実験報告書様式（一般利用課題・成果公開利用）

（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。）

CROSS TOKAI **Experimental Report** J-PARC

承認日 Date of Approval 2013/11/23
承認者 Approver Jun-ichi SUZUKI
提出日 Date of Report 2013/05/26

課題番号 Project No. 2012B0092
実験課題名 Title of experiment
Investigation of Hierarchical Structure and Hierarchical Distribution of Dopant in the Visible Light Photocatalytic Material
実験責任者名 Name of principal investigator
Daisuke Yamaguchi
所属 Affiliation
Japan Atomic Energy Agency

装置責任者 Name of Instrument scientist
Jun-ichi SUZUKI
装置名 Name of Instrument/（BL No.）
TAIKAN / BL15
実施日 Date of Experiment
December 1st 2012

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

The measured specimens of titanium dioxide (TiO_2) were fabricated and supplied by ART KAGAKU Co. Ltd. Two different types of bare and nitrogen (N) doped specimens were employed. One having a sheet-like shape of the thickness of tens to hundreds nanometers was elaborated by a specific sol-gel method: The thin layer of polytitanoxane solution extended on the water surface was calcined at 500°C. N-doping process was conducted by placing the bare TiO_2 specimen on the pipe-shaped furnace and heating at 500°C under the NH_3 atmosphere for 1 hour. The other specimens are granular type and fabricated by an ordinary sol-gel method. TiO_2 precipitation was obtained when titanium alkoxide ($Ti(O^iPr)_4$) precursor solution was hydrolyzed with the reactant consisting of 2-propanol (3eq mol), HCl (0.1eq mol), and H2O (1.1eq mol). Final product was obtained by calcination at 500°C. As for the N-doped product, N atoms were introduced by the following process: Hydrolyzed TiO_2 precipitation was crosslinked by ethylene diamine (1eq mol) before calcination at 500°C and thus, the doped N atoms were rather randomly and uniformly distributed within the specimen.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Three types of experiments were conducted in this project:

(1) Comparison and confirmation of the scattering profiles obtained by TAIKAN with those obtained by other spectrometers, concerning the structure of sheet-shaped bare TiO_2 and N-doped TiO_2.

(2) Investigation and confirmation of an inhomogenized distribution of doped N atoms by the measurements of above sheet-shaped bare and N-doped TiO_2 specimens soaked in H_2O/D_2O mixture of particular composition.

(3) Structure analysis of granular type TiO_2 specimens, via both of scattering in air and that in H_2O/D_2O mixture.

(1) In order to confirm the accessible q-range (where q denotes the magnitude of wave vector) and compare the scattering intensity profiles for some reference TiO2 specimens, which had been already measured by different contrast (i.e., x-ray contrast) and different spectroscopy. Originally, the reference TiO_2 specimen was intensively investigated toward small angle region of $3\times10^{-4} < q < 10^0$ and a characteristic scattering maximum at around

2. 実験方法及び結果（つづき） Experimental method and results (continued)

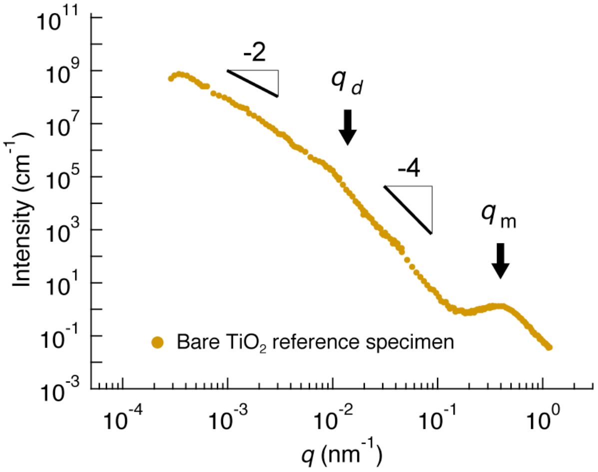

Fig.1 Wide range observation of reference TiO_2 specimen toward small-angle region obtained at JRR-3 small-angle spectrometers

