Spontaneously formed gradient chemical compositional structures of niobium doped titanium dioxide nanoparticles enhance ultraviolet- and visible-light photocatalytic performance

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Semiconductor photocatalysts showing excellent performance under irradiation of both ultraviolet (UV)- and visible (VIS)-light are highly demanded towards realization of sustainable energy systems. TiO2 is one of the most common photocatalysts and has been widely investigated as candidate showing UV/VIS responsive performance. In this study, we report synthesis of Nb doped TiO2 by environmentally benign mechanochemical reaction. Nb atoms were successfully incorporated into TiO2 lattice by applying mechanical energy. As synthesized Nb doped TiO2 were metastable phase and formed chemical compositional gradient structure of poorly Nb doped TiO2 core and highly Nb doped TiO2 surface after high temperature heat treatment. It was found that formed gradient chemical compositional heterojunctions effectively enhanced photocatalytic performance of Nb doped TiO2 under both of UV- and VIS-light irradiation, which is different trend compared with Nb doped TiO2 prepared through conventional methods. The approach shown here will be employed for versatile systems because of simple and environmentally benign process.

In the last decade, there is a numerous number of studies about functionality improvement of semiconductor photocatalysts to achieve both of ultraviolet (UV)-light and visible (VIS)-light responsive performance. Several strategies, such as band gap engineering by doping cations and/or anions, modification of surface structures, and design heterojunction with cocatalysts of metals or semiconductors, were employed to achieve UV/VIS responsive photocatalytic performance1–4. Although typical methods, such as solid state reaction5,6, solvothermal/hydrothermal reaction7–10, and vacuum deposition11,12, are successful approach to synthesize doped semiconductors and heterojunction materials, it is necessary to employ energy consuming and/or high environmental burden conditions, such as quite high temperature sintering, toxic gas flow, high pressure, and vacuum condition, which will give negative impact on environment. Mechanochemical process is known as a facile and environmentally benign method13,14. Mechanochemical reaction often produces unique metastable materials which cannot be prepared by conventional thermochemical techniques15. For example, metastable amorphous calcium carbonate phase was successfully stabilized by mechanochemical Na doping16. Synthesis of metastable Li2OHCl is another example, which showed higher ionic conductivity compared with thermodynamically stable phase17. Nowadays, mechanochemical process is widely employed to synthesize not only typical organic and inorganic compounds, but also doped compounds and composites18–21. Moreover, the mechanisms of the co-crystallization and metastable formation through mechanochemical reactions were reported in the specific systems22,23. There

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is a strong demand to develop facile and promising process by using mechanochemical reaction for highly functional materials, such as UV- and VIS-light responsive semiconductor photocatalysts.

Titanium dioxide, TiO₂, is one of the most investigated semiconductor which shows excellent photocatalytic activity under irradiation of UV-light²⁴. Doping of metals/nonmetals and/or formation of heterojunction of TiO₂/semiconductors were reported to effectively enhance photocatalytic performance²⁵,²⁶. For a preparation of doped TiO₂ through mechanochemical reaction, metals and metal salts were used as dopant sources of cations in general. However, metals tend to weld each other to form composite rather than doping and metal salts gave unexpected doping from counter anions. To avoid these drawbacks, it is necessary to optimize numerous mechanochemical reaction parameters, such as gas atmosphere, milling media, milling speed, milling time, and ball-to-powder weight ratio. Use of metal oxides instead of metals and metal salts is expected to be easier and successful way to dope metal cations into TiO₂ matrixes. In this study, we focused on the fabrication of Nb doped TiO₂ by using mechanochemical process. Commercially available TiO₂ nanoparticles (mixture of anatase and rutile phase) was employed as a starting material and synthesized TiNb₂O₇ microparticles was used as a Nb doping agent. Variety amounts of Nb atom were homogeneously incorporated into both of anatase and rutile nanoparticles by wet mechanochemical process. Nb doped anatase nanoparticles showed improved thermal stability owing to the pinning Nb atoms. It was found that heat treatment led Nb atoms distributed inhomogeneously at surface of nanoparticles to form gradient chemical compositional structures of poorly Nb doped TiO₂ and highly Nb doped TiO₂. The Nb doped TiO₂ with chemical compositional gradient showed enhanced photocatalytic activity under both of UV- and VIS-light irradiation. Although Nb doped TiO₂ were synthesized through various methods, such as pulsed laser deposition, sol–gel technique, thermal plasma processing, and spray pyrolysis, chemical compositional gradient structures have not been reported. This indicates that mechanochemically synthesized materials are key to form the gradient structure and enhance photocatalytic property. The method reported here is a simple and facile approach, hence it is expected to widely apply other dopant-semiconductor systems towards highly functionalized photocatalysts.

**Methods**

**Chemicals.** Titanium(IV) tetraisopropoxide (TTIP, 95%), niobium(V) pentaethoxide (NPE, 99.9%), diethanolamine (99%), polyethyleneimine (Mₚ = 1800), methyl orange (MO), sodium dihydrogen phosphate (NaH₂PO₄, 85%), phosphoric acid (H₃PO₄, 85%), ethanol (99.5%) were used as received. H₃PO₄ was purchased from Kanto Chemical Holdings. All other reagents were purchased from Wako Pure Chemicals Industries, Ltd. Ultrapure water of 18.2 MΩ·cm resistivity was used in all experiments.

