doi:10.1246/cl.2010.961

Supercritical Hydrothermal Synthesis of Carboxylic Acid-surface-functionalized TiO_2 Nanocrystals: pH Sensitive Dispersion and Hybridization with Organic Compounds

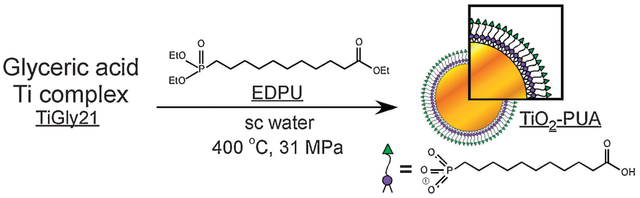
Toshihiko Arita,*[1] Ken-ichi Moriya,[2] Kimitaka Minami,[3] Takashi Naka,[4] and Tadafumi Adschiri*[3]
[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577
[2]*Department of Chemistry, Graduate School of Science, Tohoku University,*
6-3 Aramakiaoba, Aoba-ku, Sendai, Miyagi 980-8578
[3]*WPI Research Center: Advanced Institute for Materials Research, Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577
[4]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047*

(Received June 23, 2010; CL-100581; E-mail: tarita@tagen.tohoku.ac.jp, ajiri@tagen.tohoku.ac.jp)

Surface-functionalized TiO_2 (anatase) nanocrystals (NCs) (avg. $d = 6.7 \pm 1.6\,\mathrm{nm}$) were synthesized by a supercritical hydrothermal method. A phosphonic acid derivative was used as surface modifier of TiO_2 NCs. It was verified that the phosphonic acids were bound to the surface of TiO_2 with very strong binding energy. The TiO_2 NCs also exhibited extraordinarily high chemical stability. Such a strong binding between the phosphonic acid modifier and TiO_2 had not been obtained by any other methods. The TiO_2 NC showed sharp pH sensitive dispersion. Because of the functional as well as stable surface modifier layer, further manipulations on the surface using chemical reagents could be possible.

Fabrication of nanocrystals (NCs) which have well-defined crystal structure, morphology, purity, and surface structure has keen importance in nanotechnology, since these factors can affect the properties and functionalities of nanosized devises.[1] Among these principal factors of NCs, surface treatment would be the key technology for application of NCs into functional devices because surface control could lead to increased handling and functionalities of NCs. For instance, the hybridization of NCs with other functional materials, e.g., peptides,[2] amino acids,[3] polymers,[4–6] other NCs, and so on, would be one of the most promising methods to fabricate new devices, e.g., medical probes,[7] organic–inorganic composites,[8] and metamaterials.[9] Therefore, the development of a joining technique between NCs and other materials is quite important. Among other challenges and efforts for joining them, we have focused on one-pot synthesis to introduce functional substituents on a NC.

It goes without saying that TiO_2 is a quite well-known functional semiconductor which is used as, for example, photocatalyst, pigment, and high-refractive index material. Furthermore, because it is not so poisonous to humans, e.g., it can be used as sun blocks, enormous studies have been done to synthesize, characterize, functionalize, and assemble TiO_2 NCs. Functionalization by adequate surface modification is a great breakthrough point for use of TiO_2 nanoparticles (NPs). In order to obtain both chemically and thermally stable and highly functional surfaces, we have used a water-soluble Ti/glyceric acid complex as Ti source and a phosphonic acid derivative as modifier for supercritical (sc-) hydrothermal reaction. Phosphonic acids have smaller pK_a values than carboxylic acids so that they can bind to the surface of TiO_2 with much stronger interaction.[10] Applying phosphonic acids as an anchor to TiO_2 and carboxylic acid as a linker to the other materials, we developed a highly functional TiO_2 NC (Scheme 1). The carboxylic acid linker is convenient for the hybridization of TiO_2 NC because it allows us to graft other NPs, polymers, and compounds easily by esterification. In addition, because sc-hydrothermal reaction is very fast, it is suited for large-scale production of NPs. This is a huge advantage for industrial production of NPs for hybrid materials.



Scheme 1. Schematic description for the synthesis of surface-functionalized TiO_2 (anatase) nanocrystal.

Strong binding between surface modifier and TiO_2 is absolutely essential to synthesize surface-functionalized TiO_2 NCs. We chose phosphonic acid derivatives as the modifiers because phosphoric acid derivatives are well known to strongly adsorb to TiO_2 surfaces.[10] However, alkyl phosphates are easily hydrolyzed in super- and subcritical water so that they cannot be used. Phosphonic acids have a strong P–C bond instead of P–O–C bonds, therefore they are not hydrolyzed in sc-water.

