Synthesis of a metal oxide with a room-temperature photoinduced phase transition

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Photoinduced phase-transition materials, such as chalcogenides, spin-crossover complexes, photochromic organic compounds and charge-transfer materials, are of interest because of their application to optical data storage. Here we report a photoresponsive metal–semiconductor phase transition at room temperature with a unique phase of \( \text{Ti}_3\text{O}_5 \), \( \lambda\text{-Ti}_3\text{O}_5 \), \( \lambda\text{-Ti}_3\text{O}_5 \) nanocrystals are made by the combination of reverse-micelle and sol–gel techniques. Thermodynamic analysis suggests that the photoinduced phase transition originates from a particular state of \( \lambda\text{-Ti}_3\text{O}_5 \) trapped at a thermodynamic local energy minimum. Light irradiation causes reversible switching between this trapped state \( \lambda\text{-Ti}_3\text{O}_5 \) and the other energy-minimum state \( (\beta\text{-Ti}_3\text{O}_5) \), both of which are persistent phases. This is the first demonstration of a photoresponsive phenomenon at room temperature in a metal oxide. \( \lambda\text{-Ti}_3\text{O}_5 \) satisfies the operation conditions required for a practical optical storage system (operational temperature, writing data by short wavelength light and the appropriate threshold laser power).

High-density optical memory devices based on blue-laser irradiation are now being developed. In such optical memory devices, phase-change materials, such as chalcogenides, are used as the rewritable recording material. Coupled with such optoelectronic applications, studies of photoinduced phase transitions were developed aggressively. To date, several types of photoinduced phase-transition phenomena have been reported: for example, a light-induced crystalline–amorphous transformation in a chalcogenide(a,b), a light-induced excited spin-state trapping in a spin–crossover complex(c–g), a light-induced structural transformation in a photochromic compound(h–i), a light-induced charge transfer in a donor–acceptor stacked molecule(j,k), a cyano bridged metal assembly(l–p) or a perovskite manganite(q,r). Herein we report a unique phase of titanium oxide, \( \lambda\text{-Ti}_3\text{O}_5 \). \( \lambda\text{-Ti}_3\text{O}_5 \) shows a reversible, photoinduced metal–semiconductor phase transition between \( \lambda\text{-Ti}_3\text{O}_5 \) and \( \beta\text{-Ti}_3\text{O}_5 \) at room temperature. This is the first observation of a metal oxide with a photoinduced phase transition at room temperature. In this paper we report the synthesis and crystal structure of \( \lambda\text{-Ti}_3\text{O}_5 \), the magnetic, electrical and optical properties and electronic structure of \( \lambda\text{-Ti}_3\text{O}_5 \), the photoresponsive phase transition at room temperature and a thermodynamic interpretation of the photoinduced phase transition.

