Supplementary Information

Phosphor and Nitrogen Co-doped Rutile TiO$_2$ Covered on TiN for Oxygen Reduction Reaction in Acidic Media

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S1. Experimental details.

**Catalyst synthesis**: The TiO$_x$N$_y$P$_z$ catalysts were synthesised by modifying a recently reported facile combustion method$^{16-19}$ without using supports. First, 0.49 g of titanium oxysulfate powder (TiOSO$_4$·nH$_2$O; n $\approx$ 1~2, Kishida Chemical Co. Ltd., Osaka, Osaka, Japan) was dispersed in 371 cm$^3$ of distilled water by stirring at room temperature in a polytetrafluoroethylene (PTFE) beaker with a PTFE-coated magnetic bar. The outside bottom of the beaker was coated with a PTFE-carbon composite to facilitate heating on a hot stirrer. Then various amount of 85% (w/w) H$_3$PO$_4$ solution (Wako Pure Chemical Co., Osaka, Osaka, Japan) was added with continuous stirring, kept for 2 h. The atomic ratio of phosphor to titanium, $R_P$, was ranged from 0.0 to 1.0. After the 2 h-stirring, 20 g of urea powder ((NH$_2$)$_2$CO, Wako Pure Chemical Co., Osaka, Osaka, Japan) was added to set mass ratio of urea to TiOSO$_4$-derived TiO$_2$ at 100 unless otherwise noted. Next, 36 cm$^3$ of 35% (w/w) HCl solution (Kishida Chemical Co. Ltd., Osaka, Osaka, Japan) was added to the solution with continuous stirring. Then the PTFE beaker was placed on another stirrer pre-heated to 523 K, stirred continuously until the water evaporated, further dried in a convection oven overnight at 380 K. The dried powders were then ground using an agate mortar, placed in an alumina boat and the boat was set in a horizontal quartz-tube furnace. The tube was slowly evacuated, purged with N$_2$ gas, and the powder samples were heated from room temperature to 1123 K at a rate of 10 K min$^{-1}$, then the temperature was maintained for 2 h. The samples were then cooled to room temperature at an uncontrolled rate. The N$_2$ flow rate was 100 standard cubic centimetres per minute (sccm) during pyrolysis. After pyrolysis, the powders were ground in an agate mortar. Some solid by-products have attached to the inner wall of the quartz tube during pyrolysis, which can stop the gas flow if they block the narrow opening of the quartz tube, and thus can be so dangerous. We used a quartz tube more than three times longer than the heating zone, such that there is sufficient space for by-product accumulation inside the tube to avoid the blockage. It is noted that the by-products were easily removed by washing the tube with water after the pyrolysis and ejection of the alumina boat when the sample was phosphor-free TiO$_x$N$_y$. However, when the sample
contained phosphor, the by-products remained in the tube, most severely at the heating zone even after washing with water. The remained by-products which could contain phosphor affected the crystal structure, surface composition and resulting activity of the TiO$_x$N$_y$P$_z$ catalyst obtained from the next pyrolysis. Therefore, after each pyrolysis/water-washing procedure, the tube was cleaned by heating without any sample in air at 1323 K for ca. 2 h to remove the by-products. The by-products contamination became severer with increasing $R_P$ and the air annealing was performed more than twice when $R_P$ was the highest, 1.0. The TiO$_x$N$_y$P$_z$ catalysts that exhibited the highest activity level, i.e., samples at $R_P = 0.35$ and 0.5 were further annealed under NH$_3$ gas. They were placed in another horizontal quartz-tube furnace and were heated from room temperature to various temperature at a rate of 10 K min$^{-1}$, then the temperature was maintained for various durations. The flowing gases at and under the target temperature were NH$_3$ and N$_2$, respectively, and the flow rate of both gases was 100 sccm. Energy dispersive X-ray (EDX) spectroscopy analyses were performed for $R_P = 0.35$ sample before and after the second annealing under NH$_3$ gas using a EDX spectrometer (JED-2300F, JEOL Ltd., Akishima, Tokyo, Japan). The atomic ratio of phosphor to titanium did not change with the NH$_3$-annealing, and it was 0.07, lower than the precursor ratio, i.e., $R_P = 0.35$. During the first pyrolysis under N$_2$ gas in which harsh reactions including gas evolutions proceeded (S2), some phosphor species seemed to have attached to the inner wall of the quartz tube at the heating zone rather than to be doped into TiO$_x$N$_y$P$_z$ catalysts. To select another precursor will be needed for a precise control of the compositions of TiO$_x$N$_y$P$_z$.

