Effect of Preparation Conditions of Titanium Oxide on Dinitrogen Fixation to Ammonium Salt

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Dinitrogen fixation to solid needles of ammonium perchlorate was found to occur upon white light irradiation to composite systems of poly(3-methylthiophene) and titanium oxides (native, thermally-grown, and sputtered oxides) under ambient conditions of temperature and pressure.

Since Schrauzer and Guth[1] reported photocatalytic reduction of N_2 to NH_3 on a titanium oxide under an ambient condition, a great number of studies has been conducted on material screening and the mechanism for the N_2-fixation.[2] On the other hand, there still exist controversies as to whether the reaction is putative or not.[3] Those who reported unsuccessful N_2-fixation claimed that the apparent N_2-fixation comes from contamination with ammonia which is released from plastic materials by UV-light irradiation and/or from accidental contamination during its analyses[3,4] since ammonia is pervasive in the environment.[5] Such controversies seem to distinguish Schrauzer's process from the other authorized ones[6] such as Haber synthesis,[7] biological fixation,[8] coordinated dinitrogen – protonation reactions,[9] coordinated dinitrogen – coordinated hydrogen reactions,[10] electrochemical synthesis.[11] In order to settle the issue conclusively, large-scale synthesis of ammonia in excess of its natural abundance or the synthesis of easily isolable nitrogen products[9,12] may be required for the Schrauzer's process.

Quite recently, we reported the first synthesis of a solid ammonium salt using a titanium oxide/poly(3-methylthiophene) (P3MeT) system,[13] in which the oxide layer was prepared by anodic oxidation of a titanium plate. However, the questions still remain as to the extent to which environmental ammonia is involved in the formation of the solid ammonium salt and whether an electrochemically-prepared titanium oxide (ETO) is specific for our N_2-fixation or not. Here we describe photo-assisted N_2-fixation to the ammonium salt on various titanium oxide and evaporated gold layers coupled with a P3MeT film. The results reveal that our N_2-fixation also occurs on native (NTO), thermally-grown (TTO), and sputtered titanium oxides (STO), and that the contribution of environmental NH_3 is negligibly small.

Titanium plates were supplied by Sumitomo Metal Industries, Ltd. and contains impurities such as Fe (0.250%),[14] K (0.013%), O (0.200%), and N (0.050%). The plates are covered with the NTO ca. 8.5 nm thick.[15] TTO was prepared by firing of the titanium plate with a piezo gas burner (800–1300 ºC, firing time: 4 min).[16] STO was supplied by Geomatec Co., Ltd. and formed on an indium–tin–oxide coated glass. Electrochemical deposition of P3MeT (ca. 2.5 µm thick) on the titanium oxides was conducted under the same electrolysis and solution conditions as those for the deposition on ETO:[13] prior to the deposition, the oxide plates were washed ultrasonically in trichloroethylene, acetone, and ethanol. Deposition of P3MeT (ca. 1.2 µm thick) on an evaporated Au layer was done in the same manner as described before.[17]

In our previous study,[13] we found and reported time-dependent evolution and growth of $NH_4^+ClO_4^-$ needles in a P3MeT/ETO composite system under the action of white-light illumination: various control experiments and chemical analyses suggested that N_2-fixation to NH_3 and dedoping of ClO_4^- from a ClO_4^--doped P3MeT were coupled to yield $NH_4^+ClO_4^-$ needles though the mechanism of proton formation remained unsettled. Similar growth has been observed in a P3MeT/NTO system (Figure 1): unless otherwise noted, the system was stored in the vessel with a quartz window through which white-light illumination (300 lx) from a fluorescent lamp was conducted: The vessel was filled with air conditioned at ca. 20 ºC and ca. 40% relative humidity. After a definite time of illumination, the P3MeT deposite, scraped out of the NTO layer, was subjected to scanning electron microscopic (SEM) analysis. Immediately after the deposition of P3MeT, no needle was found in the deposit (Figure 1a). However, needles were recognized 12 days after the preparation. After 170 days of storage, increases in the density and length of the needles were observed (Figure 1c). Prolonged storage (270 days) led to the formation of very long needles as shown in Figure 1d. The growth rate and abundance of the needle in this system are comparable to those in the P3MeT/ETO system. In this case also, no needle formation occurred in the P3MeT deposit in the absence of white-light illumination and/or contact to an NTO underlayer. Surface density of the needles in Figure 1c was calculated to be 280 nmol/cm^2 as a concentration of $NH_4^+ClO_4^-$,[18] and ClO_4^- content in an as-grown P3MeT deposit was determined as 420