Results and discussion

A unique phase of titanium oxide, \( \lambda\text{-Ti}_3\text{O}_5 \), was obtained in two morphological types by different synthetic methods: one type was a \( \lambda\text{-Ti}_3\text{O}_5 \) nanocrystal in a SiO\(_2\) matrix and the other a flake form of \( \lambda\text{-Ti}_3\text{O}_5 \). The former was obtained by a combination of reverse-micelle and sol–gel techniques (Fig. 1a and the Methods section). The transmission electron microscope (TEM) image of \( \lambda\text{-Ti}_3\text{O}_5 \)–SiO\(_2\) shows cubic-shaped Ti\(_3\)O\(_5\) nanocrystals with an average size of 21 ± 11 nm dispersed in a SiO\(_2\) matrix (Fig. 1b). Moreover, the X-ray diffraction (XRD) pattern indicates a crystal structure of \( C2/m \) (Fig. 2a,b), which does not correspond to any reported crystal structures of Ti\(_3\)O\(_5\) (\( \alpha\text{-}, \beta\text{-}, \gamma\text{-}, \delta\text{-} \) phases)(c–g). Details of the crystal structure of \( \lambda\text{-Ti}_3\text{O}_5 \) nanocrystals in SiO\(_2\) are reported in Supplementary Table S1. In contrast, the flake form of \( \lambda\text{-Ti}_3\text{O}_5 \) was prepared by calcining the anatase form of the TiO\(_2\) nanoparticles under hydrogen at 1,200 °C. The TEM image shows that the flake (2 ± 0.5 μm) was assembled from 25 ± 15 nm nanocrystals (Supplementary Fig. S1). The XRD pattern of the sample at room temperature corresponded to the aforementioned \( \lambda\text{-Ti}_3\text{O}_5 \) in SiO\(_2\), and the Rietveld analysis showed a monoclinic structure \( (C2/m) \) (Supplementary Figs S2 and S3). Variable-temperature XRD measurements demonstrated that, as the temperature increased, the diffraction peaks of \( \lambda\text{-Ti}_3\text{O}_5 \) continuously changed to \( \alpha\text{-Ti}_3\text{O}_5 \) peaks with a crystal structure of \( Cmcm \), for example (2 0 –3) and (2 0 3) of \( \lambda\text{-Ti}_3\text{O}_5 \rightarrow (0 2 3) \) of \( \alpha\text{-Ti}_3\text{O}_5 \) (Fig. 2c). Furthermore, heating the sample to 640 K and then cooling to 300 K caused \( \alpha\text{-Ti}_3\text{O}_5 \) to return to \( \lambda\text{-Ti}_3\text{O}_5 \). The details of synthesis and crystal structure of the flake form \( \lambda\text{-Ti}_3\text{O}_5 \) are reported in the Methods section, Supplementary Fig. S4 and Table S2. Differential scanning calorimetry (DSC) measurements did not exhibit a meaningful peak (Fig. 2d), which differs greatly from the first-order phase transition between \( \beta\text{-Ti}_3\text{O}_5 \) and \( \alpha\text{-Ti}_3\text{O}_5 \) in a conventional, large Ti\(_3\)O\(_5\) crystal(h–j). Hence, the phase transition between \( \lambda\text{-Ti}_3\text{O}_5 \) and \( \alpha\text{-Ti}_3\text{O}_5 \) is classified as a second-order phase transition.

Figure 3a shows the magnetic susceptibility (χ) versus temperature (T) curve of the flake form \( \lambda\text{-Ti}_3\text{O}_5 \) as well as the χ versus T curve of a conventional large crystal of Ti\(_3\)O\(_5\). \( \lambda\text{-Ti}_3\text{O}_5 \) has χ values around 2 × 10\(^{-4}\) e.m.u. per Ti atom throughout the entire measured temperature region, which suggests that \( \lambda\text{-Ti}_3\text{O}_5 \) is a Pauli paramagnet because of metallic conduction. Spin–orbital coupling on the Ti\(^{3+}\) ion can explain the gradual decrease below 150 K, but the rapid increase below 30 K is attributed to a small amount of Curie paramagnetism (about 0.1%), which may be caused by defects in the material. The \( \lambda\text{-Ti}_3\text{O}_5 \)–SiO\(_2\) sample exhibited the same type of χ versus T curve (Supplementary Fig. S5). The electric current versus voltage curve using atomic force microscopy in the contact mode had an electrical conductivity (σ) value of about 30 S cm\(^{-1}\), which indicates that \( \lambda\text{-Ti}_3\text{O}_5 \) is a near-metallic conductor. Additionally, both the ultraviolet–visible and infrared reflectance spectra indicate that \( \lambda\text{-Ti}_3\text{O}_5 \)
Figure 1 | Synthesis procedure for \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals in a SiO\(_2\) matrix. a, A combination of reverse-micelle and sol–gel techniques is used to synthesize the \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals in a SiO\(_2\) matrix. b, TEM image of \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals in a SiO\(_2\) matrix. The inset is an enlarged image that shows the lattice planes.

