

## 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。)

 <b>Experimental Report</b> 	承認日 Date of Approval 2015/9/15 承認者 Approver Jun-ichi Suzuki 提出日 Date of Report 2015/1/5
課題番号 Project No. 2014A0128	装置責任者 Name of Instrument scientist
実験課題名 Title of experiment	Junichi Suzuki
Observation of light element by means of neutron scattering contrast in doped catalytic materials	Shinichi Takata
実験責任者名 Name of principal investigator	Kazuki Ohishi
Daisuke Yamaguchi	装置名 Name of Instrument/(BL No.)
所属 Affiliation	TAIKAN / BL15
Japan Atomic Energy Agency, Quantum Beam Science Center	実施日 Date of Experiment
	June 1 <sup>st</sup> 2014

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.

<b>1. 試料</b> Name of sample(s) and chemical formula, or compositions including physical form.
<p>Two types of bare and nitrogen (N) doped titanium dioxide (<math>TiO_2</math>) products, which were fabricated and supplied by ART KAGAKU Co. Ltd., 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 <math>TiO_2</math> specimen on the pipe-shaped furnace and heating at 500°C under the <math>NH_3</math> atmosphere for 1 hour. The other specimens are granular type and fabricated by an ordinary sol-gel method. <math>TiO_2</math> precipitation was obtained when titanium alkoxide (<math>Ti(O^iPr)_4</math>) precursor solution was hydrolyzed with the reactant consisting of 2-propanol (3eq mol), HCl (0.1eq mol), and <math>H_2O</math> (1.1eq mol). Final product was obtained by calcination at 500°C. As for the N-doped product, hydrolyzed <math>TiO_2</math> precipitation was crosslinked by ethylene diamine (1eq mol) before calcination at 500°C and thus, the doped N atoms were expected to be randomly distributed within the specimen.</p>

<b>2. 実験方法及び結果</b> (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。)
<b>Experimental method and results.</b> If you failed to conduct experiment as planned, please describe reasons.
<p>In the last experiment (Project No. 2012B0092), we tried three types of measurements to examine the hierarchical structure of <math>TiO_2</math> photocatalyst specimens, one of which conducted under the ambient atmosphere successfully detected the characteristic scattering maxima at around <math>q=0.4</math> (<math>nm^{-1}</math>) related to the distribution of pore and small particles of <math>TiO_2</math> domains. On the other hand, the measurements of the <math>TiO_2</math> specimens soaked in mixed <math>H_2O/D_2O</math> at a particular composition, of which scattering length matched <math>TiO_2</math> and selectively enhanced the contribution of doped N atoms, did not work due to the excess background scattering of unknown origin. One of the main goals of this project is to confirm the possibility of detecting the signal from a small amount of doping species by selective enhancement of scattering contrast and probably was attained in the obtained data described below. The last type of measurements related to the granular type <math>TiO_2</math> specimens both in air and mixed <math>H_2O/D_2O</math> resulted in useful data and continued in this project to deduce some conclusion.</p> <p>(1) Confirmation of the possibility of detecting the signal from a small amount of doping species by selective enhancement of scattering contrast</p> <p>In Fig. 1 the scattering profiles of both N-doped and non-doped nanosheet specimens, taken at BL-15 (TAIKAN)</p>

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

are presented. The profiles were obtained either at ambient condition (i.e. in air) or in the mixed  $H_2O/D_2O=55/45$  (w/w), of which average scattering length density is close to that of  $TiO_2$ , as depicted in Fig. 2(a), and compared. When the environmental media of  $TiO_2$  is changed from air to the  $H_2O/D_2O$  mixture (55/45), it is clearly discerned that a considerable reduction of the scattering intensity at the  $q$ -range of  $q \leq 1$  [ $nm^{-1}$ ] is brought about by the small length density difference between  $TiO_2$  and mixed  $H_2O/D_2O$ , while at the  $q$ -range of  $q > 1$  [ $nm^{-1}$ ], the scattering intensity in the  $H_2O/D_2O$  is increased due to the incoherent scattering of hydrogen atoms (H) consisting of  $H_2O$ .