**Synthesis of TiNb₂O₇ microparticles.** TTIP (1 mmol), NPE (2 mmol), and diethanolamine (2 mmol) were dissolved in 5 mL of ethanol. After stirring for 20 min, homogenous sol was obtained. Water (35 mmol) was added to the sol under vigorous stirring and keep stirring at least for 5 min to obtain gel. Gelatious precipitates were dried at 100 °C for 12 h. Dried powders were heat treated at 1150 °C for 3 h (ramp rate: 5 °C/min). Heat treated powder of TiNb₂O₇ was employed as a Nb source in subsequent mechanochemical process because TiNb₂O₇ was reportedly segregated from Nb doped TiO₂ only after high temperature heat treatment that means TiNb₂O₇ will be highly compatible with TiO₂²⁷.

**Mechanochemical synthesis of Nb-doped TiO₂ nanoparticles.** Obtained TiNb₂O₇ powders were mixed with commercial anatase–rutile TiO₂ nanoparticles (EVONIK AEROXIDE® P25, Nippon Aerosil, Tokyo, Japan) with a molar ratio of Nb/(Ti + Nb) = 0 (without TiNb₂O₇), 0.02, 0.05, and 0.10. After grounded for 30 min in a mortar, mixed powders (2.5 g) were dispersed in 20 mL of ethanol solution including polyethyleneimine (7.2 × 10⁻² mmol). Obtained suspensions were sealed in zirconia pod (inner volume of 80 mL) and milled in a tilted rotation planetary ball mill (Planet M2-3F, Nagao System Inc.) at revolution speed of 700 rpm and rotation speed of 1750 rpm (152 G) for 2 h with zirconia balls (5 mm in diameter, #243, 83.5 g). Milled suspensions were dried at room temperature for 5 days and heat treated at 500–900 °C for 3 h (ramp rate: 5 °C/min, cooling rate: 2 °C/min). The powders prepared through this process were denoted as NTO-x-y, where x and y are nominal Nb/(Ti + Nb) in percentage (0 ≤ x ≤ 10) and heat treatment temperature (500 ≤ y ≤ 900) (As dried samples before heat treatment are denoted as NTO-x-dry).

**Photocatalytic test.** The solution pH was kept at 2.1 using buffer solution to avoid agglomeration of nanoparticles during photocatalytic test, which changes background light scattering by particles. Phosphate buffer solution (0.10 mol/L, pH = 2.1) were prepared using NaH₂PO₄ and H₃PO₄. Sample powders (10 mg) were dispersed in 6 mL of buffered aqueous solution and ultrasonicated for 30 min. MO buffered aqueous solution (20 μmol/L, 20 μL) was added to the suspensions. Colored suspensions (3 mL) in close capped quartz cell (1 × 1 cm² base rectangular cell) were exposed to UV/VIS-light after stirring in dark condition. UV light and VIS light were generated by UVF-203S Type-A light source (San-Ei Electric Co., Ltd., Japan) (365 nm) and UVF–203S Type-C light source (San-Ei Electric Co., Ltd., Japan) (405 and 436 nm) with intensities of 60 and 255 mW/cm², respectively. The light probes were contacted to the quartz cell, which means the light-to-solution distance was same for all the experiments, ~ 1 mm. After appropriate irradiation time, the suspensions were left for 30 s without stirring and set in a UV–vis spectroscopy to determine MO concentration from the F(R∞) at 514 nm of diffuse reflectance spectra using calibration curve.

**Characterization.** A field emission scanning microscope (SEM; S-8020, Hitachi High-Technologies Corp., Japan) equipped with energy dispersed X-ray spectroscopy (EDS) was used for evaluation of particle size and...
elemental composition. A transmission electron microscope (TEM; JEM-2100F, JEOL Ltd., Japan) equipped with EDS and scanning TEM mode (STEM) was employed at an operating voltage of 200 kV to clarify the crystal phase and elemental composition of individual particles. Powder X-ray diffraction (XRD) (SmartLab, Rigaku Corp., Japan) using Cu Kα radiation (λ = 0.1544 nm) equipped with one dimensional detector was used to characterize crystal phases of samples. X-ray photoelectron spectrometer (XPS) analyses were carried out with ESCA-5600 (Ulvac-Phi, Japan) using a monochromatic Al Kα source (1486.6 eV, 200 W) to evaluate an elemental composition of adjacent surface of particles and an oxidation state of Ti and Nb atoms. The instrument work function was calibrated to give an Au 4f7/2 of metallic gold binding energy of 83.95 eV ± 0.1 eV. Survey spectra and high-resolution spectra were collected with a step of 0.4 and 0.05 eV, respectively. The obtained spectra were calibrated using C 1 s binding energy (284.8 eV) of the samples as an internal standard. Ultraviolet–visible (UV–Vis) spectroscopy (V-650 spectrophotometer, JASCO Corp., Japan) equipped with an integrating sphere was used to characterize optical band gap of samples and evaluation of decolorization of MO solution. The reflectance values of obtained diffuse reflectance spectra were transformed to Kubelka–Munk units, F(R∞) by using Eq. (1)

\[ F(R_∞) = 1 - \left( \frac{1}{2} F(R_{∞, s}) \right)^2 \]  

where \( F(R_{∞, s}) \) is measured reflectance value. Raman spectroscopy (RAMANtouch, Nanophoton Corp., Japan) was employed to characterize crystal phases and defects (excitation: 532 nm). The \( N_2 \) adsorption–desorption measurement using Belsorp-18 (Bel Japan Inc., Japan) was employed to evaluate specific surface area by the Brunauer–Emmett–Teller (BET) method.