We synthesized a variety of phosphonic acid derivatives for the surface modifiers.[11] In this study, ethyl 11-diethoxyphosphorylundecanoate (EDPU) was selected as the modifier for surface functionalization. Water-soluble Ti/glyceric acid complex[12] (TiGly21, [Ti]:[glyceric acid] = 2:1) was synthesized and employed as Ti source to obtain homogeneous solution. The homogeneity of the reaction system is quite important, especially for obtaining uniform reaction and products in accordance with crystal growth theory. Our TiGly21 has another advantage for sc-hydrothermal synthesis because it has quite low carbon content. Since sc-hydrothermal reaction was conducted at 400 °C, where most organic compounds are not stable for long periods, the low carbon content of TiGly21 will result in reduction of impurities in the product.

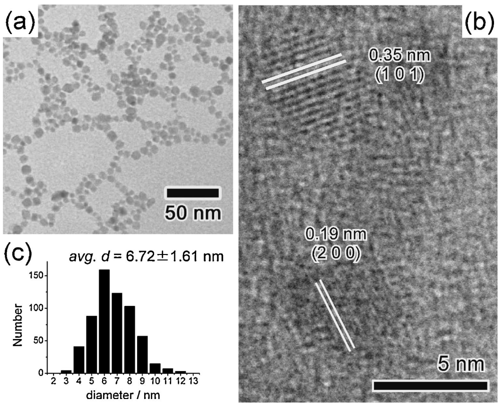


Figure 1. TEM (a), HR-TEM (b) images and histogram (c) of the EDPU-modified TiO_2 NCs. The HR-TEM image (b) displayed a cross-lattice pattern with a lattice spacing of 0.35 and 0.19 nm, corresponding to the interplane separation between the (101) or (200) lattice planes of anatase.

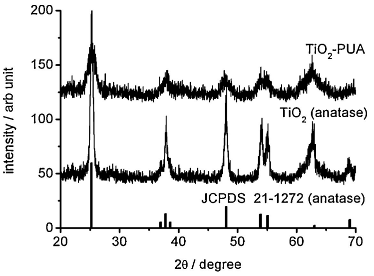


Figure 2. Powder XRD pattern of the EDPU-modified TiO_2 NCs (TiO_2–PUA). The diffraction patterns of a commercially available TiO_2 (anatase) (NanoTek®) and JCPDS file for TiO_2 (No. 21-1272) are also depicted for comparison.

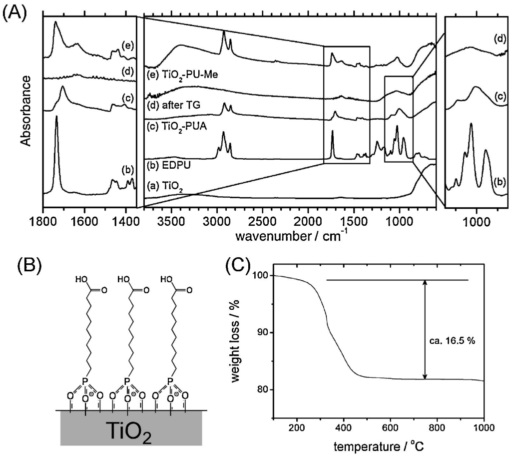


Figure 3. FTIR spectra (A), schematic illustration of possible surface structure of TiO_2–PUA deduced from FTIR (B), and the TG curve of the TiO_2–PUA (C). For FTIR spectra (A), (a) denotes the spectrum of unmodified bare TiO_2 anatase, (b) denotes pure EDPU, (c) denotes TiO_2–PUA, (d) denotes TiO_2–PUA after TG measurement, and (e) denotes TiO_2–PUA after esterification with methanol, respectively.

The synthesis of TiO_2 NCs was performed using TiGly21 as Ti source and EDPU as functional modifier. The reaction product was then collected and washed by centrifugation with methanol 3 times. The washed product was dispersed in water and freeze-dried. The obtained powder was characterized by TEM, HR-TEM, XRD, TG, and FTIR spectroscopy. The size distribution of synthesized NPs was calculated by averaging the diameter of 200 particles from 3 individual syntheses (total 600 particles). Experimental details may be found in the Supporting Information.[11]

Figure 1 depicts the TEM image of EDPU-modified TiO_2 NCs (TiO_2–PUA) synthesized in this study. The NCs had average diameter of 6.72 ± 1.61 nm. From the HR-TEM image, it was verified that the NPs synthesized in this study were all TiO_2 anatase single crystals. The crystal structure was also examined by powder XRD. The XRD results also supported that the structure of TiO_2 NCs synthesized in this study were anatase. The XRD diffraction patterns are shown in Figure 2.