**Characterization:** The morphology of the TiO$_x$N$_y$P$_z$ catalysts was investigated using a field emission scanning electron microscope and a transmission electron microscope (JSM-7000F and JEM-2100, respectively, JEOL Ltd., Akishima, Tokyo, Japan). The bulk crystal structures of catalysts were analysed using an X-ray diffractometer (MiniFlex 600, Rigaku Co., Akishima, Tokyo, Japan) with Cu-K$_\alpha$ radiation generated at 40 kV and 15 mA (scan rage = 20–80$^\circ$, step size = 0.02$^\circ$, and scan rate = 2$^\circ$ min$^{-1}$). The surface crystal structures were evaluated using a Raman spectrometer (NRS-5100, JASCO Co. Ltd., Hachioji, Tokyo, Japan) with a 532-nm
laser. The chemical states of the catalysts were determined using an X-ray photoelectron (XP) spectrometer (PHI 5000 VersaProbe, ULVAC-PHI, Inc., Chigasaki, Kanagawa, Japan) with an Al-Kα X-ray source (1486.6 eV). For some catalysts, the surface was sputtered with an Ar⁺-ion beam generated at an acceleration voltage of 500 V or 1 kV for 60 s. The spectra were obtained after the 60 s-sputtering and the procedure was repeated for five times. The peak shifts due to surface charge were corrected using the binding energy of C 1s (284.8 eV) of the hydrocarbon contaminants from the spectrometer. The spectra were acquired at least three different points for all the catalysts. Then Ti 2p, O 1s and N 1s spectra were analysed by fitting six, three and four symmetric peaks, respectively, after subtracting a Shirley-type background and then the average area fraction of each peaks was calculated.

**ORR activity and selectivity measurements:** Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) voltammograms were obtained to evaluate the ORR activity and selectivity, respectively, of the catalysts. The catalyst, 5% w/w Nafion® ionomer solution (510211, Sigma-Aldrich Co., St. Louis, Missouri, U.S.) and isopropyl alcohol were sonicated together for 1200 s and then further mixed using a planetary mixer (Mazeru Star KK-250S, Kurabo Co., Osaka, Osaka, Japan) for 180 s to obtain a homogeneous catalyst ink. The mass fraction of Nafion in the catalyst layer was set at 0.05. The catalyst loading, \( m \), was varied from 0.6 to 1.5 mg cm\(^{-2}\) by controlling the amount of the catalyst ink dropped onto a glassy carbon (GC) disk (4 mm diameter)–platinum ring (5 mm inner diameter and 7 mm outer diameter) electrode (012613, BAS Co., Sumida-ku, Tokyo, Japan). Prior to the treatment, the surface of the GC disk electrode was polished with 1.0- and 0.05-μm alumina slurries, cleaned by distilled water, ethanol, and then air-dried at 320 K for at least 600 s. A conventional three-electrode cell was used for the room-temperature electrochemical measurements performed in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\). The catalyst-coated GC disk–Pt ring electrode, a carbon rod (diameter: 5 mm, C-072591, Nilaco Co., Chuo-ku, Tokyo, Japan), and Ag/AgCl (3 M NaCl) electrode (RE-1B, BAS Co., Sumida-ku, Tokyo, Japan) were used as the working, counter, and reference electrodes, respectively. The working electrode was set on a rotator (RRDE-3A, BAS Co., Sumida-ku, Tokyo, Japan). All working electrode potentials
were referenced to the RHE. After sequentially bubbling O\textsubscript{2} and N\textsubscript{2} for 1800 s, the RDE and RRDE voltammograms were recorded by applying a disk potential ($E$) of 0.05–1.2 V at a scan rate of 5 mV s\textsuperscript{-1} and a rotation speed of 1500 rpm, using a bipotentiostat (Model 2323 or 704B, BAS Co., Sumida-ku, Tokyo, Japan). The ring potential was maintained at 1.2 V to obtain the RRDE voltammograms. The ORR was measured by $j = j_0 - j_N$, the difference between the current per unit geometrical area, $S$, of the GC disk electrode obtained in N\textsubscript{2} ($j_N = I_N S^{-1}$) and in O\textsubscript{2} ($j_O = I_O S^{-1}$). The hydrogen peroxide yield, $\chi_{H_2O_2}$ values were calculated by analysing the RRDE voltammograms according to the following equation:

$$\chi_{H_2O_2} (\%) = 100 \cdot \frac{2I_r/N}{-I_d + I_r/N}$$

where $I_d$ and $I_r$ denote the disk and ring currents, respectively, after the background correction described above, and $N$ is the collection efficiency (0.424) provided by the manufacturer (BAS Co.).