A detailed consideration of those changes of profiles on the N-doped and bare  $TiO_2$  specimens might reveal traces of signal from doping N-atoms, which were included less than 1wt% (nominally, 1.9mg/g) in the specimen. The evidential part is an enhanced difference in the scattered intensity at  $q \leq 0.8$  [ $nm^{-1}$ ], between N-doped (blue circles) and bare (red circles) specimens, which had in fact been detected the other set of measurements as shown in Fig. 2(b) and has reproduced in the current experiment. The different  $q$ -dependence between N-doped and bare  $TiO_2$  specimens is also observed on those measured in air (cf. the  $q$ -range indicated by arrow in the inset of Fig. 1), and hence it seems reasonable to claim that the different profile is not due to the doped species (N), but inherent in the own microstructure of individual specimen. This point was confirmed by comparing the profiles both taken in air and mixed water after subtraction of the incoherent scattering of hydrogen atoms (H). As shown in Fig. 3, the effective thickness of mixed  $H_2O/D_2O$  which soaks through the  $TiO_2$  specimens was estimated by comparison of the averaged scattering intensity at the  $q$ -range of  $10^0 \leq q$  ( $nm^{-1}$ )  $\leq 2 \times 10^1$ , where the incoherent scattering of H overwhelms other scattering component, and hence that intensity level can be regarded as proportional to the amount of H or equivalently to that of soaking water. The result indicates that the effective thickness of water is reduced to 0.815 in the soaked N-doped  $TiO_2$  specimen and 0.852 in the bare  $TiO_2$  specimen. Note that although in this case the  $q$ -range is restricted within  $q$ -range of  $10^0 \leq q$  ( $nm^{-1}$ )  $\leq 2 \times 10^1$  to determine the reduction rate (or effective volume fraction) of water in the cell of soaked  $TiO_2$  specimen, the obtained values (0.815 and 0.852) seem valid even at higher  $q$ -range up to  $q \sim 1.6 \times 10^2$  ( $nm^{-1}$ ) (cf. inset of Figs. 3(b) and 3(c), in which the scattered intensity was detected by backward detector). After subtraction of the contribution of incoherent scattering, the residual scattering was normalized, that is divided by the effective content of  $TiO_2$  component in the cell (0.185 for N-doped specimen and 0.148 for bare specimen), and presented in Fig. 4. Concerning small  $q$ -region (Fig. 4(a)), data points are scattered at  $q \geq 0.8$  ( $nm^{-1}$ ), which means incoherent scattering is dominant at the corresponding  $q$ -region, and therefore any argument will be neglected on this region. On the other hand, the data of  $q < 0.8$  ( $nm^{-1}$ ) can be comparable with each other as well as with those measured in the ambient condition (i.e., air). In addition, several diffraction peaks of anatase crystal

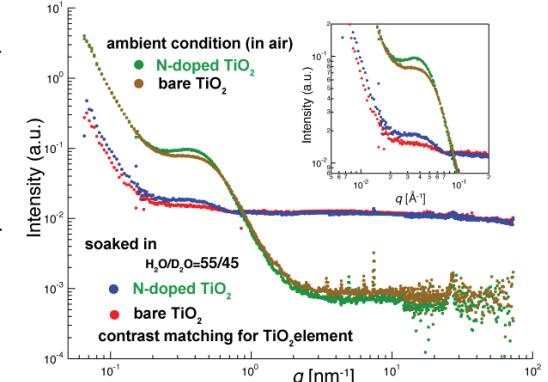


Fig. 1 Neutron scattering profile of  $TiO_2$  nanosheet specimens taken at BL-15.

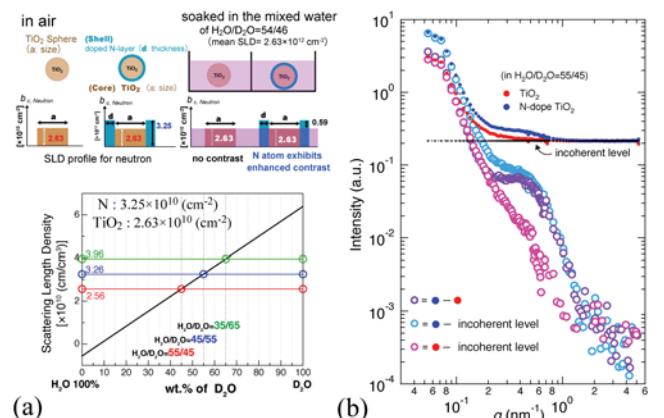


Fig. 2 (a) Estimation of scattering contrast for each component in the system, and (b) a set of data for N-doped and bare  $TiO_2$  (previously measured).

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are distinguishable at high  $q$ -region of  $2.5 \times 10^1 \leq q (\text{nm}^{-1}) \leq 4.4 \times 10^1$  (cf. Figs. 4(b) and 4(c) designated by arrow). It is discernible an opposing trend by comparing the intensity level of N-doped and bare  $\text{TiO}_2$  specimens shown in Fig. 4 at different ranges where diffraction peaks located (at high  $q$ ) and where upturn as well as a broad shoulder located (at low  $q < 0.8 (\text{nm}^{-1})$ ). At low  $q$  region ( $< 0.8 (\text{nm}^{-1})$ ) the intensity of N-doped specimen always larger than that of bare specimen, whereas at the positions of anatase peak located, intensity of those two specimens are nearly equivalent or even bare specimen is slightly larger than N-doped specimen. The tendency observed at high  $q$  region seems to make sense as those two specimens are compared under some normalized condition regarding to the content of  $\text{TiO}_2$ . Hence, in this context the observed trend at low  $q$  region may be attributed to the contrast enhancement due to doped N atoms. This argument will be further confirmed by making the same comparison of N-doped and bare  $\text{TiO}_2$  specimens measured in air. The result is shown in Fig. 5. At high  $q$ , scattered intensity was integrated within three areas as,  $q_{p1}$  ( $25.8\text{-}27.1 \text{ nm}^{-1}$  and below is same),  $q_{p2}$  ( $33.0\text{-}33.5$ ), and  $q_{p3}$  ( $41.8\text{-}42.6$ ), which correspond to 004, 200, and 204 diffraction peaks of anatase. The intensity ratio of N-doped  $\text{TiO}_2$  to bare  $\text{TiO}_2$  ( $r$ ) was obtained for 0.771 (at  $q_{p1}$ ), 0.741 (at  $q_{p2}$ ), and 0.969 (at  $q_{p3}$ ) on the soaked state in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ , while for 0.873 (at  $q_{p1}$ ), 0.767 (at  $q_{p2}$ ), and 0.834 (at  $q_{p3}$ ) in air. Further taking the average of those three area ( $r_{\text{ave}}$ ) came to 0.825 and 0.827 on the states in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  and in air, respectively. On the other hand, the averaged value of intensity ratio ( $r_{\text{ave}}$ ) at low  $q$  of  $0.07 \leq q (\text{nm}^{-1}) \leq 0.15$  where observed strong upturn consists of more than 20 data points was obtained for 1.20 and 1.01 on the states in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  and in air. Considering all the above experimental results there is not any strong evidence to exclude the possibility that an enhancement of scattered intensity due to the doped N atoms occurs at low  $q$ -region of  $q \leq 0.8 (\text{nm}^{-1})$  and is detectable when scattering contrast of  $\text{TiO}_2$  is reduced. In Fig. 5, the blue