## Results and discussion

### Incorporation of Nb into TiO₂ nanoparticles through mechanochemical treatment.

TTIP and NPE were used as precursors to synthesize TiNb₂O₇ as a Nb doping agent. Addition of water to ethanolic solution, including TTIP, NPE, and diethanolamine, triggered hydrolysis and condensation of both metal alkoxides. During reaction, diethanolamine worked as a reaction controlling agent, which hinder vigorous reaction of NPE and enabled to form homogenous Ti and Nb mixed precipitates. Dried precipitates were characterized as poorly crystalline TiNb₂O₇ by XRD measurement (Figure S1). The precipitates were heat treated at 1150 °C for 3 h. Heat treated precipitates were characterized as well-crystalline TiNb₂O₇ with a crystallite size of 63.7 nm calculated using 110 diffraction peak. Obtained TiNb₂O₇ showed angular shape with a particle size of 840 ± 359 nm (Figure 1a,d). TiNb₂O₇ microparticles and commercially available TiO₂ nanoparticles (particle diameter of 44.1 ± 16.7 nm) (Figure 1b,e) were mixed and mechanochemically treated. After mechanochemical treatment, as dried powder (NTO-5-dry, see experimental section for sample IDs) showed the particle size of 43.8 ± 20.0 nm which is comparable size to the pristine TiO₂ (Figure 1c,f). Figure 2a,b are TEM image of NTO-5-dry. The lattice fringe close to particle surface became disorder after mechanochemical treatment, which is a feature of amorphous phase. Raman spectra of pristine TiO₂, NTO-5-dry, and NTO-5-600 were shown in Figure S2. The peak around 145 cm⁻¹, assigned as \( E_g \) mode of symmetric stretching vibrations of O–Ti–O bonds of rutile phase, was shifted to 148 cm⁻¹ after mechanochemical treatment (NTO-5-dry), which indicates formation of oxygen vacancies. Grayish color of NTO-5-dry powder agrees formation of oxygen vacancies in TiO₂ matrix. The peak shifted back to 145 cm⁻¹ after heat treatment at 600 °C indicating elimination of vacancies. The atomic ratios of Nb/(Ti + Nb) evaluated by SEM–EDS and XPS were well matched with nominal molar ratio (Table S1). Figure 2c shows the local Nb/(Ti + Nb) ratio measured by STEM-EDS line scanning. The scanned line was shown as green dots, which crosses both of rutile and anatase nanoparticles. Nb atoms were detected at entire points, which implies that Nb atoms were homogeneously incorporated in both of anatase and rutile nanoparticles.

XRD patterns of powders before and after mechanochemical treatment were shown in Fig. 2d with the pattern of TiNb₂O₇ microparticles. Detected crystalline species were anatase and rutile phase with trace amount of TiNb₂O₇ after mechanochemical reaction. Crystallite size of TiNb₂O₇, anatase, and rutile before/after mechanochemical treatment were calculated as 63.7/31.7 nm, 21.4/20.7 nm, and 29.2/25.8 nm, respectively. Drastic crystallite size reduction of TiNb₂O₇ indicates that TiO₂ crystals were more stable than TiNb₂O₇ crystals against mechanochemical treatment. Lattice volume of anatase (135.98(8) Å³) and rutile (62.48(3) Å³) phases of NTO-5-dry was comparable to those of pristine TiO₂ (136.01(7) Å³ and 62.51(3) Å³). This may be result of competitive effects between lattice parameters of anatase and rutile against Nb incorporation to TiO₂. Although a phase transition from anatase to rutile by mechanochemical treatment was reported, amorphous layer formation on the surface of nanoparticles and preferential amorphization of TiNb₂O₇ may consume mechanical energy and retard phase transition of anatase. In the case of ground mixed powders of pristine TiO₂ and TiNb₂O₇ in a mortar, \( f_R \) drastically increased with temperature and reached \( f_R \sim 1.0 \)
Figure 1. (a), (c), (e) SEM images and (b), (d), (f) corresponding particle diameter distributions (statistics of 450 particles) of synthesized TiNb₂O₇ microparticles, pristine TiO₂ nanoparticles, and NTO-5-dry.

Figure 2. (a,b) TEM images and (c) Nb/(Ti + Nb) calculated from STEM-EDS line scan of NTO-5-dry. Green dots in (a) are scanned points of STEM-EDS shown in (c). (d) XRD patterns of TiNb₂O₇ microparticles, powder mixture of pristine TiO₂ and TiNb₂O₇ and mechanochemical treated powder (nominal Nb/(Ti + Nb) = 0.05). *TiNb₂O₇; JCPDS #00-072-0116.
after heat treatment at 700 °C. NTO-0-y showed smaller f_R than powder mixtures at each heat treatment temperature, which indicates formed surface amorphous layer worked as effective grain boundary and retarded phase transition. In the case of NTO-5-y, ~ 60% of anatase crystals were remained even after heat treated at 800 °C. In addition to amorphous layer formation, incorporated Nb atoms worked as pinning sites and improved thermal stability. Thermal stability of anatase phase was also improved in the case of NTO-2-y and NTO-10-y (Figure S3a), which indicates that incorporated Nb atoms effectively worked as pining sites even if small quantity.