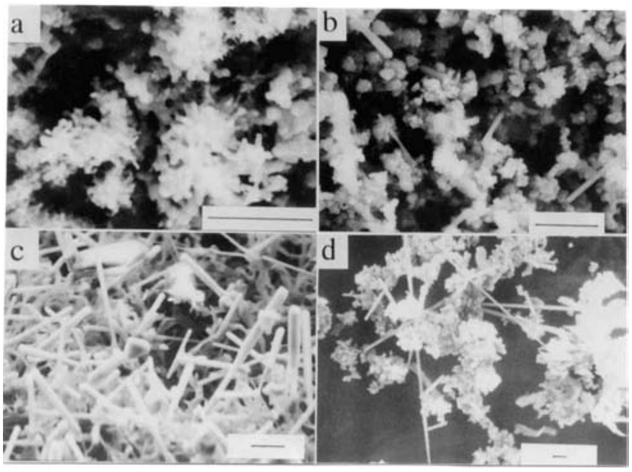

Figure 1. Scanning electron microscope (SEM) images of a P3MeT deposit prepared on NTO. The deposit was exposed to white light illumination for (a) 0 (unexposed), (b) 12, (c) 170 and (d) 270 days in an ambient atmosphere. The bright conglomerates in the image are the P3MeT deposit, and the dark image background is due to the carbon adhesive tape on which the deposit was mounted. Scale bars: 10 µm.

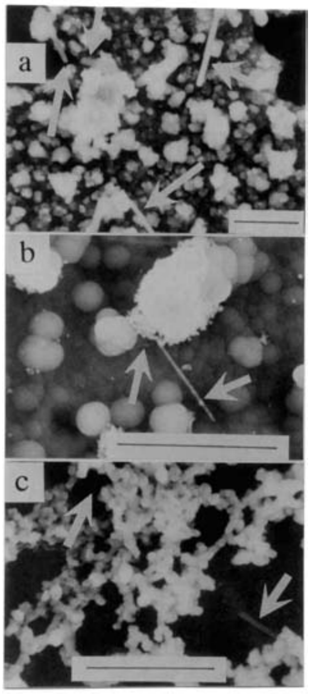

Figure 2. SEM images of the P3MeT deposits grown on (a) TTO, (b) STO, and (c) evaporated Au substrate electrodes. The images a, b, and c were taken after 310, 990, and 510 days of white-light illumination, respectively. Needles are indicated by arrows in the images. Scale bars: 10 μm.

nmol/cm^3.[19] Accordingly, ca. 70 mol% of ClO_4^- was dedoped to participate in the needle formation, but this efficiency is the lowest limit since needles in the bulk of the deposit were not counted; needles were also found on the rear surface of the deposit, i.e., at the interface of P3MeT/NTO though their size and abundance were relatively small. This finding led us to use titanium oxides prepared by alternative methods, TTO and STO.

Figure 2 shows SEM images of P3MeT deposits formed on TTO (a) and STO (b). Although not as distinct as the cases in Figure 1, needle formation was also observed in the P3MeT surfaces. The growth rate and relative yields of the needle, however, seem to be rather low compared with those for the P3MeT/NTO system despite the longer illumination time (310 days for the P3MeT/TTO and 990 days for the P3MeT/STO), and one would expect the catalytic activity of the oxides for needle formation to be different, depending on the preparation method of the oxide. If we assume that oxygen deficiencies on the oxide surface contribute to N_2-fixation and that less deficiencies are formed on titanium oxides prepared by hard (energy-consuming) processes, TTO and STO, than on those by soft processes, ETO and NTO, a large difference in the fixation efficiency among the oxides may be explained. Our rationale for the fixation described above predicts needle formation even in the absence of titanium oxide since NH_3 and NH_4^+ are pervasive in the environment.[5] Actually, tiny amounts of needles were observed in the P3MeT film on an Au layer (Figure 2c): only two seamless nano-needles were detectable in the film surface of 4.5 mm^2 upon exposure to light (510 days), in contrast to abundant needle formation in the presence of titanium oxide. We believe this may be the background of needle formation shown in Figures 1, 2a, and 2b, and the contribution of those environmental species to the fixation is negligibly small.

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