Figure 3A depicts the FTIR spectra of unmodified TiO_2, TiO_2–PUA, and EDPU. The spectrum of the TiO_2 NCs without surface modifier had no peaks corresponding to organic compounds, only a broad peak of adsorbed water (3700–3000 cm^{-1}) was seen. The spectrum of EDPU exhibits strong peaks due to the free P=O stretching mode (1240 cm^{-1}) and PO–C stretching mode (1050 and 950 cm^{-1}). The spectrum of TiO_2–PUA exhibits no peaks at 1240, 1050, and 950 cm^{-1}, whereas it only exhibits a strong peak corresponding to the PO–metal stretching mode (1000 cm^{-1}).[13,14] This suggests three PO–metal bonds per modifier were formed. In addition, a peak due to the free carboxyl C=O stretching (1700 cm^{-1}) was seen in the spectrum of TiO_2–PUA, whereas a peak due to ethyl ester C=O stretching (1740 cm^{-1}) was not seen. This indicates the ester groups of the modifier were hydrolyzed during the synthesis. Actually, the hydrolysis of diethyl phosphonate and ethyl carboxylate of EDPU in sc-water was performed. Both the diethyl phosphonate and ethyl carboxylate of EDPU were perfectly hydrolyzed after 2 min reaction at 400 °C, 31 MPa. The results are presented in the Supporting Information (Figure S1).[11] Figure 3B depicts the possible bonding form of the modifier to the TiO_2 surface deduced from the FTIR spectra. Actually, the TiO_2 NC synthesized in this study was 11-phosphonoundecanoic acid-modified TiO_2 NC (TiO_2–PUA). Such (3 footed) binding cannot be obtained by surface modifications of unmodified powder TiO_2 NPs by phosphoric acids.[15] In situ modification is absolutely necessary. This is also a benefit of the sc-hydrothermal method and an advantage of the TiO_2–PUA.

In order to measure the amount of the modifier on TiO_2–PUA, TG with air flow was measured. Figure 3C depicts the TG curve of TiO_2–PUA. The total weight loss during the TG was 16.5%. Interestingly, the FTIR spectrum of the TiO_2–PUA after TG still shows a peak corresponding to PO–metal bond. This implies the phosphoric acids were still chemisorbed on the surface of TiO_2, i.e., even after the alkyl group of the modifier was totally decomposed, PO–metal bonds survived until 1000 °C. The small blue shift of the PO–metal peak after TG may indicate PO–metal in the TiO_2–PUA was partially converted to P–OH. Since the peak corresponding to P–OH stretching mode usually appears as a broad peak around 1100–940 nm, the blue shift may be explained by the coexistence of P–OH and PO–metal groups on the TiO_2–PUA after TG. This

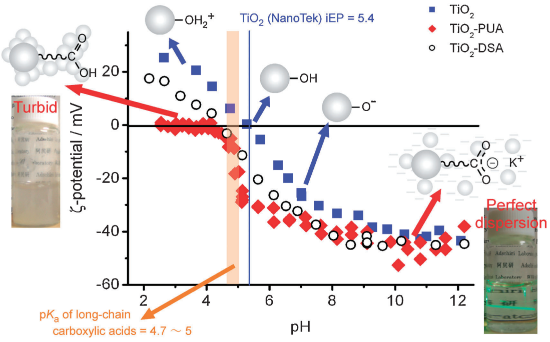


Figure 4. The titrimetric analysis of ζ potential of the unmodified TiO_2 (NanoTek®) (blue filled square), TiO_2–DSA (black circle), and TiO_2–PUA (red filled diamond). The schematic illustration of the suggested dispersion mechanism and the images of the aqueous TiO_2–PUA dispersion are also displayed.

means the binding energy between the modifier and TiO_2 is very large.

The density of the modifier on TiO_2–PUA was calculated from the average size and the TG weight loss of TiO_2–PUA. The graft density was calculated to be 3.1 chains/nm^2. The calculated graft density did not exceed the possible maximum graft density of the phosphonic acid, i.e., 4 chains/nm^2 which was calculated from the occupation area of phosphonic acid.[11]

The TiO_2–PUA was very much functional and convenient for hybridization with other materials. For example, esterification of carboxylic acid with methanol was performed. The FTIR spectrum shown in Figure 3A shows a peak due to the methyl ester (1740 cm^{-1}), this supports the successful esterification. Polymer could also be grafted to TiO_2–PUA by esterification. These facts supported the high hybridization potential of the TiO_2–PUA. Details of esterification are depicted in the Supporting Information (Figure S5).[11]

Aqueous TiO_2–PUA dispersion showed high pH sensitivity. Because the phosphonic acid formed very stable self-assembled monolayer on the TiO_2 surface, desorption of the modifier was not likely to happen in water. Figure 4 depicts the pH dependent changes of the ζ potential of the aqueous TiO_2–PUA dispersion. The ζ potential of TiO_2–PUA slightly increased with decreasing pH of the dispersion and suddenly reached zero at pH 4.8. The isoelectric point (iEP) of commercial TiO_2 (NanoTek®) was 5.4 and the pK_a values of the long chain fatty acids are 4.7–5. This switching of the surface properties cannot be achieved without full shielding of the TiO_2 surface and exhibition of carboxylic acid group to the surface of the TiO_2–PUA.