Figure 2 | Formation and crystal structure of \( \lambda \)-Ti\(_3\)O\(_5\). a, Powder XRD pattern of \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals in SiO\(_2\). Broad deviation of the baseline caused by amorphous SiO\(_2\) is eliminated. Red dots, black lines and blue lines are the observed patterns, calculated patterns and their differences, respectively, and green bars represent the calculated positions of the Bragg reflections of \( \lambda \)-Ti\(_3\)O\(_5\). b, Crystal structure for \( \lambda \)-Ti\(_3\)O\(_5\) (monoclinic \( C2/m \)). Red, light red, deep red and grey balls represent Ti(1), Ti(2), Ti(3) and O atoms, respectively, and TiO\(_6\) units are drawn as polyhedra. The central square without polyhedra represents the unit cell. c, Peak position versus temperature graph of the XRD pattern in the angle range 32.0°–33.0° for the flake form \( \lambda \)-Ti\(_3\)O\(_5\). d, DSC charts of the flake form \( \lambda \)-Ti\(_3\)O\(_5\) (red line) and conventional crystal Ti\(_3\)O\(_5\) (dashed black line) with increasing temperature.
The bands near the Fermi level were consistent with Fig. 3ci. The energy between these two bands (that is, the states were split by coupling with neighbouring Ti ions. In ab initio first principles using the Vienna simulation package, the band structures of Ti(3) provided an empty state for a charge-localized system of Ti(3) and its band was located at –0.60 eV. The conduction band consisted mainly of an empty orbital on Ti(3) at +0.71 eV (Fig. 3ci). The energy between these two bands (that is, the bandgap) was estimated to be 0.13 eV, consistent with the 0.14 eV observed in the optical reflection spectrum. In λ-Ti3O5, slipped π-stacking (like a zigzag chain) between the dxy orbital on Ti(2) and the dxy orbital on Ti(3) formed. The band was located at the position of the Fermi level (EF), and resulted in λ-Ti3O5 becoming a metallic conductor. As for the Ti(1)–Ti(1) dimer, its band was located at –1.35 eV in β-Ti3O5 and at –0.58 eV in λ-Ti3O5. The details of the band structures and density of states (DOS) plots are reported in the Methods section and Supplementary Figs S6 and S7.

When the flake form λ-Ti3O5 was irradiated with 532 nm nanosecond laser light (6 ns, five shots, 1.5 × 10−3 mJ μm−2 pulse−1) at room temperature, the irradiated area changed from black to brown (Fig. 4a,b, Supplementary Movie S1). Subsequent irradiation with 410 nm laser light (8 × 10−3 mW μm−2) caused the irradiated spots to return to black (Fig. 4c,d). Alternatively, repeated irradiation at 532 nm and 410 nm induced these colour changes (Fig. 4e–i). The XRD pattern showed that the brown area was the β-phase (monoclinic structure C2/m). Hence, the change from black to brown was caused by the transition from λ-Ti3O5 to β-Ti3O5, and the converse was caused by the transition from the β-Ti3O5 to λ-Ti3O5. Furthermore, irradiation with different nanosecond-pulsed laser lights, 355 or 1,064 nm, caused a similar phase transition.

Figure 3 | Magnetic and optical properties, and electronic structures of λ-Ti3O5. a, χ (× 10−4 emu per Ti atom) versus T graph of the flake form λ-Ti3O5 (red line) and single-crystal β-Ti3O5 (black line) under an external field of 0.5 T. b, Optical absorption spectra of the flake form λ-Ti3O5 (red line) and β-Ti3O5 (black line) in the ultraviolet–visible and infrared regions. K.M. = Kubelka–Munk transformation. c, Band structures of β-Ti3O5 and λ-Ti3O5 using VASP, showing the DOS around the Fermi level (EF) for β-Ti3O5 (i) and λ-Ti3O5 (ii). Below these are the electron-density maps around the Fermi level.

possesses metallic absorption over ultraviolet and infrared wavelengths (Fig. 3b). In contrast, the impedance measurement and reflectance spectra suggest that β-Ti3O5 is a semiconductor with σ = 3 × 10−2 S cm−1 and a band gap of 0.14 eV.

