Metastability of anatase: size dependent and irreversible anatase-rutile phase transition in atomic-level precise titania

Norifusa Satoh¹, Toshio Nakashima² & Kimihisa Yamamoto²

¹Photovoltaic Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 Japan, ²Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503 Japan.

Since crystal phase dominantly affects the properties of nanocrystals, phase control is important for the applications. To demonstrate the size dependence in anatase-rutile phase transition of titania, we used quantum-size titania prepared from the restricted number of titanium ions within dendrimer templates for size precision purposes and optical wave guide spectroscopy for the detection. Contrary to some theoretical calculations, the observed irreversibility in the transition indicates the metastability of anatase; thermodynamics cannot explain the formation of metastable states. Therefore, we take into account the kinetic control polymerization of TiO₆ octahedral units to explain how the crystal phase of the crystal-nucleus-size titania is dependent on which coordination sites, cis- or trans-, react in the TiO₆ octahedra, suggesting possibilities for the synthetic phase control of nanocrystals. In short, the dendrimer templates give access to crystal nucleation chemistry. The paper will also contribute to the creation of artificial metastable nanostructures with atomic-level precision.

The size dependence of nanocrystals during a solid-solid phase transition has attracted much attention¹⁻²⁻¹, because phase control is a key step to improve functionalities in photovoltaics³⁻⁴, ferroelectricity⁵, magnetics⁶, and oxygen permeability⁷ for various applications, such as solar cells, memories, and fuel cells. In terms of the melting point of nanocrystals, the thermal behaviours of nanocrystals have an inverse size dependence in the phase transition temperature due to the direct correlation to the volume and surface ratio⁸⁻¹３. However, irreversible solid-solid phase transitions from metastable states to the stable states cannot define any specific transition temperature based on thermodynamics due to the absence of any phase equilibrium. Therefore, the discussions on melting point can primarily apply to reversible solid-solid phase transitions at the equilibrium state, but not for irreversible transitions. Similarly, it is also not possible to define any phase diagram for irreversible phase transitions. During the irreversible transitions, however, the atoms obtain freedom in motion from the metastable phase structure and then irreversibly transform into the most stable phase structure. Based on the similarity between melting and the initiation of the transition process, we presume that the transition initiation temperature for the irreversible process is the temperature at which the atoms start moving freely toward the thermal stable states as the phase transition through the melting-like process. For the above-mentioned conditions, we can hypothesize the transition initiation temperature depending on size in a similar manner to melting as follows:

\[ T(r) = T_{\text{bulk}} - \frac{A}{r} \]  

where \( r \) is radius of nanocrystals, \( T(r) \) is size-dependent transition initiation temperature, \( T_{\text{bulk}} \) is the transition initiation temperature in bulk, and \( A \) is a constant. The transition initiation temperature for irreversible solid-solid phase transitions also decreases inversely with the size.

Although nano-size titania (TiO₂), an attractive material for photocatalysts, dye-sensitized solar cells (DSCs), and organic thin film solar cells¹⁴⁻¹⁶, has shown irreversible anatase-rutile phase transition at low temperature, a clear size dependence has not yet been observed in the transition initiation temperature. The phase control of anatase or rutile is also important in these performances due to the different band diagram and surface chemical activities. Thus, many researches have attempted to reveal the influences on the thermal phase transition from anatase to rutile caused by impurities¹⁷, heat conditions¹⁸⁻¹⁹, and the sample preparation conditions²⁰. Approximately 10 nm TiO₂ nanoparticles prepared by sol-gel method gradually transition from anatase into rutile during 550–650 °C annealing²¹. The transformation of TiO₂ particles around 200 nm in diameter occurs in
the range of 750–850°C. Curiously, 8–21 nm particles has also
given a constant transition initiation temperature at 520°C. To
the contrary, 45 nm particles transition at relatively high temper-
ature 900–1200°C when prepared by metalorganic chemical vapor
deposition (MOCVD) at 700°C. Generally, reactions at high tem-
peratures tend to consume unreacted precursors and accelerate crys-
tallization from the amorphous phase. Thus, one of the possible
reasons for this mismatch would be that sol-gel samples may contain
the tiny particles or unreacted precursors. Based on equation (1),
since small particles have a low transition initiation temperature,
we may have misconceived the transition of the smallest-size con-
tamination at the low temperature as the transition initiation for
the sample during the heating measurement; and besides, it is difficult
to detect small-size contaminants. X-ray diffraction (XRD) gives strong
evidence for existence of crystalline materials with sharp reflection
peaks but not for absence of amorphous and small-size contaminants
that show broad and unclear peaks. Similarly, these small contain-
mina gives undetectable foggy images in transmission electron
microscopy (TEM) when we focus on the mean-size particles, espe-
cially for light-element materials like TiO₂. The undetectable con-
taminants can mislead the discussions for the size dependence based
on the mean size. On the other hand, some theoretical simulations
predict that the anatase phase is conversely more stable than the
rutile phase for various crystal shapes and surface passivation to discuss
transition initiation temperature using a multi-data set instead of the conventional ana-
lyses incompetent in the crystal-nucleus-scale.