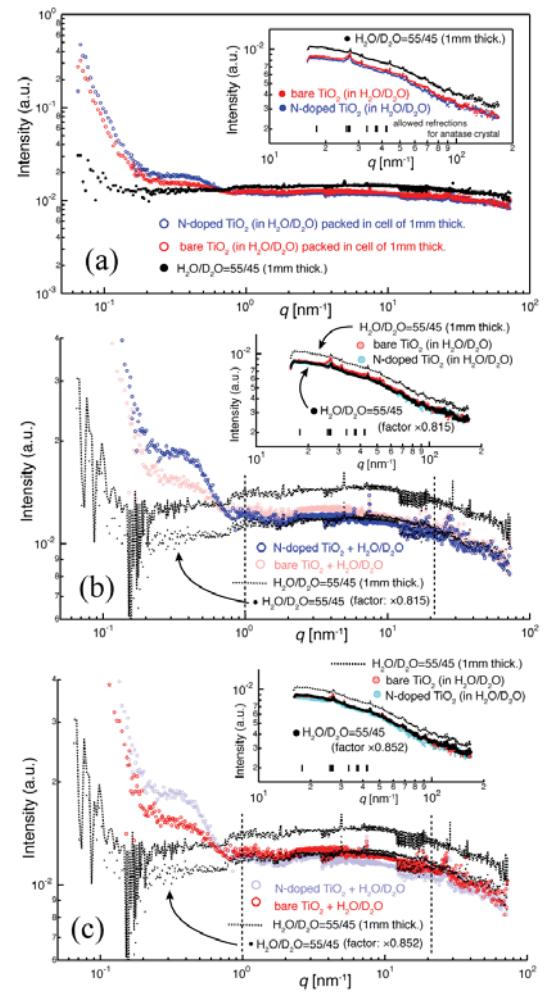


Fig. 3 Subtraction process of background scattering consisting of  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ . Scattering profiles of the same thickness (1mm) of the three specimens, two of which contain  $\text{TiO}_2$  powder soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ , and the other one contains solely the mixed water of  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ , are compared in part (a). The effective soaker  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  content (i.e., thickness) was estimated at 0.815 (mm) in N-doped  $\text{TiO}_2$  specimen (b), and at 0.852 (mm) in bare  $\text{TiO}_2$  specimen (c), by the ratio of the level of scattered intensity of soaked  $\text{TiO}_2$  specimens to that of pure  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  specimen compared at the  $q$ -range of  $10^0 \leq q (\text{nm}^{-1}) \leq 2 \times 10^1$ , where the incoherent scattering of H is dominant.

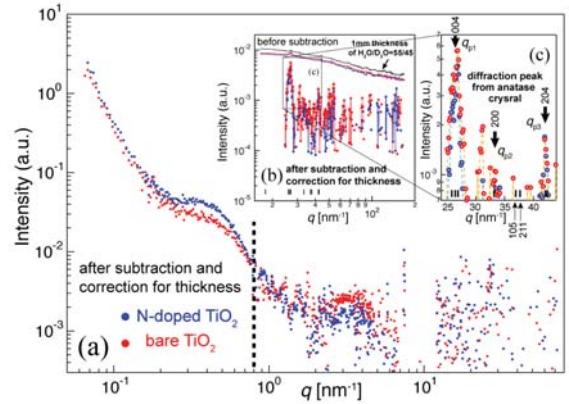


Fig. 4 Comparison of the profiles of N-doped and bare  $\text{TiO}_2$  specimens soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  after the subtraction of incoherent scattering from H atoms in soaking water. The profiles are further reduced by the effective content (i.e., volume fraction) of  $\text{TiO}_2$  in the cell which makes the comparison more rational under some normalized condition. Part (a) shows the small  $q$ -region, part (b) shows diffraction patterns of high  $q$ -region obtained by backward detector, and part (c) focuses some principal peaks from anatase. In parts (a)-(c), blue and red symbols denote N-doped and bare  $\text{TiO}_2$ , respectively.