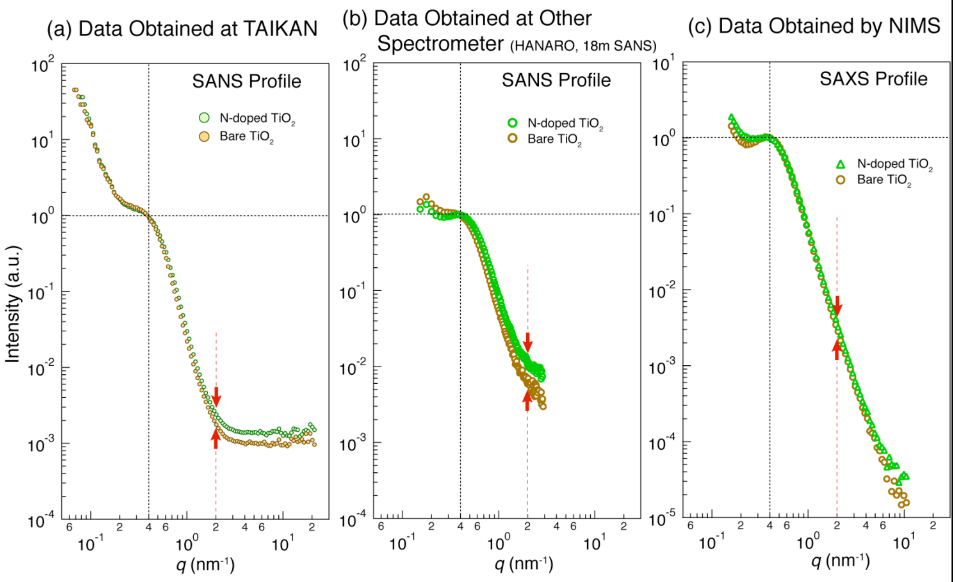

Fig. 2 Comparison of scattering profiles for the reference bare TiO_2 and N-doped TiO_2 specimens

q=0.4 nm^{-1} (denoted by q_m) was observed as shown in Fig. 1. Later on, this investigation was extended to N-doped TiO_2 and we found the fact that (i) the scattering profile of N-doped TiO_2 is similar to that of bear TiO_2 specimen, whereas (ii) at the higher q-region of the scattering maximum the decay rate of the scattering intensity is slightly but distinctly different between bare TiO_2 and N-doped TiO_2 specimens (Fig. 2(b)). On the other hand, by the measurement of small-angle x-ray scattering (SAXS) the scattering profiles of bare and N-doped TiO2 specimens are nearly identical even at the q-range of $q > 0.4$ nm^{-1} (Fig. 2(c)). The different tendency of SAXS and SANS profiles at $q > 0.4$ nm^{-1} can be attributed to the different scattering contrast of N atoms to x-ray and those to neutron. Resultant profiles obtained at TAIKAN (Fig. 2(a) were consistent with previous scattering results. For instance, at the position of q = 2 nm^{-1} (designated by arrows), the difference in intensity between bare and N-doped TiO_2 observed on Figs. 2(a) and 2(b) is larger than that observed on Fig. 2(c). This tendency is further clarified by taking the ratio of scattering intensity of N-doped TiO_2 specimen to that of bare TiO_2 specimen as shown in Fig. 3(a). Bose of the cases for SANS measurements the ratio increase rapidly at the q-range of $q > 0.4$ nm^{-1} and are close to constant at around 1.6 (for the measurement at 18m SANS of HANARO) and 1.35 (for the measurement at TAIKAN), respectively. While in the case of SAXS measurement, the ratio seems to keep at around unity or to show a slight increase even at the q-values of $q > 0.4$ nm^{-1}. In the end, at sufficiently high q of $q \sim 5$ nm^{-1}, the ratio of SAXS measurement becomes comparable to that of SANS data obtained at TAIKAN, however the level of SAXS intensity at this q-range is rather small and the obtained data is not reliable due to the statistical error. Thus, we conclude that the effect of N-dope can be certainly detectable by SANS contrast, while in

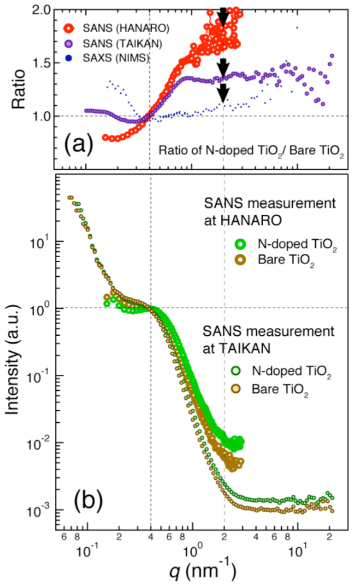

Fig. 3 Comparison of intensity and ratio of N-doped to bare TiO_2 specimens

2. 実験方法及び結果（つづき） Experimental method and results (continued)