Chemical compositions of heat-treated powders were investigated by using SEM–EDS and XPS techniques (Figure 4a). Nb/(Ti + Nb) ratio calculated from SEM–EDS (filled symbol with solid lines) and XPS (open symbol with dot lines) spectra of NTO-2-y (black), NTO-5-y (red) and NTO-10-y (blue). (b) Ti 2p and (c) Nb 3d XPS spectra of NTO-5–600 (open circles, black dot line, blue/green area, and red solid line denote experimental data, background, fitted curves, and cumulative curves of fitted curves.

Figure 3. (a) XRD patterns of NTO-5-y (y = 500 – 900). 101_A and 110_R correspond to 101 diffraction peak of anatase and 110 diffraction peak of rutile, respectively. (b) Rutile phase weight fraction, f_R, against anatase phase calculated from corresponding XRD patterns. As mixed pristine TiO_2 and TiNb_2O_7, NTO-0-dry, and NTO-5-dry are plotted at temperature of 25 °C.

Figure 4. (a) Nb/(Ti + Nb) values calculated from SEM–EDS (filled symbol with solid lines) and XPS (open symbol with dot lines) spectra of NTO-2-y (black), NTO-5-y (red) and NTO-10-y (blue). (b) Ti 2p and (c) Nb 3d XPS spectra of NTO-5–600 (open circles, black dot line, blue/green area, and red solid line denote experimental data, background, fitted curves, and cumulative curves of fitted curves.)
increased with increasing the heat treatment temperature, which means that heat treated Nb doped TiO₂ have inhomogeneous chemical composition between surface and core of the particles. The Nb/(Ti + Nb) increased with increasing heat treatment temperature independently of the integrated area of diffraction peak of TiNb₂O₇, except NTO-10-900 (Figure S3b). This implies that Nb atoms were still incorporated in the TiO₂ lattice and/or in amorphous like Nb-rich oxide phases at the surface of nanoparticles. Figure 4b,c were XPS Ti 2p and Nb 3d core level spectrum of NTO-5-600. Both spectra were fitted with two of peak functions. The fitted peak positions of Ti 2p₁/₂ and Ti 2p₃/₂ were 464.6 eV and 458.9 eV, respectively, which is a good agreement with reported value of Ti⁴⁺⁴³. The fitted peak positions of Nb 3d₃/₂ and Nb 3d₅/₂ were 210.0 eV and 207.2 eV, respectively. The Nb 3d₅/₂ peak position is intermediate of Nb⁴⁺ (205.9 eV) and Nb⁵⁺ (207.5 eV)⁴⁴. In the case of titanium niobium oxides family (TiNbₘO₂₊₂.₅ₘ), relatively Ti rich compounds, such as TiNb₂O₇ (ₘ = 2)⁴⁵ and Ti₂Nb₁₀O₂₉ (ₘ = 5)⁴⁶ showed Nb 3d₅/₂ peak position same as mixture of Nb⁴⁺ and Nb⁵⁺ in Nb-doped TiO₂⁴³ and relatively Nb rich compounds, such as TiNb₆O₁₇ (ₘ = 6)⁴⁷ and TiNb₂₄O₆₂ (ₘ = 24)⁴⁸ showed the peak position same as Nb⁵⁺ in Nb₂O₅. Considering Nb/(Ti + Nb) of NTO-5–600 was 0.11, it is reliable that Nb was exist as a mixture of Nb⁴⁺ and Nb⁵⁺. All the samples showed Ti 2p₃/₂ = 458.8 ± 0.2 eV and Nb 3d₅/₂ = 207.1 ± 0.2 eV which indicate that the oxidation states of Ti and Nb were stable during heat treatment.

Further analysis was demonstrated using TEM and STEM-EDS. Figure 5a–d were STEM and STEM-EDS mapping images. Although Ti atoms were homogenously distributed in the individual particles, Nb atoms inhomogeneously distributed around the edges of the particles. Figure 5e is the result of line scanned STEM-EDS analysis. Nb/(Ti + Nb) clearly increased at the scan point of the particle edges. Figure 5f–h are TEM image of the location where STEM-EDS mapping and line scan were taken. The start and end points of STEM-EDS line scan were located at the nanoparticles of anatase and rutile, respectively. Therefore, Nb rich TiO₂ (Nb/(Ti + Nb) ~ 0.25) were formed at the surface of both anatase and rutile nanoparticles. The changes of lattice fringes were analysed by fast Fourier transform method (Figure S4). Clear spots corresponding to anatase 101 and rutile 101 lattice fringes were obtained at the analysis area enough distant from the particle surface. On the other hand, the fast Fourier transform images prepared using the analysis area around surface showed blurred spots with broad ring patterns, which indicates segregation of Nb atoms at the surface made the lattice disordered. XPS, STEM-EDS, and TEM analyses indicate that gradient chemical composition was spontaneously developed; poorly Nb doped TiO₂ at the core of the nanoparticles and highly Nb doped TiO₂ at the surface of nanoparticles.