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dotted line at the range of  $0.15 \leq q (\text{nm}^{-1}) \leq 0.8$  denotes the trace of the data corresponding to the ratio of N-doped  $\text{TiO}_2$ /bare  $\text{TiO}_2$  which is shifted up by a factor of  $\times 1.2$ . Thus, it seems possible to make a reasonable coincidence for the data of low  $q$  region simply by shift up (or down) the data points of red (or ash) circles. In that case, however, it is necessary to rationalize the discrepancy at high  $q$  region, namely the reason why the intensity (ratio) of anatase diffraction peaks varies by surrounding (from water to air). There are still some contradictions between expectation and experimental result; from the viewpoint of scattering contrast, supposing the following ideal condition a porous  $\text{TiO}_2$  object having stoichiometrically averaged uniform scattering length density ( $2.63 \times 10^{10} (\text{cm}/\text{cm}^3)$ ) is surrounded by  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  (as shown in Fig. 2), the scattering length density difference, which is proportional to the square root of scattering intensity, decreases at  $7 \times 10^8 (\text{cm}/\text{cm}^3)$  and which in turn, brings about a reduction of scattering intensity at the rate of  $\sim 10^{-3}$ . However, in the experimental result the reduction of scattered intensity was only limited to  $\sim 1/18.6$ , that is, the real contrast is ca. 7 times larger than the expectation based on the above ideal situation. This indicates that the supposition of uniform scattering length density is obviously broken and, considerable internal inhomogeneities due to density fluctuations between anatase crystal and amorphous phase or impurities and contaminations involved during synthesis and calcination process contribute to the scattering. The influence of doped N atoms, also acting as a kind of impurity whose contribution to scattering might turn out unexpectedly large in particular at low  $q$  region, should be considered in such an inhomogenized system. In another point, further possibility like overlooked adsorption (of N atoms) might be open to re-examination.

### (2) Examination on the granular type $\text{TiO}_2$ specimens both in air and mixed $\text{H}_2\text{O}/\text{D}_2\text{O}$

Scattering measurements for  $\text{TiO}_2$  specimens other than nanosheet were performed in air and in water whose scattering contrast was tempered at three conditions as shown in Fig. 2(a) (Figs. 6 and 7). As for the profiles measured at different scattering contrast (Fig. 7) it is discerned that the specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  exhibited the lowest scattering intensity at the  $q$ -region of  $q \leq 10^0 (\text{nm}^{-1})$  for the both N-doped and bare  $\text{TiO}_2$  specimens. This trend is unanticipated from the calculation result for the scattering length density of  $\text{TiO}_2$  component being equivalent to that of  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  mixture (cf. Fig. 2(a)) and implying the following fact: There are other components than  $\text{TiO}_2$  not only in N-doped specimen but also in bare specimen, or otherwise the real scattering length density of  $\text{TiO}_2$  is somewhat different from the calculated value. Although in the case of N-doped  $\text{TiO}_2$  product, the difference between the scattering profiles of the specimens

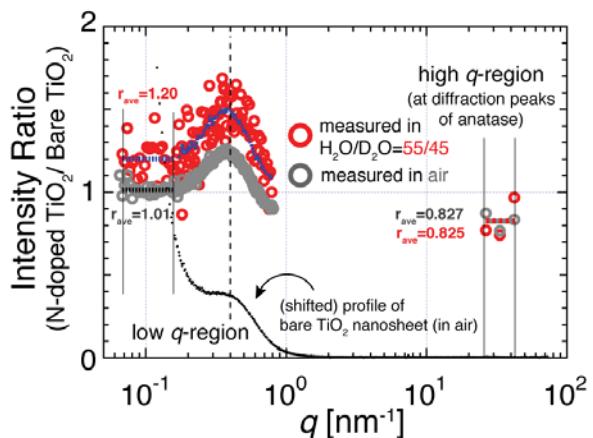


Fig. 5 The ratio of scattered intensity from N-doped  $\text{TiO}_2$  to that from bare  $\text{TiO}_2$  estimated at different  $q$ -region, particularly at low  $q$  of  $\leq 0.8 (\text{nm}^{-1})$  and high  $q$  where diffraction peak of anatase located is shown. The ratio of those two specimens is taken at different conditions, one of which is soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  (nearly the matching point of  $\text{TiO}_2$ ) and the other is in air. At high  $q$  region the ratio ( $r_{\text{ave}}$ ) is similar to each other at 0.82–0.83, while at lowest  $q$  of  $0.07 \leq q (\text{nm}^{-1}) \leq 0.15$ ,  $r_{\text{ave}}$  measured in  $\text{H}_2\text{O}/\text{D}_2\text{O} = 55/45$  is slightly larger (1.20) than that in air (1.01).

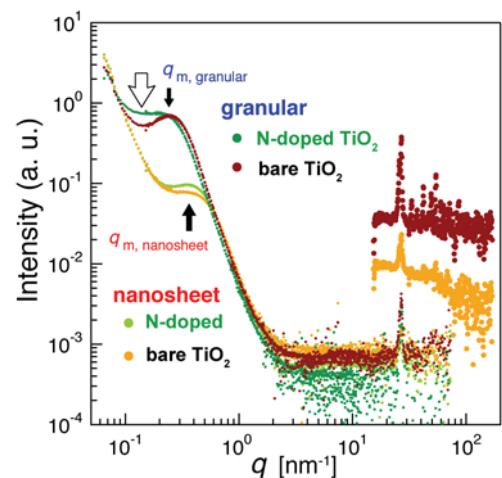


Fig. 6 Scattering profiles are compared for the granular and nanosheet  $\text{TiO}_2$  specimens. Because of the larger size of the crystal grains in the granular specimens, either diffraction peaks at high  $q$ -region ( $q > 2 \times 10^1 \text{ nm}^{-1}$ ) or scattering maximum denoted by  $q_m$  are more pronounced than those observed on nanosheet specimens.