In this paper, we identify whether the irreversible anatase-rutile phase transition exists in the crystal-
nucleus scale or not by the size dependence in transition initiation
temperature using a multi-data set instead of the conventional anal-
asies incompetent in the crystal-nucleus-scale.

Results
The assembling process of Ti(acac)Cl₃ into TPM-DPA is confirmed
by the previously established procedures (Supplementary Fig. S2)²⁹,₃₃,₃₇–₃₉, particularly the observation of isosbestic points in UV-
vis absorption spectra: observing iso-points indicating isosbestic points is a strong tool to distinguish stepwise processes in complex
systems. The isosbestic points observed in UV-vis absorption spec-
tra indicate the radial stepwise coordination of Ti(acac)Cl₃ within
TPM-DPA until an addition of a stoichiometric amount (per imine
site) of Ti(acac)Cl₃. Since Ti(acac)Cl₃ has an absorption around 300–
400 nm at which DPA derivatives show the isosbestic points during
the coordination, we can subtract the absorption for the added
Ti(acac)Cl₃ from all figures to clarify the stoichiometry with the
isosbestic points. After this subtraction, the isosbestic points appear

Figure 1 | Schematic protocol for preparation and thermal treatment of Q-size TiO₂. To prevent molecular aggregation, we control the cast amount of the dendrimer templates assembling Ti(acac)Cl₃ based on the molecular size and spread the solution on substrates. Thus, the size of the dendrimer templates determines the maximum dot density, ca. 10¹³ cm⁻². The chemical conversions using hydrolysis and thermolysis provide rutile and anatase

| Chemical conversion | Thermal treatment |

| 2r | T(r) |

$$E(r) = E_{\text{bulk}} + \frac{\hbar^2}{2m} \left( \frac{1}{r^2} \right) - \frac{1.8e^2}{er}$$
to identify four distinct transitions: 363 nm for 0–4 equiv.; 358 nm for 5–12 equiv.; 354 nm for 14–28 equiv.; and 351 nm for 32–60 equiv., indicating that the coordination proceeds in a stepwise manner. The existence of an isosbestic point reveals the quantitative equiv., indicating that the coordination proceeds in a stepwise manner. The number of distinct isosbestic points indicates the successive four different coordination processes upon the Ti(acac)Cl₃ addition. The number of added equivalents of Ti(acac)Cl₃ at each transition agrees with that of the binding sites present in the different layers programmed in TPM-DPA. These results are consistent with those in the case of titration of Ti(acac)Cl₃ into DPA₂⁹. The titration results indicate that the coordination also proceeds in a stepwise fashion from the core to the terminal imines of TPM-DPA.

Figure 2 shows a TEM image of hydrolysed 60TiO₂ and Table 1 summarizes the other size characteristic data for 60TiO₂. The diameter of the particle observed in TEM is 1.97 ± 0.15 (s.d., n = 100) nm, which agrees with the modelling sizes cleaved from the bulk crystal structures (Supplementary Fig. S3). The AFM images of the hydrolysed and thermostabilised 60TiO₂ reveal that the chemical conversion process does not affect the heights (Supplementary Fig. S4). As observed in 14 and 30TiO₂, E(r) estimated from the Tauc plot of OWG spectra depends on the chemical conversion process (Supplementary Fig. S5). The experimental E(r) of hydrolysed and thermostabilised 60TiO₂ corresponds with E(r) calculated using equation (2) for the rutile and anatase parameters, respectively (Supplementary Fig. S6). These results indicate that the TPM-DPA serves as a template for precise size control of size of 60TiO₂ and that rutile phase as well as anatase phase forms in nano scale less than 2 nm.