Nyquist plots of some selected catalysts were measured by an electrochemical impedance spectroscopy (EIS) using a potentiostat equipped with a frequency response analyser (SP-150, Bio-Logic Science Instruments, Seyssinet-Pariset, Isère, France), which was connected to the three-electrode cell used for the abovementioned ORR activity/selectivity measurements. The Nyquist plots were obtained by applying a root mean square alternating current voltage at 5 mV in the frequency range from 0.1 to 1.0 MHz at an open circuit potential in O\textsubscript{2}-saturated 0.1 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4}. 

S2. Changes in crystal structure during the synthesis processes of TiO$_x$N$_y$P$_z$ catalysts.

The TiO$_x$N$_y$P$_z$ catalysts were synthesised by two steps: (1) mixing the precursors at 523 K, (2) pyrolysis at 1123 K under N$_2$ gas in a quartz tube furnace and solid by-products have attached to the inner wall of the quartz tube after (2), as described in section S1. Fig. S1 shows X-ray diffraction (XRD) patterns of dried precursor powders before (2) and the by-products collected from the tube end outside of heating zone after (2). Before heating to 523 K, the HCl concentration in the precursor dispersion was set at 1.0 mol dm$^{-3}$, strongly acidic to decompose urea into ammonium ions and carbonic acid.$^{S1}$

\[
\text{Urea} \rightarrow \text{NH}_4^+\text{CNO}^- \\
\text{NH}_4^+\text{CNO}^- + 2\text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{H}_2\text{CO}_3
\]

Fig. S1(i)–(v) indicates that the main product was NH$_4$Cl at any $R_p$, which should be originated from the reaction between NH$_4^+$ ions from urea and Cl$^-$ ions from the HCl solvent. Although some unknown weak peaks appeared between 30 and 32$^\circ$ when $R_p > 0$, all these precursors were converted to a single TiN phase as shown in Fig. 1(A) of the main text. The NH$_4$Cl was therefore suggested to be a source of nitrogen in TiN formed during the N$_2$-pyrolysis at 1123 K, via various routes including sublimation to decompose into NH$_3$ and HCl.$^{S2}$ Fig. S1(vi) manifests that the amount of NH$_4$Cl was large enough to produce TiN and extra NH$_4$Cl deposited as powders on the inner wall of quartz tube end located outside of heating zone. Thus, the surface of catalyst in the heating zone was with huge amount of evolved reactive gases. The quartz tube outside of the heating zone was not lagged with heat insulators and the temperature at the end of the tube where the by-products were collected was much lower than the sublimation temperature of NH$_4$Cl, 611 K.
Fig. S1 X-ray diffraction (XRD) patterns of TiO$_x$N$_y$P$_z$ precursors with five different phosphor-to-titanium atomic ratio, $R_P$, (i) 0.0, (ii) 0.2, (iii) 0.35, (iv) 0.5 and (v) 1.0 before pyrolysis and (vi) by-products attached to the inner wall of the quartz tube end at outside of the heating zone after N$_2$-pyrolysis of (iii) at 1123 K for 2 h.
S3. Depth profile of TiO$_x$N$_y$P$_z$ catalysts.