The empirical relationship between the bond length and valence states35 gives estimated valence states for Ti(1), Ti(2) and Ti(3) in λ-Ti3O5 of +3.37, +3.20 and +3.32, respectively, which are close to the maximum Ti3+ orbital on Ti ions. The electronic structure of λ-Ti3O5 is a semiconductor with a band gap of 0.14 eV. The electronic structure of β-Ti3O5 and λ-Ti3O5 are close to Ti3+ at –1.35 eV in β-Ti3O5 and at –0.58 eV in λ-Ti3O5. The details of the band structures and density of states (DOS) plots are reported in the Methods section and Supplementary Figs S6 and S7.
Figure 4 | Reversible photoinduced phase transition in $\lambda$-Ti$_3$O$_5$. a–i, Photographs of $\lambda$-Ti$_3$O$_5$ at irradiations of 532 nm and 410 nm laser lights. When the flake form $\lambda$-Ti$_3$O$_5$ was irradiated with 532 nm nanosecond-pulsed laser light at room temperature, the irradiated area changed from black (a) to brown (b). Subsequently, on irradiating with 410 nm laser light the spots returned from brown to black (c,d). Photoinduced colour changes were observed repeatedly by alternating 532 nm and 410 nm laser-light irradiation (e–i).

Figure 5 | Phase transition between $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ induced by one-shot laser pulses. a, A mixed sample of $\lambda$- and $\beta$-phases ($\lambda/\beta = 2/1$) was irradiated with 532 nm pulsed laser light at various laser-power densities. b, The change in amount of $\lambda$-Ti$_3$O$_5$ from the ratio 2/1, $\Delta(\lambda$-Ti$_3$O$_5$), versus laser-power density. Clear thresholds for laser-power densities were observed. c, Difference XRD patterns of the alternating phase transition between $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ by irradiation of pulsed-laser (532 nm, 6 ns) shots at room temperature.
To investigate the threshold value of nanosecond laser power, a mixed sample of \( \lambda \)-Ti\(_3\)O\(_5\) and \( \beta \)-Ti\(_3\)O\(_5\) (ratio of 2/1) was irradiated with 532 nm pulsed laser light (one shot) at various laser-power densities. As shown in Fig. 5a,b, the threshold laser-power of \( \beta \)-Ti\(_3\)O\(_5\) to \( \lambda \)-Ti\(_3\)O\(_5\) was \( 2.7 \times 10^{-6} \) mJ m\(^{-2}\) and, conversely, that of \( \lambda \)-Ti\(_3\)O\(_5\) to \( \beta \)-Ti\(_3\)O\(_5\) was above \( 6.9 \times 10^{-6} \) mJ m\(^{-2}\). The existence of clear thresholds with the laser-power density indicates cooperative interaction between photoexcited sites and neighbouring sites. Such a threshold is important for long-lasting memory in recording storage media. The observed threshold values of the laser-power densities used are the same as those used on digital versatile discs\(^{35,36}\). Based on this knowledge, using XRD we demonstrated alternating switching between \( \lambda \)-Ti\(_3\)O\(_5\) and \( \beta \)-Ti\(_3\)O\(_5\) induced by one-shot, nanosecond-pulsed, laser-light irradiation (532 nm, 6 ns, \( 7 \times 10^{-5} \) mJ m\(^{-2}\) pulse\(^{-1}\)) (Fig. 5c).