Table 1 | Characteristics of 60TiO₂

| Modelling (nm) | Hydrolysis | Thermostabilysis |
|----------------|------------|------------------|
| AFM (height, nm) | 1.31 ± 0.21 | 1.38 ± 0.17 |
| Eₗ (eV) | 3.24 | 3.34 |
| 2r (nm) | 1.84 | 1.87 |

*Assuming the spherical growth of the bulk crystal structure of the rutile and anatase forms (Supplementary Fig. S3).
*AFM images are shown in Supplementary Fig. S4. Error bar denotes ± s.d. (n = 30).
*Estimated from the Tauc plots of the OWG spectra (Supplementary Fig. S5).
*Calculated from Eₗ using equation (2).

Discussion

These results support the hypothesis that the irreversible phase transition occurs after the melting-like process of the anatase structure. Since Q-size TiO₂ binds with the substrate strongly enough to resist a mechanical wipe with methanol, the solid Q-size TiO₂ is likely to grow in size with the melting-like process for diffusion on the substrate during the thermal treatment at T(r). Considering the cast amount of the Ti-assembling dendrimer templates and both sizes of the templates as well as formed Q-size TiO₂, the diffusion distances of Q-size TiO₂ are estimated to be ca. 1 nm, a reasonable distance for the diffusion during 1-hr thermal treatment based on the diffusion constant⁴¹. Furthermore, the transition initiation temperature reveal that E(r) sharply drop within 50°C at size dependent temperature. The experimental system figures that 14, 30 and 60TiO₂ grow from 1.3, 1.6, and 2.0 nm to 2.8, 3.6, and 4.9 nm after the anatase-rutile phase transitions at 600, 650, and 750°C, respectively (Fig. 3). All observed E(r) is less than 3.2 eV, which is an evidence of the irreversible phase transition from anatase to rutile. According to the cleaved models for these size particles, the sizes estimated from the dropped E(r) agree with sizes after three of each dot merges. Since the OWG spectra are observed after cooling to room temperature, the observations reveal that the rutile phase irreversibly occurs without returning to the anatase phase even though the size of the grown particles is less than 5 nm.

Figure 3 | Thermal bandgap shift of 14, 30, and 60TiO₂ observed in OWG spectra. Since equation (2) correlates the size and bandgap of anatase and rutile, the OWG spectroscopy reveals that the phase transit from anatase to rutile irreversibly, size dependently, and accompanied with the size growth through the melting-like process.
temperature decreases with $1/r$, as predicted by equation (1) (Fig. 4). The intercept, $T_{\text{bulk}}$, is 990 °C, which is comparable to $T_{\text{bulk}}$ reported for pure bulk TiO$_2$, ca. 1000 °C$^{16,19}$. Additionally, the size dependence agrees with the plot for the smallest particles in the MOCVD sample; the transformation initiation temperature for the MOCVD sample corresponds to the transformation initiation of the smallest particles in the sample. These strong agreements in the intercept and slope support that the observed size dependence would correlate with the physical parameters for the thermal phase transition from anatase to rutile through the melting-like process.

Contrary to the theoretical predictions of the phase stability based on thermodynamics, the irreversible thermal phase transition gives the rutile phase less than 5 nm through the melting-like process. As equation (1) indicates that large-size dot has higher transition initiation temperature, the grown dots cannot maintain the melting-like state and then result in solidification. As mentioned above, the observation of $E(r)$ less than 3.2 eV after the phase transition and the size dependence of $T(r)$ corresponding to $T_{\text{bulk}}$ and $T(r)$ for the MOCVD sample indicates that the rutile phase irreversibly forms from the anatase phase during the solidification. The thermal stability observed in $E(r)$ after the phase transition also agrees with the formation of rutile phase. Since the melting temperature of rutile phase is ca. 1840 °C and remarkably higher than the phase transition temperature of anatase in bulk, it is difficult to observe the further size growth caused by melting of the rutile phase in the thermal range for this experimental setup. Moreover, the anatase-rutile transformation is also confirmed by the reasonable shift in binding energy for Ti2p observed with X-ray photoelectron spectroscopy (XPS), which is a strong tool to identify Q-size TiO$_2$ (Supplementary Fig. S7)$^{29}$. The rutile formation suggests that we cannot discuss the phase stability for the irreversible transitions from the metastable anatase phase to the thermal stable rutile phase based on the thermodynamic simulations of the nano structure, surface stabilization, or phase diagram. If thermodynamic energy were the only factor to determine the stability of states, no metastable states would exist in the world.