The chemical states of the TiO$_x$N$_y$P$_z$ catalyst series were investigated from the surface to sub-surface using X-ray photoelectron spectroscopy (XPS) with Ar$^+$-ion beam sputtering, to focus on the valence of doped phosphor atoms. The XP spectra shown in Fig. S2 were obtained with an acceleration voltage for Ar$^+$-ion sputtering at 500 V, the lowest value with the use of the spectrometer. After sputtering the surface with Ar$^+$-ion beam up to 5 minutes, the P 2p spectra exhibited only the P$^{5+}$-peak at ~133 eV and were still free from P$^{3-}$ as no peaks appeared at ~129 eV$^{23,38}$ whereas the TiN peak at ~455 eV$^{32,33}$ in Ti 2p spectra grew up with increasing the sputtering time. The acceleration voltage was doubled to 1 kV for investigating the chemical states of deeper part in the bulk of some TiO$_x$N$_y$P$_z$ catalysts and the XP spectra before and after the sputtering are shown in Fig. S3. Compared with the Ti 2p spectra shown in Fig. S2(a)–(c), the area fraction of TiN peak at ~455 eV of corresponding TiO$_x$N$_y$P$_z$ catalysts displayed in Fig. S3(a)–(c) increased, which manifests that inner part was observed due to the higher acceleration voltage. The valence of phosphor was still P$^{5+}$ after the 1 kV-sputtering at any $R_p$, as only ~133 eV peak was observed in the P 2p spectra.
Fig. S2 X-ray photoelectron (XP) Ti 2p, N 1s and P 2p spectra of TiO$_x$N$_y$P$_z$ catalysts with four different $R_P$, (a) 0.2, (b) 0.35, (c) 0.5 and (d) 1.0 before and after 1$^{st}$ – 5$^{th}$ sputtering with Ar$^+$-ion beam generated at an acceleration voltage of 500 V. For reference, Ti 2p and N 1s spectra of phosphor-free catalysts ($R_P = 0.0$) without sputtering are also shown in (a). All catalysts were synthesised by pyrolysis under N$_2$ gas at 1123 K for 2 h.
**Fig. S3** XP Ti 2p, N 1s and P 2p spectra of TiO$_x$N$_y$P$_z$ catalysts after N$_2$-pyrolysis at 1123 K for 2 h with three different $R_P$, (a) 0.2, (b) 0.35, and (c) 0.5 before and after 1$^{\text{st}}$ – 5$^{\text{th}}$ sputtering with an Ar$^{+}$-ion beam generated at an accelerating voltage of 1 kV.
S4. Effect of phosphor doping on the Nyquist plots of TiO$_x$N$_y$P$_z$.

Nyquist plots of phosphor-free TiO$_x$N$_y$ ($R_P = 0.0$) and TiO$_x$N$_y$P$_z$ ($R_P = 0.2$) catalysts are shown in Fig. S4. The semicircle at high frequency region became smaller with increasing $R_P$ from 0.0 to 0.2, which indicates that the charge transfer resistance was decreased by the phosphor doping.

**Fig. S4** Nyquist plots of TiO$_x$N$_y$P$_z$ catalysts with two $R_P$, (i) 0.0 and (ii) 0.2 after N$_2$-pyrolysis at 1123 K for 2 h.

The morphology of two TiO$_x$N$_y$P$_z$ catalysts with different $R_P$ was investigated by field emission-scanning electron microscopy, FE-SEM and the images are shown in Fig. S5. The TiO$_x$N$_y$P$_z$ catalysts at $R_P = 1.0$ showed some agglomerates larger than that of $R_P = 0.35$ sample as indicated by circles or arrows.

**Fig. S5** Field emission-scanning electron microscopy (FE-SEM) images of TiO$_x$N$_y$P$_z$ catalysts with two $R_P$, (left) 0.35 and (right) 1.0 after N$_2$-pyrolysis at 1123 K for 2 h. The images were acquired at two different magnifications: (top) $\times$1,000 and (bottom) $\times$10,000.
S6. Optimisation of synthesis conditions for the ORR activity of TiO$_x$N$_y$P$_z$ catalysts.

Effects of mass ratio of urea to TiOSO$_4$-derived TiO$_2$, NH$_3$-annealing temperature and duration (hereafter denoted as $u$, $T$, and $t$, respectively) on the ORR activity of TiO$_x$N$_y$P$_z$ catalysts were investigated to maximise it at $R_P = 0.35$. First, $u$ was optimised as shown in Fig. S6. Both the activity and selectivity were maximised at $u = 100$ under the identical N$_2$-pyrolysis conditions, thus this TiO$_x$N$_y$P$_z$ catalyst was further annealed under NH$_3$ gas. The optimum values were $T = 923$ K and $t = 3$ h as shown in Fig. S7 and S8, respectively. The Tafel slope of the optimised TiO$_x$N$_y$P$_z$ catalyst was 66 mV decade$^{-1}$, obtained by fitting the Tafel plots at kinetically controlled region shown in Fig. S9.