Optical properties were investigated using UV–Vis diffuse reflectance spectroscopy (Figure S5 and S6). Obtained diffuse reflectance spectra were converted to (F(Rₐ∞hv)hv)² versus hv and (F(Rₐ∞hv)hv)½ versus hv plots for an evaluation of direct and indirect transitions, respectively. Direct band gap energies were decreased with increasing heat treatment temperature (Figure S6a). On the other hands, indirect band gap energies were slightly increased with increasing heat treatment temperature (Figure S6b). There is a rough linear relationship between fₒ and the direct band gap energy (Figure S6c) and between Nb/(Ti + Nb) and indirect band gap energy (Figure S6d). These results indicate that rutile phase and niobium titanium oxide phases are dominant factor of direct and indirect band gaps, respectively. In fact, direct and indirect band gaps were approaching to corresponding band gaps; direct band gap of rutile phase is 3.0 eV⁴⁹ and indirect band gap of TiNb₂O₇ phase is 3.1 eV⁴⁹, respectively.

In summary, mechanochemical treatment using TiO₂ nanoparticles and TiNb₂O₇ microparticles produced Nb doped TiO₂ nanoparticles as a result of preferential amorphization of TiNb₂O₇ phase. Homogenously incorporated Nb atoms diffused to the surface of nanoparticles after heat treatment. Resultant nanoparticles of both
anatase and rutile-based phase had gradient chemical composition of highly Nb doped TiO₂ and poorly Nb doped TiO₂.

**Photocatalytic performance.** The photocatalytic performances of mechanochemically prepared powders were evaluated by decoloration of methyl orange (MO) aqueous solution, which is widely employed to investigate the properties of photocatalysts. In addition to NTO-\(x-y\), pristine TiO₂ and homogeneously Nb incorporated TiO₂ synthesized by thermal plasma treatment\(^{32}\) (Nb/(Ti + Nb) ~ 0.21, TP-20)) were tested as a control. Diffuse reflectance measurements were employed to trace decoloration of MO. Figure 6 shows typical results of MO decoloration. The peaks correspond to MO were clearly decreased with light irradiation time (Fig. 6a,b). The calculated \(-\ln(\frac{C_t}{C_0})\), where \(C_0\) and \(C_t\) were MO concentrations of initial and \(t\) min light irradiated solutions, were plotted against irradiation time (Fig. 6c). According to the following Eq. (3) for first-order reaction, the rate constants were determined;

\[
-\ln \left( \frac{C_t}{C_0} \right) = k \cdot t
\]

where \(k\) and \(t\) were rate constants (\(k_{\text{UV}}\) and \(k_{\text{VIS}}\) under UV- and VIS-light irradiation, respectively) and irradiation time. Figure 7a,c are summary of \(k_{\text{UV}}\) and \(k_{\text{VIS}}\) for all the tested samples. Both of \(k_{\text{UV}}\) and \(k_{\text{VIS}}\) of NTO-0-\(y\) were decreased with increasing heat treatment temperature same as TiO₂. In the case of TiO₂ and NTO-0-\(y\), there was a relation between \(f_R\) and \(k_{\text{UV}}/k_{\text{VIS}}\) the photocatalytic activity decreased with increasing \(f_R\) (Fig. 7b,d). Decrease of \(k_{\text{UV}}\) is due to decrease of UV-light active anatase phase. The trend of \(k_{\text{VIS}}\) is different from reported studies, in which heat treated TiO₂ photocatalysts showed volcanic plot of VIS-light activity against \(f_R\)^{50–52}. The mechanism of photocatalytic activity in the case of anatase/rutile mixed phase was reported as follows; formation of heterojunction between anatase and rutile allows electrons transfer from rutile to anatase through interface that stabilizes charge separation and hinders charge recombination^{53}. It is supposed that formed amorphous layers after mechanochemical treatment inhibit formation of anatase/rutile heterojunction, which disturbs electron transfer and results decrease of photocatalytic performance.

NTO-2-dry, NTO-5-dry, and NTO-10-dry showed significant increase of \(k_{\text{UV}}\) compared with NTO-0-dry and TiO₂. Although mechanochemically synthesized samples showed increased \(k_{\text{UV}}\) with increasing Nb doping amount, TP-20 having largest amount of Nb dopant revealed lowest \(k_{\text{UV}}\). It is supposed that metastable doping by
mechanochemical treatment promoted photocatalytic performance. The $k_{\text{UV}}$ further improved after heat treatment at 600 °C only in the case of mechanochemically Nb doped samples, which indicates formed chemical compositional gradient enhanced photocatalytic reaction. The $k_{\text{UV}}$ tend to decrease with increasing heat treatment temperature above 600 °C, i.e., increasing $f_R$ as is shown in Fig. 7b. These results imply that Nb doped anatase nanoparticles having chemical compositional gradient structure are dominant component for an enhancement of UV-light photocatalytic performance. Although $k_{\text{VIS}}$ of NTO-2-dry, NTO-5-dry, and NTO-10-dry were smaller than TiO$_2$ and NTO-0-dry, those were drastically increased after heat treatment. Considering $k_{\text{VIS}}$ increased with further increasing $f_R$, it is supposed that Nb doped rutile nanoparticles gave significant enhancement of VIS-light photocatalytic performance. Surprisingly, NTO-2-800 showed significant high $k_{\text{UV}}$ and $k_{\text{VIS}}$ despite smaller specific surface area (3.21 m$^2$/g) compared with pristine TiO$_2$ (45.7 m$^2$/g), NTO-2-dry (53.6 m$^2$/g) and TP-20 (87.2 m$^2$/g). It is reported that Cu nanocluster-grafted Nb-doped TiO$_2$ showed VIS active photocatalytic performance owing to the energy level matching. Considering these, formation of chemical compositional gradient structures will result energy level matching and lead excellent photocatalytic performance under both of UV- and VIS-light irradiation.