Metastable states kinetically develop in the crystal growth reactions without reaching the stable state at each reaction step when the chemical bonds are too strong to free from the metastable states to the stable states. From this perspective, the phase of TiO$_2$ depends on which of the phases grows faster during polymerization of TiO$_6$ octahedral units as the crystal nucleation (Fig. 5). Some have already reported that anions and solvents affect the phase and shape of TiO$_2$ nanoparticles obtained from crystal growth in solution due to the adsorption on reaction sites to inhibit growth of certain crystal structures or crystal faces$^{42-45}$. As the first step of the crystal growth, tiny crystal nuclei for each crystal structure will form depending on the environmental factors. The difference in the crystal structure originates from order of TiO$_6$ octahedral units; zigzag packing for anatase and linear packing for rutile. The zigzag packing uses only the cis-coordination sites of the octahedra for the crystal growth, but the linear packing requires the trans-coordination sites bridging two octahedra too. Although the linear packing results in the thermal stable structure due to the closest packing of TiO$_6$ octahedral units, the bridging structure is unstable under the kinetic control condition. Once the metastable anatase forms, it cannot transform to rutile without melting-like process at $T(r)$ because Ti-O bonds have strong binding energy as an ionic covalent bond.

The kinetic and thermodynamic control nucleation model also explains the fact that the crystal phase of Q-size TiO$_2$ depends on the different chemical conversion processes, simply because we can consider Q-size TiO$_2$ as the crystal-nucleus-size TiO$_2$. In the other words, since the number of titanium ions in the dendrimer templates inhibits the further crystal growth after the formation of the crystal-nucleus-size TiO$_2$ with size precision, the dendrimer templates allow us to study the crystal nucleation process. These results are the first evidence that the crystal nuclei have the phase difference$^{29}$, although it has been believed that the difference would diverge crystal phase in nanocrystals because the crystal growth reactions continuously occur on the surfaces of the crystal nuclei. Considering that the ionic covalent bond maintains the metastable structure in nano scale, we can also conclude that the atomic-level precision of quantum-size TiO$_2$ would originate from the strong binding energy of Ti-O ionic covalent bonds. The nucleation model explains how the phase difference forms; still, it is unclear how the difference in the chemical conversion processes accelerates which of the kinetic or thermodynamic control nucleation. As the future works, although the importance of kinetics in nanocrystal growth has been discussed for the size distribution and shape control$^{46-49}$, the simulation and correlating experiments to understand the factors for kinetic and thermodynamic control nucleation will be requirement to control the phase formation of nanocrystals, because of the complexity. The nucleation reactions are a complex system to give different crystal phases based on difference in the first reaction setup through multiple interactions$^{8}$; for example, in a chemical system to synthesize nano-size TiO$_2$, the

---

**Figure 4 | Size dependence in the transition initiation temperature from anatase to rutile.** Error bar for ref. 20 denotes the size distribution observed in the TEM image. The regression line gives $T_{\text{bulk}} = 990$ and $A = 276$. The coefficient of determination is 99%. The obtained $T_{\text{bulk}}$ strongly agrees with the reported $T_{\text{bulk}}$. 

---
nucleation correlates with strength in dehydration defined by the reaction condition and with multiple interactions between TiO₆ octahedral units, ligands of Ti precursors, anions, solvents, and/or additives.

In conclusion, we have demonstrated the size dependence of the irreversible anatase-rutile phase transition in TiO₂ using the dendrimer templates for the atomic-level size control of Q-size TiO₂ and OWG spectroscopy for the detection sensitive to the crystal-nucleus-scale changes. As a result of the combination with OWG spectroscopy, the dendrimer templates give access to crystal nucleation chemistry. The sol-gel samples contain the unreacted precursors and small-size contaminants, which cannot be detected with the conventional analyses, such as XRD and TEM. These obstacles had blinded us to the size dependent phase transition and misdirected the theoretical model to discuss the phase stability. The size dependence observed in the transition initiation temperature and rutile phase formed with the size growth supports the hypothesis that the anatase phase irreversibly transits to the rutile phase through the melting-like process. To explain the metastability of anatase and the phase difference in the crystal-nucleus-size titania, we have proposed a kinetic control nucleation model from a combinational viewpoint of polymer chemistry and coordination chemistry instead of thermodynamics. The basic understanding of the thermal properties contributes to improving the energy conversion efficiency of DSCs by 10% through the thermal annealing process of TiO₂ nanocrystalline film for better connection between nanocrystals without the phase change and size growth, as recently reported. Since the phase control is important for nano materials and devices, we still need the further works to understand and control the crystal phase of nanocrystals. It will probably result in direct phase control during the synthesis of nanocrystals consisting of strong chemical bonds. In addition, the paper suggests that ionic covalent bond of oxide is beneficial to construct nanostructure in atomic-level precision due to the strong binding energy, even if the nanostructure is thermodynamically unstable. Owing to the atomic-level precision, Q-size TiO₂ shows the clear size dependences in both of optical and thermal measurements for the same samples, although these measurements easily detect large-size and small-size contaminants, respectively. The concepts will contribute to the creation of artificial metastable nanostructures that we have not achieved yet with atomic-level precision.

