Electronic Supporting Information (ESI)

# Surface Modification Effects of Graphite for Selective Hydrogen Absorption of Titanium at Room-Temperature

Keita Shinzato,[a] Yuki Nakagawa,[b] So Hamamoto,[a] Yuya Hayashi,[c] Hiroki Miyaoka,[d] Shigehito Isobe,[b] Tamaki Shibayama,[b] Norio Ogita[e] and Takayuki Ichikawa*[a, d, e]

[a.] *Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan*

[b.] *Faculty of Engineering, Hokkaido University, N-13, W-8, Sapporo, 060-8628, Japan*

[c.] *Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo, 060-8628, Japan*

[d.] *Natural Science Center for Basic Research and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan*

[e.] *Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima, 739-8521, Japan*

*Corresponding author

E-mail: tichi@hiroshima-u.ac.jp

# Experimental Section

All sample preparation and analyses described below were performed under high purity Ar (6N) or $H_2$ (7N) by using glove box and special vessels to minimize air contamination. Ti (99.7%, 100 mesh, Sigma Aldrich), and graphite (99.9995%, 2-15 micron, Alfa Aesar) were purchased and used without further purification. Acetone, xylene, and 4-methyl-2-pentanone, which include water below 0.001% as an impurity, were purchased from FUJIFILM Wako Pure Chemical. *cis*-1,2-Dimethylcyclohexane (98.0 %) was purchased from Tokyo Chemical Industry. Ti and graphite were mixed with 1:0.5 molar ratio. Total 300 mg of the mixture and 20 pieces balls made of $ZrO_2$ (8 mm in diameter) were put into Cr steel milling pot (30 $cm^3$ inner volume). The mixture was ball-milled under 0.1 MPa Ar at 200 rpm for 3 h by using a planetary ball-milling apparatus (Fritsch P7). To avoid increasing temperature in the milling pot, the ball-milling was stopped for 1 min every 10 min ball-milling. Here, the Ti ball-milled with graphite is denoted as $Ti_{Graphite}$ in this work. Ti ball-milled with 20 wt.% acetone, xylene, *cis*-1,2-dimethylcyclohexane, and 4-methyl-2-pentanone were prepared by the ball-milling with the same conditions of $Ti_{Graphite}$. Here, the volatile by-products are observed in 200 to 300 °C during TG measurement for Ti ball-milled with acetone and 4-Methyl-2-pentanone, which are not related to hydrogenation properties. Therefore, after ball-milling of Ti with each organic solvent, the samples were vacuumed at 300 °C for 2 h to remove the residual solvents and volatile by-products generated by the ball-milling. Ti ball-milled with acetone, xylene, *cis*-1,2-dimethylcyclohexane, and 4-methyl-2-pentanone are denoted as $Ti_{Acetone}$, $Ti_{Xylene}$, $Ti_{\textit{cis}\text{-1,2-Dimethylcyclohexane}}$, and $Ti_{4\text{-Methyl-2-pentanone}}$, respectively.

The $H_2$ absorption of the prepared samples was carried out by using a thermogravimetry with differential thermal analysis equipment (TG-DTA, Rigaku, TG8120). The TG-DTA equipment is located in glove box (Miwa MFG, MDB-2BL, $H_2O$ < 0.2ppm). The TG-DTA measurements were performed by the following processes. Sample was heated up to 40 °C under 0.1 MPa Ar flow with heating rate of 5 °C/min. Then, the carrier gas was changed from Ar to $H_2$ at 40 °C to investigate $H_2$ absorption properties around room temperature, where this point was drawn in Fig. 1 and S1 as the zero point (0 min, 0 wt.%). After changing carrier gas, the temperature was kept around 40 °C for 10 min. After that, the sample was heated up to 400 °C under 0.1 MPa $H_2$ flow.

Powder x-ray diffraction pattern (XRD, Rigaku RINT 2000, Cu-K$\alpha$: $\lambda$ = 1.54 Å) was measured for the phase identification of the samples. The obtained XRD pattern was analyzed by comparing to powder diffraction files (PDF) using the PDXL software. The sample was fixed on glass plate by using grease (Apiezon® H grease, Leef Energy Co. Ltd.) and sealed by polyimide sheet (Kapton, Du Pont-Toray Co. Ltd.) to protect the samples from oxidation during the measurements. The Raman spectrometry was carried out in order to analyze the chemical state of the samples. The light source was an Ar ion laser (Spectra-physics, Inc., Stabilite 2017) operated at 488.0 nm with an output power of 4 mW. The scattered light was analyzed by a triple monochromator (JASCO, TRS-600) with a liquid-$N_2$ cooled charge coupled device (CCD) detector (Princeton Instruments, Inc., model LN/CCD-1100-PB). The sample was pressed at 180 MPa to make a pellet for the Raman spectrometry. The pellet was put on a carbon tape to fix on a hand-made sample holder. The morphology of $Ti_{Graphite}$ and $Ti_{Acetone}$ were analyzed using scanning transmission electron microscope (STEM, FEI Titan$^3$ G2 60-300) with an acceleration voltage of 200 kV. The sample was dispersed on a quantifoil Mo TEM grid (EM Japan Co. Ltd., R2/1 type, 200 mesh). The sample was transferred from glove box to TEM by using the atoms defend holder (Mel-build corporation).