To understand the mechanism of the observed photoinduced phase transition, the thermodynamic energy of Ti\(_3\)O\(_5\) was calculated using the Slichter and Drickamer mean-field model (see Methods section\(^{32}\)). The first-order phase transition between \( \beta \)-Ti\(_3\)O\(_5\) and \( \alpha \)-Ti\(_3\)O\(_5\) on a conventional large-crystal Ti\(_3\)O\(_5\) was regarded as a metal–semiconductor phase transition between charge-localized (\( Ti^{3+} \rightarrow Ti^{4+} \)) and charge-delocalized (\( Ti^{3+} / Ti^{4+} \)) systems. Also, the metal–semiconductor phase transition between \( \beta \)-Ti\(_3\)O\(_5\) and \( \alpha \)-Ti\(_3\)O\(_5\) for conventional Ti\(_3\)O\(_5\) was reproduced, as shown in Supplementary Fig. S8. In contrast, to analyse the phase transition between \( \lambda \)-Ti\(_3\)O\(_5\) and \( \alpha \)-Ti\(_3\)O\(_5\), the thermodynamic parameters of the phase transition in a Ti\(_3\)O\(_5\) nanocrystal are necessary, but unknown. In this work, \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals showed a pressure-induced phase transition from \( \lambda \)-Ti\(_3\)O\(_5\) to \( \beta \)-Ti\(_3\)O\(_5\). That this \( \beta \)-Ti\(_3\)O\(_5\) nanocrystal was produced by an external pressure indicates that the transition enthalpy (\( \Delta H \)) from \( \beta \)-Ti\(_3\)O\(_5\) to \( \alpha \)-Ti\(_3\)O\(_5\) is small and caused by the surface energy of the nanocrystal form. The details of the pressure-induced phase transition and nanoscopic effect are reported in the Methods section and in Supplementary Figs S9 and S10. The observed \( \Delta H \) (4.8 kJ mol\(^{-1}\)) and the transition entropy (\( \Delta S \)) (10.4 J K\(^{-1}\)mol\(^{-1}\)) values were used, assuming an interaction parameter (\( \gamma \)) of 9.0 kJ mol\(^{-1}\), to calculate the Gibbs free energy (\( G \)) versus \( x \) plots for Ti\(_3\)O\(_5\) nanocrystals given by the Slichter and Drickamer model (Supplementary Fig. S11). Energy barriers exist between the charge-localized and charge-delocalized systems throughout the temperature range. Therefore, as the temperature decreases from the high calcination temperature, the system maintains a charge-delocalized state (Fig. 6, red line). This calculation supports \( \lambda \)-Ti\(_3\)O\(_5\) as a metal conductor through both charge delocalization and paramagnetism, and the phase transition between \( \lambda \)-Ti\(_3\)O\(_5\) and \( \alpha \)-Ti\(_3\)O\(_5\) is classified as a second-order phase transition. Furthermore, \( \beta \)-Ti\(_3\)O\(_5\) is a true stable phase below 460 K (Fig. 6, dark blue line).

Thermodynamic analysis of \( \lambda \)-Ti\(_3\)O\(_5\) suggests that the photoinduced metal–semiconductor phase transition results from the phase transition from \( \lambda \)-Ti\(_3\)O\(_5\), a metastable phase thermodynamically trapped at a local energy-minimum state, to \( \beta \)-Ti\(_3\)O\(_5\), a truly stable phase, by irradiation (Fig. 6, top inset). The metallic absorption allows \( \lambda \)-Ti\(_3\)O\(_5\) to absorb light effectively over a wide wavelength range from ultraviolet to near-infrared, so this metal–semiconductor phase transition was observed by irradiating 353, 332, and 1,064 nm nanosecond-pulsed laser light. The reverse photoinduced phase transition from \( \beta \)-Ti\(_3\)O\(_5\) to \( \lambda \)-Ti\(_3\)O\(_5\) was induced by excitation from the valence band to the conduction band on \( \beta \)-Ti\(_3\)O\(_5\), and then the excited state changed directly to \( \lambda \)-Ti\(_3\)O\(_5\) in the pulsed laser irradiation (Fig. 6, middle inset), or photothermally to \( \lambda \)-Ti\(_3\)O\(_5\) through \( \alpha \)-Ti\(_3\)O\(_5\) (that is, \( \beta \)-Ti\(_3\)O\(_5\) \( \rightarrow \) \( \alpha \)-Ti\(_3\)O\(_5\) \( \rightarrow \) \( \lambda \)-Ti\(_3\)O\(_5\)) in continuous-wave laser-light irradiation (Fig. 6, bottom inset).

**Conclusion**

In this paper we report a photoreversible metal–semiconductor phase transition at room temperature with a new phase of Ti\(_3\)O\(_5\). This phenomenon originates from a particular state of \( \lambda \)-Ti\(_3\)O\(_5\) trapped at thermodynamic local energy minimum. Light irradiation causes a phase transformation from this trapped state (\( \lambda \)-Ti\(_3\)O\(_5\)) into another energy-minimum state (\( \beta \)-Ti\(_3\)O\(_5\)). This is the first demonstration of a photoreversible phenomenon at room temperature in a metal oxide. \( \lambda \)-Ti\(_3\)O\(_5\) satisfies the operation conditions (an operational temperature around room temperature, writing data by short wavelength, near ultraviolet light for high memory density and the appropriate threshold laser power to maintain long-term memory). Moreover, a \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystal is a candidate for optical storage using near-field light. Its memory density is expected to achieve 1 terabit inch\(^{-2}\) (Supplementary Fig. S12). Furthermore, Ti is environmentally benign, and the elements used to construct \( \lambda \)-Ti\(_3\)O\(_5\) are very economical. Hence, \( \lambda \)-Ti\(_3\)O\(_5\) is a high-performance, photoinduced phase-transition material with harmless, sustainable and economic features suitable for the next generation of optical storage media with super-high density.