SAXS contrast ascertainment of the N-dope effect is rather difficult. Nevertheless, the combined measurement of SANS and SAXS is the most effective and brings a richest information. That is, if N atoms distributed uniformly in the specimen, there would be no difference between bare and N-doped even in SANS contrast. In this case the different feature obtained between in SANS and SAXS contrast suggests some inhomogenized distribution of N atoms in the specimen. Effectively, one of the aims of experiment (2) was to capture and confirm a signal arising from inhomogeneity of N atoms in different contrast. An additional remark for experiment (1) is that a certain discrepancy was also observed on the SANS profiles obtained at different spectrometers as shown in Fig. 3(b). The origin of this discrepancy is not yet specified, but the difference in accessible q-range in those spectrometers is one possibility. In particular, for the other spectrometer from TAIKAN, the accessible range toward high-q is rather limited (for instance, in the case of Fig. 3(b) the scattering profile terminates at around q ~ 2nm^{-1}) and hence, the accuracy of the intensity value might become lower due to a varieties of factors such as some kind of non-uniformity of the sensitivity at the edge of the detector or statistical error.

(2) In the second experiment measurements were conducted on the bare and N-doped TiO_2 soaked in mixed water of H_2O/D_2O=55/45. This experiment also aimed comparison and confirmation with the previous experiment. However, those measurements at TAIKAN did not work well after all. The grounds for judging a miss of measurements are described below (but the data is not shown here): There is a serious discrepancy between the resultant profiles of TAIKAN and those of the previous experiment (performed at FRM-II in Germany). At the region of q > 2nm^{-1} scattering is nearly constant for both experiments, indicating an incoherent scattering from mixed water of H_2O/D_2O=55/45. Whereas at the region of q < 2nm^{-1}, the scattering intensity obtained at TAIKAN starts to increase gradually even in the case of background, i.e., 2mm thick of mixed water, whereas the scattering intensity obtained by the previous experiment keeps constant before q decrease to 0.7nm^{-1}. Consequently, the difference between bare and N-doped TiO_2 specimens (red and blue circles) observed on the profiles of previous experiment at lower q-region (q < 0.7nm^{-1}), seems to be hidden by the excess scattering on the obtained profiles (dark yellow and green circles) at TAIKAN. The origin of the excess scattering till now remains unexplained.

(3) Structural investigation for another type of granular TiO_2 specimens was performed both in air and in mixed water of H_2O/D_2O=55/45. The comparison of bare and N-doped specimens revealed different features of granular specimens from the above sheet-shaped specimens. The most significant feature is that when the granular specimens were soaked in mixed water of H_2O/D_2O=55/45, of which scattering length density is tuned to TiO_2, bare TiO_2 specimen (filled yellow circles) exhibited a considerable scattering intensity (even larger than that of N-doped specimen). While the specimens put in air, exhibited a likely behavior. Namely, the N-doped specimen possessed a larger scattering intensity at small q-range of q < 0.4nm^{-1}, probably due to the existence of doped N atoms. Since the distribution of doped N atoms in the granular specimen might be different from that of sheet-shaped specimen, the different scattering contrast between those two N-doped specimens can be attributed to the local structure or distribution of doped N-atoms.

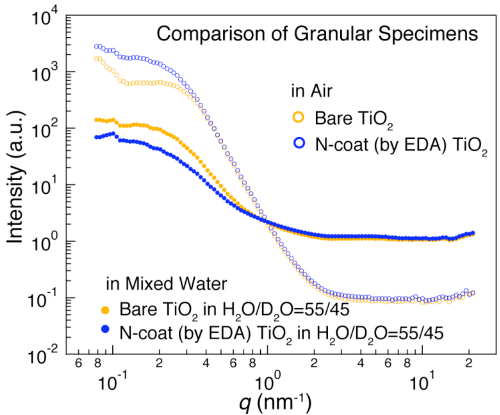

Fig. 4 Comparison of bare and N-doped nitrogen for granular specimens