## Figures

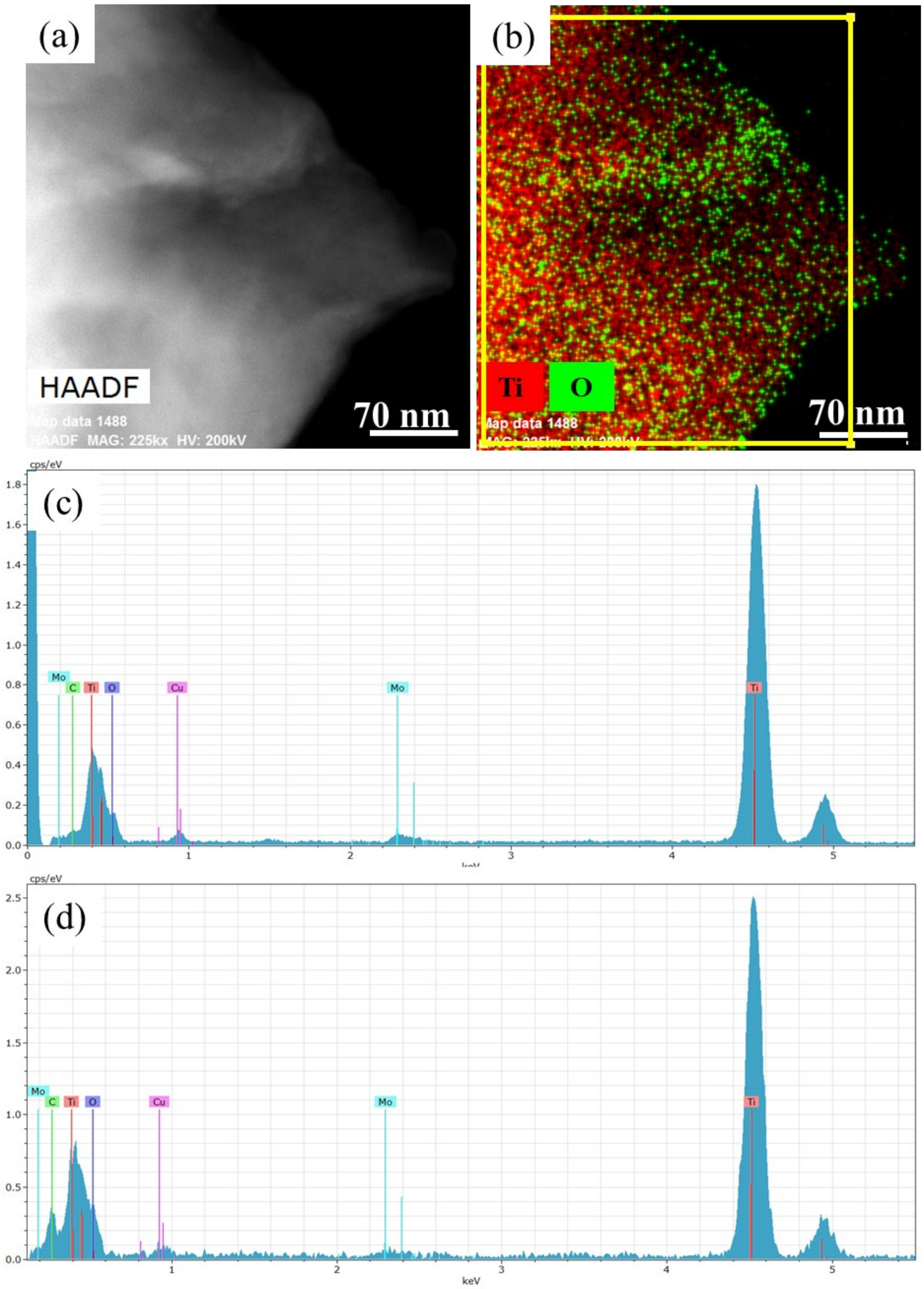

Fig. S1 (a-c) TEM observation results of as-received Ti, and (d) EDS spectrum of $\mathrm{Ti}_{\mathrm{Acetone}}$. (a) HAADF-STEM image, (b) EDS mapping of Ti and

O, and (c) EDS spectrum of the area expressed as square in Fig. S1b. The EDS spectrum of $Ti_{Acetone}$ was obtained in the similar observation conditions to as-received Ti. The peaks of Mo and Cu are corresponding to TEM grid and the specimen holder, respectively. Carbon is included in TEM grid as supporting film of sample. The peak intensity of carbon for as-received Ti is quite low compared to that of $Ti_{Acetone}$. The results indicate that carbon on the surface of as-received Ti should be negligible.