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soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O} = 55/45$  and 45/55 seems more pronounced as compared with the case of bare  $\text{TiO}_2$ , this issue should be discussed after correcting the influence of the incoherent scattering of  $\text{H}_2\text{O}$  as well as net irradiated volume (or thickness) occupied by granular  $\text{TiO}_2$  product. The correction process was same as performed on the  $\text{TiO}_2$  nanosheet specimen (cf. Fig.3). The levels of incoherent scattering were obtained by taking an average over the  $q$ -range of  $2 \leq q (\text{nm}^{-1}) \leq 2 \times 10^1$  for both pure mixed  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (net 1mm thickness) and granular  $\text{TiO}_2$  specimens soaked in the mixed  $\text{H}_2\text{O}/\text{D}_2\text{O}$  and compared them each other. The ratio of averaged intensity level of incoherent scattering for soaked  $\text{TiO}_2$  specimen to that for pure mixed  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (denoted as  $r_{\text{soak}/1\text{mm}}$ ) was obtained at the range of 0.5-0.7 for  $\text{H}_2\text{O}/\text{D}_2\text{O} = 55/45$ , 45/55, and 35/65 mixtures (further in detail, individually,  $r_{\text{soak}/1\text{mm}} = 0.54$  (N-doped  $\text{TiO}_2$ ), 0.55 (bare  $\text{TiO}_2$ ) for  $\text{H}_2\text{O}/\text{D}_2\text{O} = 55/45$ ;  $r_{\text{soak}/1\text{mm}} = 0.59$  (N-doped  $\text{TiO}_2$ ), 0.57 (bare  $\text{TiO}_2$ ) for  $\text{H}_2\text{O}/\text{D}_2\text{O} = 45/55$ ;  $r_{\text{soak}/1\text{mm}} = 0.67$  (N-doped  $\text{TiO}_2$ ), 0.62 (bare  $\text{TiO}_2$ ) for  $\text{H}_2\text{O}/\text{D}_2\text{O} = 35/65$ ). In consequence, net volume fraction occupied by  $\text{TiO}_2$  entity in the cell can be given by  $(1 - r_{\text{soak}/1\text{mm}})$  on the premise that there is no cavities but filled with either  $\text{TiO}_2$  or water throughout the irradiated volume inside of the cell and the scattering profiles of soaked specimen ( $I(q)_{\text{soaked TiO}_2}$ ), subtracted incoherent scattering ( $I(q)_{\text{pure H}_2\text{O/D}_2\text{O}}$ ) by  $[I(q)_{\text{soaked TiO}_2} - r_{\text{soak}/1\text{mm}} I(q)_{\text{pure H}_2\text{O/D}_2\text{O}}]$ , was divided by the factor of  $(1 - r_{\text{soak}/1\text{mm}})$  for normalization. Fig. 8 shows the profiles after subtraction of the incoherent scattering and normalization for the effective thickness occupied by  $\text{TiO}_2$  product. It is discernible that the reduction of scattering intensity of specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  to that soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  is still more distinct for the case of N-doped  $\text{TiO}_2$  (Fig. 8(a)) as compared with the case of bare  $\text{TiO}_2$  (Fig. 8(b)) at the  $q$ -region of  $0.15 \sim 0.4 (\text{nm}^{-1})$  (designated by thick open arrow). While at higher  $q$ -region detected by backward detector (cf. Figs. 8(c)-8(e)), the trend turned out to be different from that of low  $q$  area. For instance, concerning the three diffraction peaks from anatase crystal designated by filled arrows in Figs. 8(c)-8(e), their intensity on the specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  is not smaller but larger than that soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ . Furthermore, the enhancement rate of those peak intensity is nearly the same or even slightly larger for the case of N-doped  $\text{TiO}_2$  as compared

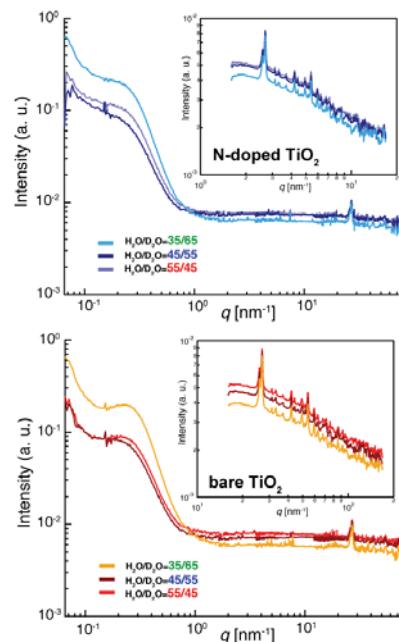


Fig. 7 Scattering profiles of granular  $\text{TiO}_2$  specimens (N-doped and bare) measured at different contrast where the specimens are soaked in mixtures of  $\text{H}_2\text{O}/\text{D}_2\text{O} = 55/45$ , 45/55, and 35/65.