![Fig. S6](image_url) (left) Rotating disk electrode (RDE) voltammograms and (right) hydrogen peroxide yield versus potential ($X_{H_2O_2} - E$) curves of TiO$_x$N$_y$P$_z$ ($R_P = 0.35$) catalysts with three different mass ratios of urea to TiOSO$_4$-derived TiO$_2$, $u$, 70, 100 and 130 after pyrolysis under N$_2$ gas at 1123 K for 2 h. The scans are performed under N$_2$ and O$_2$ atmospheres, with a rotation speed of 1500 rpm and a scan rate of −5 mV s$^{-1}$ (cathodic) in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. The catalyst loading, $m$, was 0.86 mg cm$^{-2}$.
Fig. S7  (left) RDE voltammograms and (right) $X_{H_2O_2} - E$ curves of TiO$_x$N$_y$P$_z$ ($R_P = 0.35$) catalysts with four different NH$_3$-annealing temperatures, $T$, 873 K, 923 K, 973 K and 1073 K. The catalysts were synthesised by two step heating processes; the first under N$_2$ at 1123 K for 2 h then the second under NH$_3$ at $T$ for a fixed duration, $t$, of 3 h. The scans are performed under N$_2$ and O$_2$ atmospheres, with a rotation speed of 1500 rpm and a scan rate of $-5$ mV s$^{-1}$ (cathodic) in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. The $m$ was 0.86 mg cm$^{-2}$.

Fig. S8  (left) RDE voltammograms and (right) $X_{H_2O_2} - E$ curves of TiO$_x$N$_y$P$_z$ ($R_P = 0.35$) catalysts with three different $t$, 1.5 h, 3.0 h and 4.5 h. The catalysts were synthesised by two step heating processes; the first under N$_2$ at 1123 K for 2 h then the second under NH$_3$ at a fixed $T$ of 923 K for $t$ h. The scans are performed under N$_2$ and O$_2$ atmospheres, with a rotation speed of 1500 rpm and a scan rate of $-5$ mV s$^{-1}$ (cathodic) in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. The $m$ was 0.86 mg cm$^{-2}$.
**Fig. S9** A Tafel plot of TiO$_x$N$_y$P$_z$ ($R_p = 0.35$) catalyst synthesised by two step heating processes; the first under N$_2$ at 1123 K for 2 h then the second under NH$_3$ at 923 K for 3 h. The kinetically controlled current density, $j_k$, was calculated by $j_k = |j| \cdot |j_l| / (|j_l| - |j|)$ where $j$ is the background corrected disk current density described in S1 and $j_l$ is the limiting current density. The solid line is the fitting result.
S7. The ORR mass activity of oxynitride-based catalysts.

As summarised in a recent paper (Table S1 in section S5 of reference 18), the highest activity among the ever reported oxide, oxynitride and nitride catalysts is from ZrO$_x$N$_y$-MWCNT$^{14}$ and the second highest one is from support-free TiO$_x$N$_y$$^{18}$ whereas $m$ values used for the activity measurements of these catalysts were different. To compare the activity of these two catalysts and present TiO$_x$N$_y$P$_z$, the mass activity, $j_m = (j_O - j_N)$ $m^{-1}$, of the three catalysts were plotted as a function of $E$ in Fig. S10. The used rotation speed as well as three-electrode cell and resulting solution resistance were different between ZrO$_x$N$_y$-MWCNT$^{14}$ and TiO$_x$N$_y$/TiO$_x$N$_y$P$_z$. As reported by van der Vliet et al., effect of the solution resistance on RDE voltammograms is not negligible to change the slope of RDE voltammograms before reaching diffusion limiting plateau$^{33}$ whereas the diffusion limiting current increases with increasing rotation speed. Although the rotation speed was smaller for TiO$_x$N$_y$P$_z$ than ZrO$_x$N$_y$-MWCNT, higher $j_m$ was observed from the former at the diffusion controlled region, indicating the larger active surface area. When compared with phosphor-free TiO$_x$N$_y$$^{18}$, $j_m$ of TiO$_x$N$_y$P$_z$ was more than double at any $E$.

![Fig. S10](image_url) The mass activity versus potential ($j_m - E$) curves of TiO$_x$N$_y$P$_z$, TiO$_x$N$_y$ and ZrO$_x$N$_y$-MWCNT calculated from RDE voltammograms in Fig. 4(I) of this paper, Fig. 6(a) of reference 18 and Fig. 2(a) of reference 14, respectively. The scans are performed under N$_2$ and O$_2$ atmospheres and a scan rate of −5 mV s$^{-1}$ (cathodic) in 0.1-mol dm$^{-3}$ H$_2$SO$_4$. The rotation speed was 1500 rpm for TiO$_x$N$_y$P$_z$ and TiO$_x$N$_y$$^{18}$ whereas 1600 rpm for ZrO$_x$N$_y$-MWCNT.$^{14}$ The $m$ values were 0.86, 2.00 and 1.39 mg cm$^{-2}$ for TiO$_x$N$_y$P$_z$, TiO$_x$N$_y$ and ZrO$_x$N$_y$-MWCNT, respectively.
Supplementary references