**Methods**

**Materials.** TPM-DPA G4 was prepared according to a previous method. Ti(acac)Cl₃ was synthesized following a literature method. Q-size TiO₂ were obtained using the previous method. All other chemicals were purchased from Kantoh Kagaku Co. and used as received.

**Measurements.** UV-vis spectra were recorded using a Shimadzu UV-3100PC spectrometer with a closed quartz cell (optical path length: 1 cm). AFM was performed using a SII SPA400 instrument under ambient conditions with the tapping mode of imaging (DFM). Si cantilevers having a spring constant of 42 N/m (SII SIFD40F for DFM) were used at a resonance frequency of 300 kHz. A 20-μm scanner (SPA400-PZT (FS-20A), 970P3202) was used. The TEM images were obtained at 120 kV with a JEOL JEM-2100 instrument. The OWG spectra were obtained using a System Instruments Co., Ltd., SIS-5000 spectrophotometer. The XPS spectra were measured using a JEOL JPS-9000MC photoelectron spectrometer without the plasma etching process. The binding energy calibration is based on the measurement of the mica O(1s) signal, E₀ = 531.61 eV.

---

![Figure 5](https://www.nature.com/scientificreports/images/2015/01959/figure5.png)

**Figure 5 |** Schematic image for the kinetic and thermodynamic control polymerization of TiO₆ octahedral units as the nucleation of anatase and rutile in TiO₂. Geometrically, the ratio of the cis-coordination sites for anatase to for rutile is 7 : 1 in the octahedral dimer. Since the symmetry is broken at the anatase trimer, only half of the cis-coordination sites are arrowed on the anatase dimer. The high probability for the cis-coordination polymerization is the reason why anatase tends to form easily as the metastable structure.

1. Tolbert, S. H. & Alivisatos, A. P. Size dependence of a first order solid-solid phase transition: the wurtzite to rock salt transformation in CdSe nanocrystals. *Science* **265**, 373–376 (1994).
2. Jacobs, K., Zazinski, D., Scher, E. C., Herhold, A. B. & Alivisatos, A. P. Activation volumes for solid-solid transformations in nanocrystals. *Science* **293**, 1803–1806 (2001).
3. Rivest, J. B., Fong, L.-K., Jain, P. K., Toney, M. F. & Alivisatos, A. P. Size dependence of a temperature-induced solid–solid phase transition in copper(I) sulfide. *J. Phys. Chem. Lett.* **2**, 2402–2406 (2011).
4. Li, Y., Qi, W., Li, Y., Janssens, E. & Huang, B. Modeling the size-dependent solid–solid phase transition temperature of Cu₃S nanosolids. *J. Phys. Chem. C* **116**, 9800–9804 (2012).
5. Szwarcman, D., Vestler, D. & Markovich, G. The size-dependent ferroelectric phase transition in BaTiO₃ nanocrystals probed by surface plasmons. *ACS Nano* **5**, 507–515 (2011).
6. Takahashi, Y. K., Ohkubo, T., Ohnuma, M. & Hono, K. Size effect on the ordering of FePt granular films. *J. Appl. Phys.* **93**, 7166 (2003).
7. Abdala, P. M., Craievich, A. F. & Lamas, D. G. Size-dependent phase transitions in nanostructured zirconia–scandia solid solutions. *RSC Advances* **2**, 5205–5213 (2012).
8. Buffat, P. & Borel, J.-P. Size effect on the melting temperature of gold particles. *Phys. Rev. A* **13**, 2287–2298 (1976).
9. Goldstein, A. N., Echer, C. M. & Alivisatos, A. P. Melting in semiconductor nanocrystals. *Science* **256**, 1425–1427 (1992).
10. Cleveland, C. L., Luedtke, W. D. & Landman, U. Melting of gold clusters: icosahedral precursors. *Phys. Rev. Lett.* **81**, 2036–2039 (1998).
11. Cleveland, C. L., Luedtke, W. D. & Landman, U. Melting of gold clusters. *Phys. Rev. B* **60**, 5065–5077 (1999).
12. Olson, E. A., Yu, M., Zhang, E. M., Zhang, Z. & Allen, L. H. Size-dependent melting of Bi nanoparticles. *J. Appl. Phys.* **97**, 034304 (2005).
13. Dick, K., Dhannasekaran, T., Zhang, Z. & Meisel, D. Size-dependent melting of silica-encapsulated gold nanoparticles. J. Am. Chem. Soc. 124, 2313–2317 (2002).

14. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).

15. O’Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 353, 737–740 (1991).

16. Kim, J. Y. et al. Efficient tandem polymer solar cells fabricated by all-solution processing. Science 13, 222–225 (2007).

17. Gennari, F. C. & Pasquievich, D. M. Kinetics of the anatase–rutile transformation in TiO2, in the presence of Fe3+. J. Mater. Sci. 33, 1571–1578 (1998).

18. Shannon, R. D. Phase transformation studies in TiO2 supporting different defect mechanisms in vacuum-reduced and hydrogen-reduced Battie. J. Appl. Phys. 35, 3414–3416 (1964).

19. Gemba, J. A. & Pasquievich, D. M. Effect of additives on photocatalytic activity of titanium dioxide powders synthesized by thermal plasma. J. Am. Ceram. Soc. 75, 2934–2938 (1992).

20. Sun, Y., Egawa, T., Zhang, L. & Yao, X. High anatase–rutile transformation temperature of anatase titanate nanoparticles prepared by metalorganic chemical vapor deposition. Jpn. J. Appl. Phys. 41, L 945–L 948 (2002).

21. Zhang, H. & Banfield, J. F. Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO2. J. Phys. Chem. B 104, 3481–3487 (2000).

22. Pal, M., Serrano, J. G., Santiago, P. & Pal, U. Size-controlled synthesis of spherical TiO2 nanoparticles: morphology, crystallization, and phase transition. J. Phys. Chem. C 111, 96–102 (2007).

23. Zhang, H. & Banfield, J. F. Size dependence of the kinetic rate constant for phase transformation in TiO2 nanoparticles. Chem. Mater. 17, 3421–3425 (2005).

24. Lu, H. M., Zhang, W. X. & Jiang, Q. Phase Stability of Nanonanotube. Adv. Eng. Mater. 5, 787–788 (2003).

25. Barnard, A. S. & Curtiss, L. A. Prediction of TiO2 nanoparticle phase and shape transitions controlled by surface chemistry. Nano Lett. 5, 1261–1266 (2005).

26. Guisbiers, G., Van Overschelde, O. & Wantelet, M. Theoretical investigation of size and shape effects on the melting temperature and energy bandgap of TiO2 nanostructures. Appl. Phys. Lett. 92, 103121 (2008).

27. Barnard, A. S. & Xu, H. An environmentally sensitive phase map of titania nanocrystals. ACS Nano 2, 2237–2242 (2008).

28. Takahashi, H., Fujita, K. & Ohno, H. Direct visible spectral analysis of solid samples by optical waveguide spectroscopy due to adsorbed sample molecules after sublimation. Chem. Lett. 36, 116–117 (2007).

29. Satoh, N., Nakashima, T., Kamikura, K. & Yamamoto, K. Quantum size effect in TiO2 nanoparticles prepared by finely controlled metal assembly on dendrimer templates. Nature Nanotechn. 3, 106–111 (2008).

30. Tomalà, D. A. Dendrons/dendrimers: quantized, nano-element like building blocks for soft-soft and soft-hard nano-compound synthesis. Soft Matter. 6, 456–474 (2010).

31. Astruc, D., Boisselier, E. & Ormelas, C. Dendrimers designed for functions: from physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics, and nanomedicine. Chem. Rev. 110, 1857–1899 (2010).

32. Myers, V. S. et al. Dendrimer-encapsulated nanoparticles: New synthetic and characterization methods and catalytic applications. Chem. Sci. 2, 1632–1646 (2011).