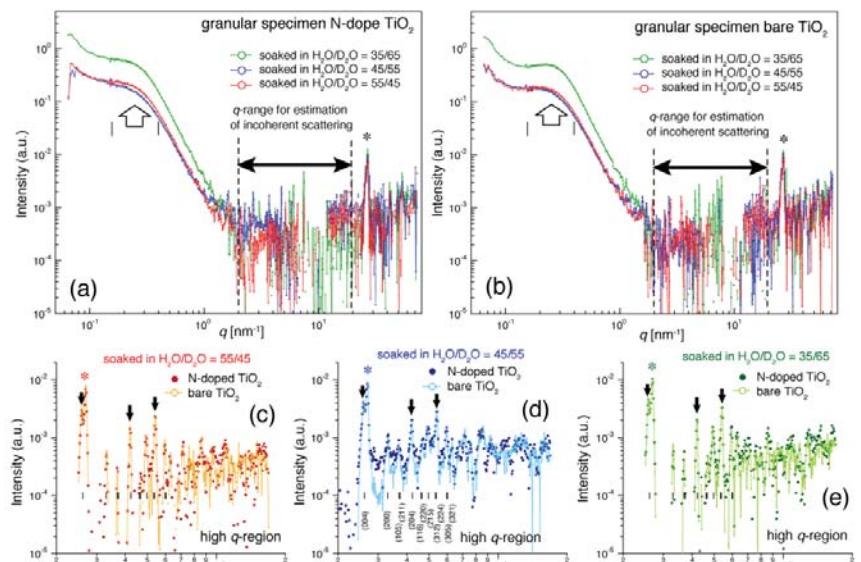


Fig. 8 Scattering profiles of granular  $\text{TiO}_2$  specimens (N-doped and bare) after the correction for subtracting incoherent scattering and for normalizing the net volume (i.e., thickness) of  $\text{TiO}_2$  products in the cell: (a) and (b) present smaller  $q$  region where the range for taking the average of incoherent scattering is sectionalized by broken line, (c)-(e) present higher  $q$  region where diffraction peaks from anatase are compared between N-doped and bare  $\text{TiO}_2$  specimens soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  of the same composition.

peaks from anatase crystal designated by filled arrows in Figs. 8(c)-8(e), their intensity on the specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  is not smaller but larger than that soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ . Furthermore, the enhancement rate of those peak intensity is nearly the same or even slightly larger for the case of N-doped  $\text{TiO}_2$  as compared

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with the case of bare  $\text{TiO}_2$ . Note, though the data in Figs. 8(c) and 8(d) do not explicitly indicate the difference, the mean value of the peak intensity ratio of above three peaks on the specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  to that in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  is 1.55 for the case of N-doped  $\text{TiO}_2$  and 1.43 for the case of bare  $\text{TiO}_2$ , of which situation is presented in Fig. 9. At the range of  $q \leq 1 (\text{nm}^{-1})$ , data of N-doped  $\text{TiO}_2$  (green) is smaller than that of bare  $\text{TiO}_2$  (ochre) reflects the trend in Figs. 8(a) and 8(b), on the other hand, there is no good explanation for the trend of ratio of the intensity of three peaks at  $q = 2.56, 4.18 and  $5.37 (\text{\AA}^{-1})$ . As those peaks are assigned to 004, 204, and 224 diffraction peaks of anatase crystal, their intensity should be independent of the scattering contrast between  $\text{TiO}_2$  crystalline grains and surrounding  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture. Nevertheless, here a certain tendency that those peak intensity was somewhat reduced when the specimen was soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  was observed. However, the possibility that the content of  $\text{TiO}_2$  product in the irradiated volume is still misestimated during the process of above correction (i.e., subtracting incoherent scattering and dividing with estimated fraction) is not excluded. Hence, the whole scattering profile is re-normalized with the height of  $\text{TiO}_2$  diffraction peaks appeared at high- $q$  and on backward detector, which can be a kind of expedient according to the assumption that the diffraction peak intensity depends on the irradiated volume but never on the surrounding media. In either case, the trend that reduction of low- $q$  ( $\leq 1 (\text{nm}^{-1})$ ) scattering is larger for N-doped  $\text{TiO}_2$  than for bare  $\text{TiO}_2$  is common in Fig. 9.$

Like nanosheet specimen (cf. Fig. 5), taking the ratio of the scattered intensity between N-doped and bare  $\text{TiO}_2$  specimens under the same condition seems to have some reason to examine the structural modification due to doped N atoms (Fig. 10). In this case, the ratio of peak height at high- $q$  region (designated by arrows in Fig. 10(a)) comes close to unity, suggesting that doped effect does not appear on the crystalline structure. While at low- $q$  region, variation of  $q$ -dependence is different among each condition of granular specimen as well as between granular and nanosheet product. Concerning four different conditions prepared for granular specimen, i.e., in air, in water with three types of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  composition as 55/45, 45/55, and 35/65, the intensity ratio (hereafter, denoted as  $R(q)$ ) in air and in  $\text{H}_2\text{O}/\text{D}_2\text{O}=35/65$  exhibit quite similar  $q$ -dependence, meaning that the  $q$  position of broad maximum observed on  $R(q)$  is nearly the same. While, broad maximum observed on  $R(q)$  in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  (red curves) locates at lower  $q$  (designated by open arrow in Fig. 10(c)) as compared with the case in air or in  $\text{H}_2\text{O}/\text{D}_2\text{O}=35/65$ , and furthermore  $R(q)$  in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$

