsorption, activation, and reduction. The fixation mechanism of Scrauzer's process is still not totally elucidated,[7] but experimental evidence is presented to show that Ti^{3+}□ (□ = oxygen vacancy) acts as an N_2-adsorption and activation site that is generated from the hydroxylated surface of TiO$_2$: [Eq. (4)]

$$Ti^{4+}-OH^- \rightarrow Ti^{3+}-OH\cdot \rightarrow Ti^{3+}\square + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \qquad (4)$$
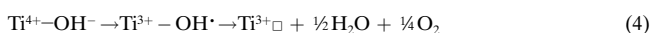
The TiO$_2$-powdered materials doped with Fe, Cr, Ni, Rh, etc.[24–26] show much higher activity for the N_2 fixation than the nondoped powders, the reason for which being considered as the formation of the Ti^{3+} species by the doping or the formation of a permanent space charge region whose electric force improves the efficiency of the hole–electron separation [Eq. (4)].

The N_2-fixation to $NH_4^+ClO_4^-$ is also affected by the nature of titanium oxide.[12] The P3MeT layer was deposited on ETO, NTO, thermally-grown (TTO), and sputtered titanium oxide layers (STO), followed by photoirradiation of the composites. Comparison of the SEM images taken after the photoirradiation revealed a much higher fixation efficiency of the first two composites (see Figures 3–5) compared to the last two (Figure 6). A large difference in the fixation efficiency
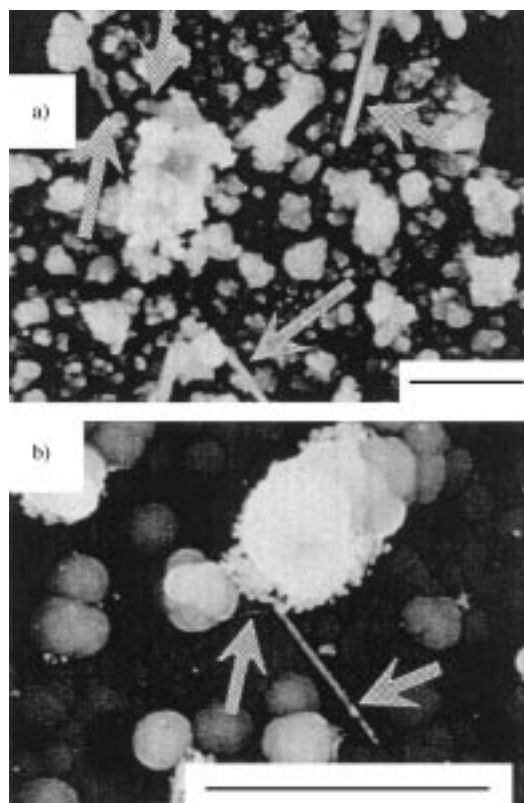

Figure 6. SEM images of the P3MeT deposits grown on a) TTO and b) STO in air. Images a) and b) were taken after 310 and 990 days of white-light illumination (300 lx), respectively. Needles are indicated by arrows in the images. Scale bar: 10 μm.

among the composites was temporarily explained by assuming that the Ti^{3+}□ deficiency (Ti^{3+} site adjacent to oxygen vacancy) on the oxide surface contributes to the N_2 adsorption and activation, and that fewer deficiencies are formed on titanium oxides prepared by hard (energy-consuming) processes, TTO and STO, than on those by soft (energy-efficient) processes, ETO and NTO.

If we assume that the fixation mechanism of the current process is based on Schrauzer's route, the reaction scheme involves the photogeneration of NH_3 at the TiO$_x$/P3MeT interface followed by its conversion to $NH_4^+ClO_4^-$. Under this assumption, the second conversion step is expected to offer a

mechanism to maintain the first photogeneration step of NH_3 in a steady state. The fixation rate of the latter process declines in a few hours (Table 1) probably due to the deactivation of the TiO_2 and/or photodecomposition (photo-oxidation) of NH_3 that is generated and accumulated on the TiO_2 surface:[7, 27] Such a rapid decline in the reaction rate is considered as one of the causes for the noncatalytic nature of the process.[28] On the other hand, no decline in the former fixation rate ($NH_4^+ClO_4^-$ needle formation and growth) was observed for at least a few weeks. This observation may be explained by assuming that the injection of NH_3 formed at the TiO_x/P3MeT interface into the P3MeT layer occurs and prevents accumulation of NH_3 in the vicinity of the TiO_x, leading to a suppression of the back reaction and/or the photodecomposition. However, the longer period of fixation is not an indication of the catalytic nature of the route. The anionic part of the fixation product, ClO_4^-, is provided by the dedoping of the ClO_4^--doped P3MeT,[11] and, therefore, the fixation reaction should cease when the P3MeT is fully dedoped. Repeated use of the TiO_x/P3MeT system would require the recovery of the $NH_4^+ClO_4^-$ needles from the system and re-doping of the P3MeT: Phoirradiation to the TiO_x/P3MeT system (cultivating), recovery of $NH_4^+ClO_4^-$ needles by washing with water (reaping), and electrochemical redoping of the P3MeT with a perchlorate salt (sowing).

Conclusion

A novel N_2-fixation process by using conducting polymer/titanium oxide composites has been reviewed. The process is characterized by its fixation product, $NH_4^+ClO_4^-$, and most likely by reaction kinetics to drive a reacting system. We believe that these characteristics come from the coupling of the titanium oxide (TiO_x) with a conducting polymer material (P3MeT); this donates an anionic part of the fixation product, prevents accumulation of ammonia at the TiO_x/P3MeT interface, and assists the hole–electron separation at the junction interface. Current experiments are directed towards material screening of the conducting polymers, preparation of TiO_x under various electrolysis conditions, fixation over the composite systems under visible light irradiation, etc. While we are not certain of the N_2-fixation mechanism, the fact that conducting, polymeric materials coupled with TiO_x modify and assist the fixation should open new avenues for both fundamental and applied research.

Acknowledgements

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