The effects of Nb doping on physical properties of TiO$_2$ have been reported; with increasing amount of Nb dopant, band gap energy became large and electron conductivity enhanced. In addition, Nb doping leads generation of Ti$^{3+}$ improving photocatalytic activity, which is not detected by XPS but detected by electron paramagnetic resonance technique. Considering these reports, the hypothetic mechanism of mechanochemically prepared photocatalysts is summarized in Fig. 8. Electron–hole pair will generate at the poorly Nb doped TiO$_2$ (core part of nanoparticles) due to their smaller band gap energy compared with highly Nb doped TiO$_2$ (surface part of nanoparticles). Electrons will move to highly Nb doped TiO$_2$ because of larger conductivity. In addition, electron will transfer from rutile to trapping site of anatase around heterointerface, which is reported to be 0.8 eV lower than the conduction band edge of anatase. These processes will stabilize charge separation and retard charge recombination. Considering Nernstian shift of conduction bands of TiO$_2$, O$_2^-$ radical formation through single-electron reduction reaction may be minor reaction. HO$_2^-$ radical and H$_2$O$_2$ formed and attacked to MO molecules leading decoloration. The reported energy levels of valence band maximum and conduction band minimum of anatase, rutile, and TiNb$_2$O$_7$ (as a typical example of Nb-rich titanium oxides) consistent with our hypothesis.

**Conclusion**

Nb doped TiO$_2$ were synthesized through mechanochemical reaction between TiO$_2$ (rutile/anatase) nanoparticles and TiNb$_2$O$_7$ microparticles owing to the relatively lower elastic modulus of TiNb$_2$O$_7$. Homogeneously distributed Nb atoms tended to move to particle surface after high temperature heat treatment, which indicates initially
formed Nb doped TiO₂ was metastable phase. Resultant materials had gradient chemical compositional structure of poorly Nb doped TiO₂ core part and highly Nb doped TiO₂ surface part. It was found that the materials with gradient chemical compositional heterojunction structure showed enhanced photocatalytic activity under both of UV- and VIS-light irradiation. Obtained results in this study indicate metastable materials prepared by mechanochemical treatment will show unique functions which are different from materials prepared by conventional thermal processes. It is expected to enhance not only photocatalytic property but also other functionalities, such as catalytic and electrochemical activity, by design materials through mechanochemical treatment.