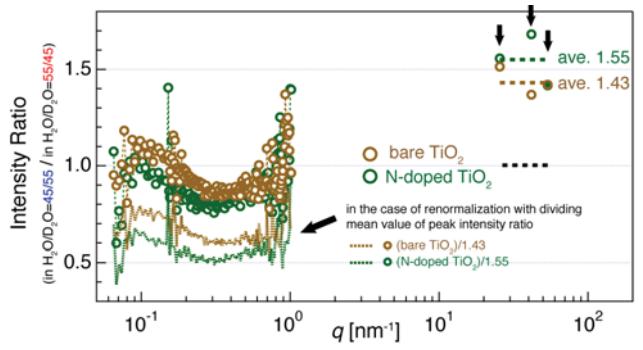


Fig. 9 Intensity ratio of the specimen soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  to that in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  is taken for both of N-doped and bare  $\text{TiO}_2$  product to examine the effect of tuning scattering length density (or contrast) to  $\text{TiO}_2$  and impurity. The effect was appeared in different way at each of low- and high- $q$  region. At low- $q$  it acts reducing the intensity ratio, while at high- $q$  the ratio somehow becomes larger than unity. In any case, reducing of intensity ratio at low- $q$  is more effective on N-doped  $\text{TiO}_2$  product.

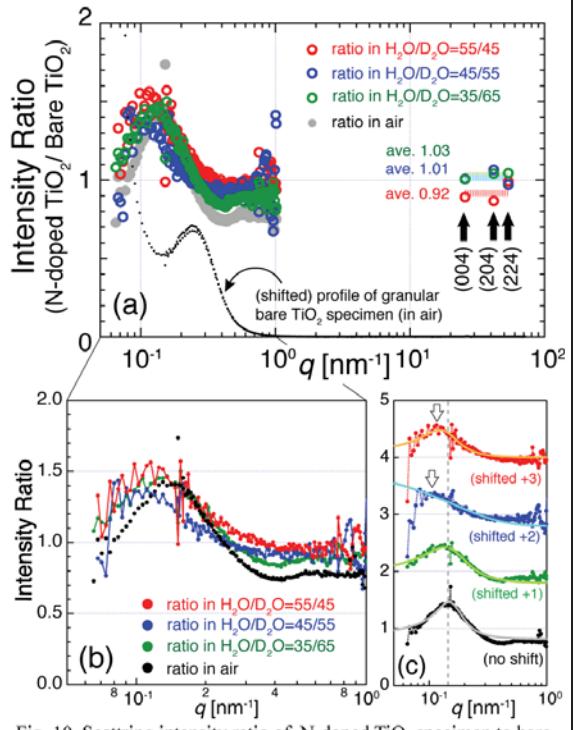


Fig. 10 Scattering intensity ratio of N-doped  $\text{TiO}_2$  specimen to bare  $\text{TiO}_2$  specimen is taken at various conditions, namely in air, in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$ , 45/55, and 35/65. Part (a) shows both low- and high- $q$  region at which three diffraction peaks of anatase (assigned to 004, 204, and 224) were employed for the comparison. Parts (b) and (c) focus on low- $q$  region.

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

(blue curves) exhibits an upturn ambiguous with a shoulder peak at the region of  $q \leq 0.2$  ( $\text{nm}^{-1}$ ), though an open arrow in Fig. 10(c) is confusing to indicate the top of broad maximum. Turning to comparison with nanosheet product (cf. Fig. 5), it is discerned that the character of broad maximum appeared at low- $q$  region on  $R(q)$  (curves of intensity ratio) is different between granular and nanosheet product. That is, in both of Figs. 5 and 10(a), besides the curves of intensity ratio ( $R(q)$ ), the (shifted) scattering profile,  $I(q)$ , of bare  $\text{TiO}_2$  taken in air is presented (by black dotted curve) for the sake of the reference, which also possesses a broad maximum due to the characteristic length among network structure consisting of  $\text{TiO}_2$  nano-particles or porous nano-channels, and for nanosheet products (Fig. 5),  $q$ -position of the maximum is common to the curves of intensity ratio ( $R(q)$ ) and  $I(q)$  of reference specimen. Whereas for granular products (Fig. 10(a)), the position of maximum is distinctly different between  $R(q)$ s and  $I(q)$ . This indicates that the doping process of N atoms did not change the basic porous structure for nanosheet products, but not the case for granular products. Since doping process for granular product is rather different from that for nanosheet product, in particular, addition of ethylene diamine, acting as N doping reagent and simultaneously as cross-linking reagent has a possibility to affect the porous structure, above difference in  $R(q)$  between granular and nanosheet product is not unanticipated. Return to  $I(q)$  (scattering intensity profile) of granular N-doped and bare  $\text{TiO}_2$  specimen (cf. Fig. 6), the different  $q$  behavior at  $0.1 \leq q$  ( $\text{nm}^{-1}$ )  $\leq 0.25$  is obvious, at which N-doped specimen possesses nearly constant  $I(q)$ , whereas bare specimen exhibits an depression of intensity. Therefore a hump appeared in  $R(q)$  of granular specimen measured in air can be concluded as a “ghost” peak reflecting the depression part on  $I(q)$  of bare specimen as schematically stressed in Fig. 11(a). Then, some curiosity still remains on the fact that such a “ghost” peak shifts or disappears under some specific condition soaked in  $\text{H}_2\text{O}/\text{D}_2\text{O}=55/45$  or  $45/55$ . A possible explanation for such behaviors of “ghost” peak is depicted in Fig. 11(b). Namely, to erase the peak on  $R(q)$  it is necessary that the shape (i.e.,  $q$ -dependence) of  $I(q)$  profile comes to resemble each other between N-doped and bare  $\text{TiO}_2$  specimen, which in turn requires that not uniform but selective reduction of scattered intensity at particular  $q$ -range (specifically, in the current situation it correspond to  $0.1 \leq q$  ( $\text{nm}^{-1}$ )  $\leq 0.25$ ) should occur on N-doped specimen with the change of contrast. Though the results in Figs. 7-9 do not exhibit such an extreme feature as depicted in Fig. 11, the tendency seems basically consistent. Especially, in Fig. 9 indicates (not constant but) an excess reduction occurs at around  $0.1 \leq q$  ( $\text{nm}^{-1}$ )  $\leq 0.3$  for N-doped specimen. It should be maximally emphasized here that such a selective depression of  $I(q)$  at a limited  $q$ -range never happens as long as the scattering contrast inside the sample is kept constant.