The ζ potential of the *n*-octylsuccinic anhydride-modified TiO_2 NPs (TiO_2–DSA) were also displayed in Figure 4 as a reference. The synthesis of TiO_2–DSA is described in the Supporting Information (Figure S4).[11] The TiO_2–DSA has ionized *n*-octylsuccinic acid monolayer on the surface. The dispersion of TiO_2–DSA did not show quick response to pH. Ligand exchange is well known for fatty acid-modified ceramic NPs, it is not an exception for TiO_2–DSA.[16] Because of the ligand exchange, i.e., some of the *n*-octylsuccinic acids were desorbed from the TiO_2 surface, part of the TiO_2 surface would be directly posed to water. Then small amounts of TiO_2–DSA can disperse even though the surface of TiO_2–DSA is hydrophobic. This could also be the reason why immediate switching of ζ potential was not seen for the TiO_2–DSA dispersion. Taguchi et al.[17] also reported similar pH-mediated dispersion of dicarboxylic acid-modified CeO_2 NCs in water. In their case, the anchor group was also (ionized) carboxylic acid. According to this, the strong binding of the phosphonic acid to TiO_2 was also deduced. The pH sensitive switching would be attractive for biocompatible materials.

In conclusion, in situ surface-modified TiO_2 (anatase) NCs (TiO_2–PUA) by a phosphonic acid derivative (EDPU) were synthesized via sc-hydrothermal method. Because of the large binding energy between phosphonic acids and TiO_2 formed by sc-hydrothermal method, the modifier layer on the TiO_2–PUA showed very good stability to heat and chemical reagents. In addition, since TiO_2–PUA exhibits carboxylic acids on the surface, it showed sharp pH dependent switching on its dispersion and tunability of the surface properties by esterification of the carboxylic groups with alcohols. The surface-functionalized TiO_2 NC (TiO_2–PUA) synthesized in this study can be applied to a wide variety of purposes, e.g., for polymer composites and biocompatible NCs.

This work was supported by a Scientific Research Grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan. This research was also partly supported by New Energy and Industrial Technology Development Organization Japan (NEDO). The author (T. Arita) thanks Grant-in-Aid for Young Scientists (B) No. 19750094 for their financial support.

References and Notes

1 G. Schmid, *Nanoparticles*, WILEY-VCH Verlag GmbH & Co. KGaA, **2004**.
2 P. Pengo, Q. B. Broxterman, B. Kaptein, L. Pasquato, P. Scrimin, *Langmuir* **2003**, *19*, 2521.
3 M. T. Zin, H. Ma, M. Sarikaya, A. K.-Y. Jen, *Small* **2005**, *1*, 698.
4 B. Hojjati, P. A. Charpentier, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3926.
5 C. Boyer, V. Bulmus, P. Priyanto, W. Y. Teoh, R. Amal, T. P. Davis, *J. Mater. Chem.* **2009**, *19*, 111.
6 R. Darkow, T. Groth, W. Albrecht, K. Lützow, D. Paul, *Biomaterials* **1999**, *20*, 1277.
7 C. Kumar, *Nanomaterials for Cancer Therapy*, WILEY-VCH Verlag GmbH & Co. KGaA, **2006**.
8 G. Kickelbick, *Hybrid Materials*, WILEY-VCH Verlag GmbH & Co. KGaA, **2007**.
9 T. J. Cui, D. R. Smith, R. Liu, *Metamaterials: Theory, Design, and Applications*, Springer, **2009**.
10 E. Bae, W. Choi, J. Park, H. S. Shin, S. B. Kim, J. S. Lee, *J. Phys. Chem. B* **2004**, *108*, 14093.
11 Detail is shown in Electronic Supporting Information (ESI). Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
12 M. Kakihana, K. Tomita, V. Petrykin, M. Tada, S. Sasaki, Y. Nakamura, *Inorg. Chem.* **2004**, *43*, 4546.
13 M. J. Pellerite, T. D. Dunbar, L. D. Boardman, E. J. Wood, *J. Phys. Chem. B* **2003**, *107*, 11726.
14 L. C. Thomas, *Interpretation of the Infrared Spectra of Organophosphorous Compounds*, Heyden, London, **1974**.
15 S. Hayashi, *Chem. Lett.* **2009**, *38*, 960.
16 T. Arita, J. Yoo, Y. Ueda, T. Adschiri, *Nanoscale* **2010**, *2*, 689.
17 M. Taguchi, S. Takami, T. Naka, T. Adschiri, *Cryst. Growth Des.* **2009**, *9*, 5297.