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References

1. Chen, X., Shen, S., Guo, L. & Mao, S. S. Semiconductor-based photocatalytic hydrogen generation. Chem. Rev. 110, 6503–6570 (2010).
2. Kumar, S. G. & Devi, L. G. Review on modified TiO₂ photocatalysis under UV/visible light: Selected results and related mechanisms on interfacial charge carrier transfer dynamics. J. Phys. Chem. A 115, 13211–13241 (2011).
3. Wang, H. et al. Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. Chem. Soc. Rev. 43, 5234–5244 (2014).
4. Miyauchi, M. et al. Visible-light-sensitive photocatalysts: Nanocluster-grafted titanium dioxide for indoor environmental remediation. J. Phys. Chem. Lett. 7, 75–84 (2016).
5. Li, Y., Hwang, D. S., Lee, N. H. & Kim, S. J. Synthesis and characterization of carbon-doped titania as an artificial solar light sensitive photocatalyst. Chem. Phys. Lett. 404, 25–29 (2005).
6. Hou, Y. D. et al. N-doped SiO₂/TiO₂ mesoporous nanoparticles with enhanced photocatalytic activity under visible-light irradiation. Chemosphere 72, 414–421 (2008).
7. Perera, S. D. et al. Hydrothermal synthesis of graphene-TiO₂ nanotube composites with enhanced photocatalytic activity. ACS Catal. 2, 949–956 (2012).
8. Zhu, J., Zheng, W., He, B., Zhang, J. & Anpo, M. Characterization of Fe-TiO₂ photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water. J. Mol. Catal. A Chem. 216, 35–43 (2004).
9. Xiao, X. et al. One-pot solvothermal synthesis of three-dimensional (3D) BiOI/BiOCl composites with enhanced visible-light photocatalytic activities for the degradation of bisphenol-A. J. Hazard. Mater. 233–234, 122–130 (2012).
10. Huang, D. G., Liao, S. J., Liu, J. M., Dang, Z. & Petrik, L. Preparation of visible-light responsive N-F-codoped TiO₂ photocatalyst by a sol-gel-solvothermal method. J. Photochem. Photobiol. A Chem. 184, 282–288 (2006).
11. Suda, Y., Kawasaki, H., Ueda, T. & Oshshima, T. Preparation of high quality nitrogen doped TiO₂ thin film as a photocatalyst using a pulsed laser deposition method. Thin Solid Films 453–454, 162–166 (2004).
12. Sato, Y., Akizuki, H., Kamiyama, T. & Shigesato, Y. Transparent conductive Nb-doped TiO₂ films deposited by direct-current magnetron sputtering using a TiO₂-x target. Thin Solid Films 516, 5758–5762 (2008).
13. James, S. L. et al. Mechanochemistry: Opportunities for new and cleaner synthesis. Chem. Soc. Rev. 41, 413–447 (2012).
14. Garay, A. L., Pichon, A. & James, S. L. Solvent-free synthesis of metal complexes. Chem. Soc. Rev. 36, 846–855 (2007).
15. Lea, M. C. Disruption of the silver haloid molecule by mechanical force. Am. J. Sci. 43, 527–531 (1892).
16. Leukel, S. et al. Mechanochemical access to defect-stabilized amorphous calcium carbonate. Chem. Mater. 30, 6040–6052 (2018).
17. Yamamoto, T. et al. Synthesis of the metastable cubic phase of Li₃OHCl by a mechanochemical method. Inorg. Chem. 59, 11901–11904 (2020).
18. Suryanarayana, C. & Al-Aqeeli, N. Mechanically alloyed nanocomposites. Prog. Mater. Sci. 58, 383–502 (2013).
19. Prochowicz, D., Saksi, M., Yadav, P., Grätzel, M. & Lewinski, J. Mechanochemicals for photovoltaic applications: Preparation, characterization, and device fabrication. Acc. Chem. Res. https://doi.org/10.1021/acs.accounts.9b00454 (2019).
20. MacNicol, C. E., Fu, F., Jing, L., Chen, P. Y. & Wong, I. Y. Mechanochanical engineering of 2D materials for multiscale biointerfaces. J. Mater. Chem. B 7, 6293–6309 (2019).
21. Palazon, F., El Aijouri, Y. & Bolink, H. J. Making by grinding: Mechanochemistry boosts the development of halide perovskites and other multinary metal halides. Adv. Energy Mater. 1902499, 1–13 (2019).
22. Rana, R. et al. Insights into the mechanism of the mechanochemical formation of metastable phases. ACS Appl. Mater. Interfaces 13, 6785–6794 (2021).
23. Germain, L. S., Arhangelski, M., Etter, M., Dinnebier, R. E. & Friščić, T. Challenging the Ostwald rule of stages in mechanochemical cocrystallisation. Chem. Sci. 11, 10092–10100 (2020).
24. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).
25. Zhang, J., Wu, Y., Xing, M., Leghari, S. A. K. & Saïdaj, S. Development of modified N-doped TiO2 photocatalyst with metals, nonmetals and metal oxides. Energy Environ. Sci. 3, 715–726 (2010).
26. Marschall, R. Semiconductor composites: Strategies for enhancing charge carrier separation to improve photocatalytic activity. Adv. Funct. Mater. 24, 2421–2440 (2014).
27. Jaiswal, R., Patel, N., Kothari, D. C. & Mostello, A. Improved visible light photocatalytic activity of TiO2 co-doped with Vanadium and Nitrogen. Appl. Catal. B: Environ. 126, 47–54 (2012).
28. Murakami, M. et al. Anatase TiO2 thin films grown on lattice-matched LaAlO3 substrate by laser molecular-beam epitaxy. Appl. Phys. Lett. 78, 2664–2666 (2001).
29. Furubayashi, Y. A transparent metal: Nb-doped anatase TiO2. Appl. Phys. Lett. 86, 1–3 (2005).
30. Tsuzuki, A., Murakami, H., Kani, K., Kawakami, S. & Tori, Y. Preparation of Nb-doped TiO2 films by the sol-gel method. J. Mater. Sci. Lett. 9, 624–626 (1990).
31. Ruiz, A. M., Dezanneau, G., Arbiol, J., Cornet, A. & Morante, J. R. Insights into the structural and chemical modifications of Nb additive on TiO2 nanoparticles. Chem. Mater. 16, 862–871 (2004).
32. Zhang, C. et al. High-concentration niobium (V) doping into TiO2 nanoparticles synthesized by thermal plasma processing. J. Mater. Res. 26, 658–671 (2011).
33. Saito, K., Yi, E., Laine, R. M. & Sugahara, Y. Preparation of Nb-doped TiO2 nanopowder by liquid-feed spray pyrolysis followed by ammonia annealing for tunable visible-light absorption and inhibition of photocatalytic activity. Chem. Int. 46, 1314–1322 (2020).
34. Ohkawa, T., Izumi, F. & Fujiki, Y. Raman spectrum of anatase, TiO2. J. Raman Spectrosc. 7, 321–324 (1978).