**Methods**

**Synthesis of \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals in SiO\(_2\) matrix and isolation of \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals.** Microemulsion systems were formed by cetyltrimethylammonium bromide (CTAB) and 1-butanol in \( \beta \)-octane with a H\(_2\)O/CTAB molar ratio of 17/1. The microemulsion, which contained an aqueous solution of TiCl\(_4\) (0.50 mol dm\(^{-3}\)), was mixed (rapid stirring) with another microemulsion that contained 11 mol dm\(^{-3}\) NH\(_3\) aqueous solution. Si(C\(_2\)H\(_5\)O\(_4\))\(_2\) (22 mmol) was injected into the white solution and produced a precipitate composed of Ti(OH)\(_4\). The TEM image showed spherical Ti(OH)\(_4\) particles (5 nm) covered by SiO\(_2\). The precipitate was collected by centrifugation, washed with CH\(_2\)Cl\(_2\) and CH\(_3\)OH, and then heated at 1,200 °C for five hours in a hydrogen flow of 0.3 dm\(^3\) min\(^{-1}\) (Fig. 1). Elemental analysis confirmed the ratio of Ti\(_3\)O\(_5\)/SiO\(_2\), as 13/87 weight per cent. X-ray fluorescence (XRF) analysis confirmed that an impurity element did not exist (<0.1%). The isolated \( \lambda \)-Ti\(_3\)O\(_5\) nanocrystals were obtained by etching the SiO\(_2\) matrix with a KOH ethanol solution (1 mol dm\(^{-3}\)) for 24 hours at 60 °C (Supplementary Fig. S12a).
Synthesis of the neat-flake form of $\lambda$-Ti$_3$O$_5$ assembled by nanocrystals. The anatase form of the TiO$_2$ nanoparticles (7 nm) was calcinating under hydrogen with a flow speed of 0.3 dm$^3$ min$^{-1}$ at 1,200 °C for two hours, which produced the flake form TiO$_2$ (Supplementary Fig. S1). XRF analysis confirmed that an impurity element did not exist (<0.1%). Inductively-coupled plasma mass spectrometry (ICP-MS) indicated that the formula was Ti$_{0.9965}$O$_{5.0006}$ (calculated Ti, 64.2%; found Ti, 64.2%).

Physical measurements. Elemental analyses on the prepared samples were carried out with ICP-MS (Agilent Technologies, HP 4500) and XRF spectroscopy (SII-SEA2120L). The TEM measurements were conducted using a JEOL JEM-2000EXII and JEM-4000FXII. The morphologies of the compounds were measured with a JEOL JSM-7000F scanning electron microscope (SEM) with a 20 kV accelerating voltage. The XRD measurements were conducted on a Rigaku Ultima IV and RINT-RAPID-CMF and Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). Rietveld analyses were performed using the RIETAN-FP program. Magnetic properties were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS 7). The ultraviolet–visible reflectance spectra were measured with a Shimazu UV–3100 spectrometer. The infrared spectra were recorded on a JASCO FT-IR-4100 and IRT-3000 spectrometer. DSC was performed on a Rigaku DSC 8230. The electrical conductivity was measured in contact mode using an SII SPI-3000/SPA300HV atomic force microscope.

First-principal calculation using VASP. Density functional method calculations based on a plane wave were carried out for $\beta$-Ti$_3$O$_5$ and $\lambda$-Ti$_3$O$_5$ by the ab initio total energy method. Molecular dynamics program VASP was used to study the wave functions and potentials of the core orbitals were replaced by the projector-augmented wave of Blochl, and the exchange-correlation energy was calculated by the generalized gradient approximation. The DOS and band structures were calculated with an energy cut-off of 520 eV. In our calculations, we use the Coulomb interaction parameter ($U$) and exchange coupling ($J$) as $U = J = 5.0$ eV.