33. Yamamoto, K., Higuchi, M., Shiki, S., Tsuruta, M. & Chiba, H. Stepwise radial complexation of imine groups in phenylzamethine dendrimers. Nature 415, 509–511 (2002).

34. Peng, H., Li, J., Li, S.-S. & Xia, J.-B. First-principles study on rutile TiO2 quantum dots. J. Phys. Chem. C 112, 13964–13969 (2008).

35. Iacomino, A., Cantele, G., Ninno, D., Marr, I. & Ossicini, S. Structural, electronic, and surface properties of anatase TiO2 nanocrystals from first principles. Phys. Rev. B 78, 075405 (2008).

36. Sahoo, S. K., Pal, S., Sarkar, P. & Majumder, C. Size-dependent electronic structure of rutile TiO2 quantum dots. Chem. Phys. Lett. 516, 68–71 (2011).

37. Yamamoto, K. et al. Size-specific catalytic activity of platinum clusters enhances oxygen reduction reactions. Nature Chem. 1, 397–402 (2009).

38. Satoh, N., Nakashima, T. & Yamamoto, K. Metal-assembling dendrimers with a triarylamino core and their application to a dye-sensitized solar cell. J. Am. Chem. Soc. 127, 13030–13035 (2005).

39. Satoh, N. & Yamamoto, K. Self-assembled monolayers of metal-assembling dendron thiolate formed from dendrimers with a disulfide core. Org. Lett. 11, 1729–1732 (2009).

40. Satoh, N. & Han, L. Chemical input and 1–V output: stepwise chemical information processing in dye-sensitized solar cells. Phys. Chem. Chem. Phys. 14, 16014–16022 (2012).

41. Hoshino, K., Peterson, N. L. & Wiley, C. I. Diffusion and point-defects in TiO2-X. J. Phys. Chem. Solid. 46, 1397–1411 (1985).

42. Jun, Y.-W. et al. Surfactant-assisted elimination of a high energy facet as a means of controlling the shapes of TiO2 nanocrystals. J. Am. Chem. Soc. 125, 15981–15985 (2003).

43. Yam, M., Chen, F., Zhang, J. & Anpo, M. Preparation of controllable crystalline titanium and study on the photocatalytic properties. J. Phys. Chem. B 109, 8673–8678 (2005).

44. Yang, H. G. et al. Anatase TiO2 single crystals with a large percentage of reactive facets. Nature 453, 638–641 (2008).

45. Yang, H. G. et al. Solvolothermal synthesis and photoreactivity of anatase TiO2 nanosheets with dominant [001] facets. J. Am. Chem. Soc. 131, 4078–4083 (2009).

46. Peng, X., Wickham, J. & Alivisatos, A. P. Kinetics of II–VI and III–V colloidal semiconductor nanocrystal growth: “focusing” of size distributions. J. Am. Chem. Soc. 120, 5343–5344 (1998).

47. Manna, L., Scher, E. C. & Alivisatos, A. P. Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals. J. Am. Chem. Soc. 122, 12700–12706 (2000).

48. Jun, Y.-W., Choi, J.-S. & Cheon, J. Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes. Angew. Chem. Int. Ed. 45, 3414–3439 (2006).

49. Yu, Y., Zhang, Q., Xie, J. & Lee, J. Y. Engineering the architectural diversity of heterogeneous metallic nanocrystals. Nat. Commu. 4, 1453 (2013).

50. Fabbri, F. et al. Thermal processing and characterizations of dye-sensitized solar cells based on nanostructured TiO2. J. Phys. Chem. C 117, 3729–3738 (2013).

51. Enoki, O., Kato, H. & Yamamoto, K. Synthesis and properties of a novel phenylzamethine dendrimer with a tetraphenylmethane core. Org. Lett. 8, 569–571 (2006).

52. Serpone, N., Bird, P. H., Somogyvari, A. & Bickley, D. G. Five-coordinate titanium(V) complexes. Infrared spectral studies on XiTi(diketonato) and XY2Ti(diketonato) complexes and the crystal and molecular structure of di-μ-chloro-tetrachlorobis(2,4-pentanedionato)dititanium(IV). Inorg. Chem. 16, 2381–2386 (1977).

53. Liu, Z. H. & Brown, N. M. D. XPS characterization of mica surfaces processed using a radio-frequency (rf) argon plasma. J. Phys. D, Appl. Phys. 31, 1771 (1998).