35. Chen, X., Liu, L., Yu, P. Y. & Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. Science 311, 746–750 (2011).
36. Wachtman, J. B., Telf, W. E. & Lam, D. G. Elastic constants of rutile (TiO2). J. Res. Natl. Bur. Stand. Sect. A. Phys. Chem. 66A, 465 (1962).
37. Perfler, L. et al. Nanodentation, high-temperature behavior, and crystallographic/spectroscopic characterization of the high-refractive-index materials TiTa2O7 and TiNbO2. Inorg. Chem. 54, 6836–6848 (2015).
38. Santara, B., Giri, P. K., Imakita, K. & Fujii, M. Microscopic origin of lattice contraction and expansion in undoped rutile TiO2 nanostructures. J. Phys. D Appl. Phys. 47, 215302 (2014).
39. Kamisaka, H., Hitosugi, T., Suenaga, T., Hasegawa, T. & Yamashita, K. Density functional theory based first-principle calculation of Nb-doped anatase TiO2, and its interactions with oxygen vacancies and interstitial oxygen. J. Chem. Phys. 131, 034702 (2009).
40. Lee, H.-Y. & Robertson, J. Doping in and nanoscale morphology of Nb-doped rutile TiO2. J. Appl. Phys. 113, 213706 (2013).
41. Spurr, R. A. & Myers, H. Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. Anal. Chem. 29, 766–767 (1957).
42. Begin-colin, S., Caer, G. L., Moccelin, A. & Zandonà, M. Polymorphic transformations of titania induced by ball milling. Philos. Mag. Lett. 69, 1–7 (1994).
43. Sayers, C. N. & Armstrong, N. R. X-ray photoelectron spectroscopy of TiO2 and other titane electrodes and various standard Titanium oxide materials: Surface compositional changes of the TiO2 electrode during photoelectrolysis. Surf. Sci. 77, 301–320 (1978).
44. Darlinski, A. Angle resolved XPS studies of oxides at Nb- NbN-, NbC- and NbSn- surfaces. IEEE Trans. Magn. 23, 1381–1384 (1987).
45. Yu, Z. et al. Dual modification of TiNbO2 with nitrogen dopants and oxygen vacancies for selective aerobic oxidation of benzylamine to imine under green light. J. Mater. Chem. A 5, 4607–4615 (2017).
46. Yao, Z. et al. Superior high-rate lithium-ion storage on TiNb2O7 arrays via synergistic TiC/C skeleton and N-doped carbon shell. Nano Energy 54, 304–312 (2018).
47. Sun, R. et al. High rate capability performance of ordered mesoporous TiNb2O7 microsphere anodes for lithium ion batteries. Dalt. Trans. 46, 17061–17066 (2017).
48. Li, S., Chen, J., Gong, X., Wang, J. & Lee, P. S. Hole graphene-wrapped porous TiNb2O7 nanoparticles as high-performance intercalation pseudocapacitive anode materials for lithium-ion capacitors. NPC Asia Mater. 10, 406–416 (2018).
49. Cardona, M. & Harbeke, G. Optical properties and band structure of wurztite-type crystals and rutile. Phys. Rev. C137, A1467–A1476 (1965).
50. Su, R. et al. How the anatase-to-rutile ratio influences the photoreactivity of TiO2. J. Phys. Chem. C 115, 24287–24292 (2011).
51. Nair, R. G., Paul, S. & Sandarski, S. K. High UV-visible light activity of mixed phase titania: A generic mechanism. Sol. Energy Mater. Sol. Cells 95, 1901–1907 (2011).
52. Ishigaki, T. et al. Enhanced visible-light photocatalytic activity of anatase-rutile mixed-phase nano-size powder given by high-temperature heat treatment. R. Soc. Open Sci. 7, 191539 (2020).
53. Hurum, D. C. et al. Probing reaction mechanisms in mixed phase TiO2 by EPR. J. Electron Spectros. Relat. Phenomena 150, 155–163 (2006).
54. Liu, M., Qiu, X., Hashimoto, K. & Miyaschi, M. Cu(ii) nanocluster-grafted, Nb-doped TiO2 as an efficient visible light-sensitive photocatalyst based on energy-level matching between surface and bulk states. J. Mater. Chem. A 2, 13571–13579 (2014).
55. Kurita, D., Ohta, S., Sugikura, K., Ohta, H. & Komoto, K. Carrier generation and transport properties of heavily Nb-doped anatase TiO2 epitaxial films at high temperatures. J. Appl. Phys. 100, 1–4 (2006).
56. Zhang, S. et al. Niobium doped TiO2: Intrinsic transparent metallic anatase versus highly resistive rutile phase. J. Appl. Phys. 102, 1–5 (2007).
57. Wolfenstein, J. & Allen, J. L. Electrical conductivity and charge compensation in Ta doped Li2TiO3. J. Power Sources 180, 582–585 (2008).
58. Kiwi, J., Suss, J. T. & Szapio, S. P. Spectra of niobium-doped TiO2 and impurities for water photo cleavage processes. Chem. Phys. Lett. 106, 135–138 (1984).
59. Vázquez, M. et al. A structural, thermogravimetric, magnetic, electron spin resonance, and optical reflectance study of the Nb2O5-TiO2 system. J. Solid State Chem. 77, 255–263 (1988).
60. Biedrzycki, J., Livraghi, S., Giamello, E., Agnoli, S. & Granonzi, G. Fluorine- and niobium-doped TiO2: Chemical and spectroscopic properties of polycrystalline n-type-doped anatase. J. Phys. Chem. C 118, 8462–8473 (2014).
61. Leytner, S. & Hupp, J. T. Evaluation of the energetics of electron trap states at the nanocrystalline titanium dioxide/aqueous solution interface via time-resolved photoacoustic spectroscopy. *Chem. Phys. Lett.* **330**, 231–236 (2000).
62. O’Regan, B., Graetzel, M. & Fitzmaurice, D. Optical electrochemistry. 2. Real-time spectroscopy of conduction band electrons in a metal oxide semiconductor electrode. *J. Phys. Chem.* **95**, 10525–10528 (1991).
63. Kavan, L., Grätzel, M., Gilbert, S. E., Klemenz, C. & Scheel, H. J. Electrochemical and photoelectrochemical investigation of single-crystal anatase. *J. Am. Chem. Soc.* **118**, 6716–6723 (1996).
64. Park, K. W. & Kolpak, A. M. Optimal methodology for explicit solvation prediction of band edges of transition metal oxide photocatalysts. *Commun. Chem.* **2**, 1–10 (2019).

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**Author contributions**

Study design: N.T., T.U., T.I. Experimental analyses: N.T., R.K. Data evaluation: N.T., R.K., T.I. All authors read and approved the final version. N.T. and T.I. are corresponding authors because they gave equal contribution.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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