Slichter and Drickamer mean-field model. The Gibbs free energy ($G$) of the phase transition is expressed as $G = \Delta H + \chi(1 - x) + TR\ln(x + (1 - x)\ln(1 - x)) - \Delta G$, by taking $G$ of the charge-localized system as the origin of the energies, where $x$ is the fraction of the charge-delocalized unit (Ti$^{3+*}$)$_2$O$_5$, $\Delta H$ is the transition enthalpy, $\Delta S$ is the transition entropy, $R$ is the gas constant and $\gamma$ is an interaction parameter.

Pressure-induced phase transition from $\lambda$-Ti$_3$O$_5$ to $\beta$-Ti$_3$O$_5$. An external pressure applied to $\lambda$-Ti$_3$O$_5$ induced a phase transition. When the flake form $\lambda$-Ti$_3$O$_5$ was pressed with an external pressure of 0.3 GPa, 25% of $\lambda$-Ti$_3$O$_5$ was converted into $\beta$-Ti$_3$O$_5$ (Supplementary Fig. S9), and this sample exhibited a $\Delta H$ value from the $\beta$- to $\alpha$-phase of 4.8 kJ mol$^{-1}$ in the DSC measurement, which is smaller than that of a conventional large-crystal $\beta$-Ti$_3$O$_5$ (Supplementary Fig. S10).

Nanosopic effect on Ti$_3$O$_5$ phase. For a nanoparticle, the contribution of the charge or interface energy perturbs the free energy ($G = H - TS$), and $G = G_0 + \langle 6V_r/G\rangle$, where $G_0$ is the bulk free energy, $V_r$ is the surface (or interface) free energy, $V_m$ is the molar volume and $n$ is the diameter of the nanoparticle. As $\lambda$-Ti$_3$O$_5$ in the low temperature phase, $G_0(\alpha) > G_0(\beta)$ in the Ti$_3$O$_5$ system. If $G_0$ satisfies the condition $G_0(\alpha) > G_0(\beta)$, the value of $G(\beta) - G(\alpha)$ shrinks. This nanoscopic effect may contribute to the decreased $\Delta H$ value in the phase transition from $\beta$- to $\alpha$-phases in a Ti$_3$O$_5$ nanocrystal. Hence, the decrease in the $\Delta H$ value in the aforementioned pressure-induced phase-transition experiment is explained by this nanoscopic effect. Such an effect was observed in Al$_2$O$_3$ (ref. 39) and Fe$_2$O$_3$ (ref. 40). A similar nanoscopic effect was observed in superionic AgI (ref. 41).

Received 30 November 2009; accepted 13 April 2010; published online 23 May 2010

References
40. Ohkoshi, S., Sakurai, S., Jin, J. & Hashimoto, K. The addition effects of alkaline earth ions in the chemical synthesis of $\gamma$-Fe$_2$O$_3$ nanocrystals that exhibit a huge coercive field. J. Appl. Phys. 97, 10K312 (2005).


Acknowledgements
This work was performed under the management of the Project to Create Photocatalyst Industry for Recycling-oriented Society supported by the New Energy and Industrial Technology Development Organization. We are grateful to T. Nuida and K. Takeda for drawing the colour figures, K. Tomono for measuring the infrared spectra, Y. Kakegawa, H. Tsunakawa and M. Adachi for collecting TEM images, S. Ohtsuka and T. Monoyama for collecting SEM images, and T. Takasaki, Y. Namatame, M. Saigo and M. Yasaka (Rigaku Corporation) for measuring the XRD patterns. We are thankful for a Grant-in-Aid for the Global COE Program, ‘Chemistry Innovation through Cooperation of Science and Engineering’ from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and the Center for Nano Lithography & Analysis, The University of Tokyo, supported by MEXT, Japan.

Author contributions
S.O. designed and coordinated this study and contributed to all measurements and calculations, and wrote the paper. Y.T. carried out synthesis, DSC and first-principle band calculation. T.M. carried out synthesis. A.N. performed XRD measurements, Rietveld analysis and ICP-MS. F.H. carried out synthesis and TEM, SEM and SQUID measurements. K.H. contributed to the discussion. H.T. carried out synthesis and thermodynamic analysis, and carried out the photoirradiation and pressure-effect experiments. All authors commented on the manuscript.

Additional information
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