Instead, it is a natural notion that there is another component (or phase) possessing the characteristic length corresponding to that limited  $q$ -range and the characteristic contrast to be matched out with that of some tuned specific surrounding made of an inert solvent mixture of isotopic molecules. In the current situation, we are not so optimistic to simply conclude that the granular N-doped  $\text{TiO}_2$  product contains N-rich  $\text{TiO}_2$  nano-domains having the size distribution from tens to hundreds nanometers, tracing the distribution of cross-linker ethylene diamine before the calcinations and removing their contribution to  $I(q)$  by soakage in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$ . However, the current dataset of profiles at different four contrast is quite profitable to make an decomposition of

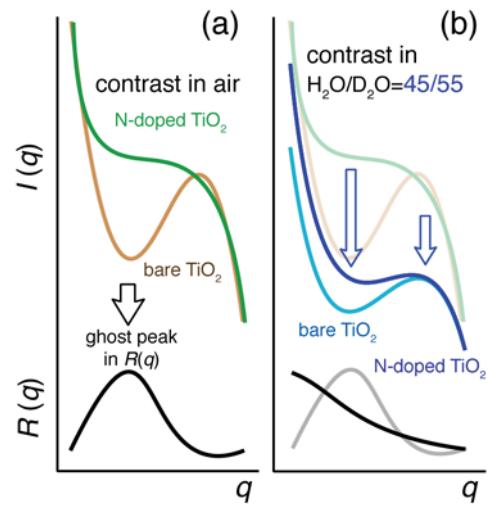


Fig. 11 Schematic depiction to give a possible explanation for some strange behavior observed on the scattering profile  $I(q)$  and its ratio  $R(q)$  of N-doped and bare granular  $\text{TiO}_2$  product.

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scattering profile into the partial contributions of each component, meaning  $\text{TiO}_2$  and other impurities of which major part is most probably nitrogen. This project is still undergoing and not included in this report.

A summary remark of this report is that small- (and wide-) angle neutron scattering measurement was conducted on two types of  $\text{TiO}_2$  product, for both of which nitrogen doping was performed to enhance the applicability of the material and prepared specimens with and without (i.e., “bare”) nitrogen (N) doping for comparison, to study nano-structural features of each product and the feasibility for capture of the trace of doped N species being contained rather small by a typical contrast variation method. Both types of  $\text{TiO}_2$  products were fabricated by sol-gel method and are distinguished as follows; one of which possessing an extra process in fabrication of extending the sol before calcination on the water surface to control the shape, in particular the thickness of the final product is called “nanosheet” while, the other prepared in ordinary process is called “granular”. Doping process for nitrogen differs each other between “nanosheet” and “granular”  $\text{TiO}_2$  products; in the former case, after the calcination of sol an extra annealing (e.g., at 773K) under  $\text{NH}_3$  atmosphere accomplish it, while in the latter case, cross-linking of sol with  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (ethylene diamine) before calcination led to the final product. Following results (or features) are extracted from measured profiles:

- (1) Comparing the “nanosheet” and “granular” product, granular specimen exhibits the larger grain size of which average is ~26 nm and at the same time the diffraction peaks of anatase with larger number (more than ten) as well as higher intensity indicating better ordered crystalline structure, while nanosheet specimen possesses grains of which average size is ca. 18 nm and the crystalline order inside them seems poor judging by less intense and smaller number of diffraction peaks (cf. Figs. 1 and 6).
- (2) Comparison between N-doped and “bare” specimens reveals that the doping process basically does not affect on the crystalline structure either “nanosheet” or “granular” product. While in regard to the nano-scale structure, granular product suggests that addition of cross-linking reagent (in the current case, ethylene diamine) has a possibility to alter the size and its distribution of the  $\text{TiO}_2$  grains (cf. for instance, Figs. 3, 4, 6, 8, and 10).
- (3) Other traces of doped N species on the scattering profiles might be brought out from invisible differences with contrast variation method employing the soakage in tuned  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture and for the case of “nanosheet” product doped N, which never alters the base porous structure and is anticipated to concentrated on the surface area, has a contribution to slightly enhance the scattering contrast of the grain structure being larger than nanometer scale by a factor of ~1.2 in scattering intensity (cf. Fig. 5). While, doped N in “granular” product may have a tendency to be accumulated in the grains where the cross-linker molecules existed before the calcination and such grains may be (slightly) more invisible under some specific condition of soakage in  $\text{H}_2\text{O}/\text{D}_2\text{O}=45/55$  (cf. Figs. 9, and 10).