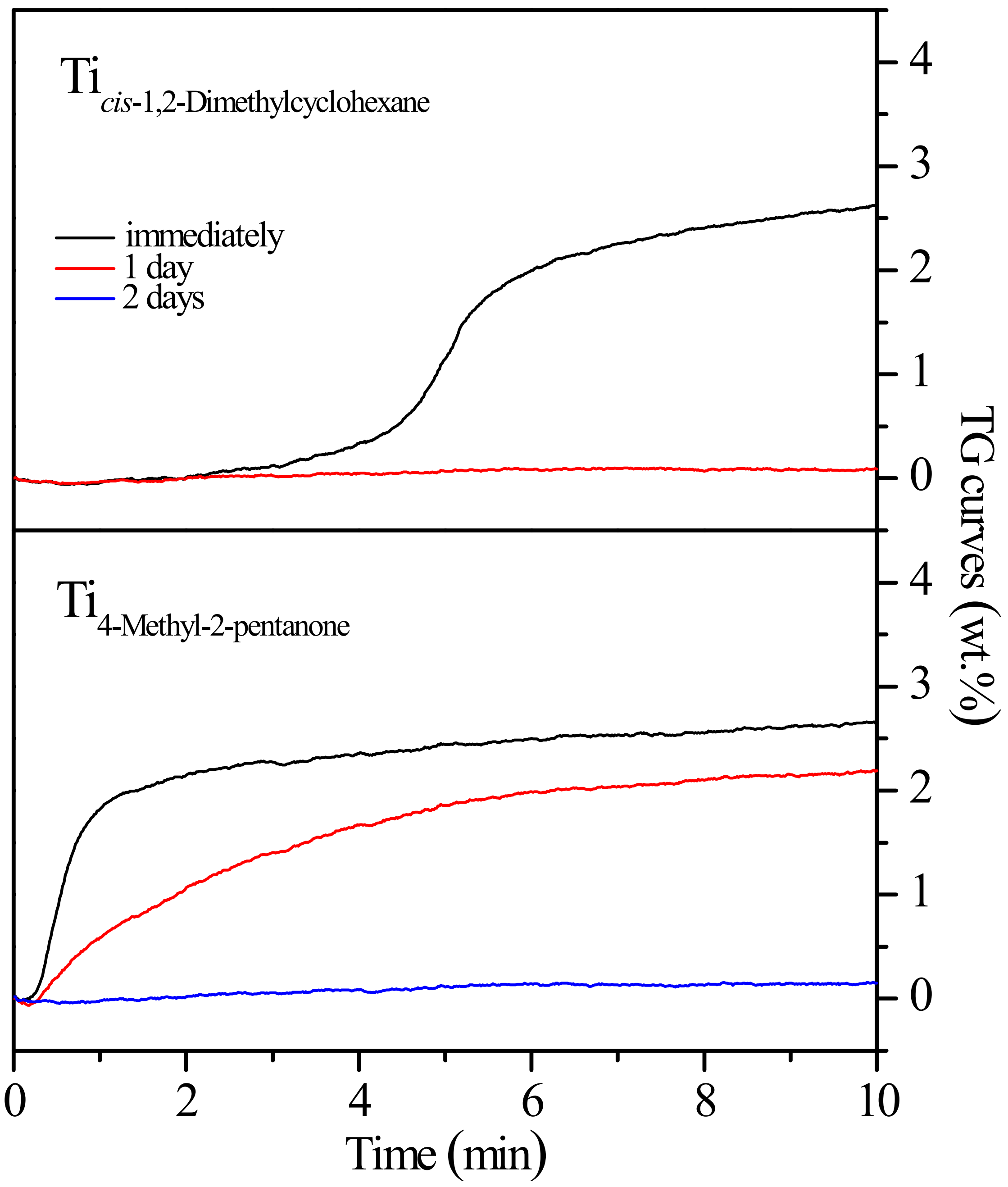

Fig. S2 Hydrogen absorption profiles of Ti$_{cis\text{-1,2-Dimethylcyclohexane}}$ and Ti$_{\text{4-Methyl-2-pentanone}}$, performed by TG apparatus under 0.1 MPa $H_2$ around 40 °C.

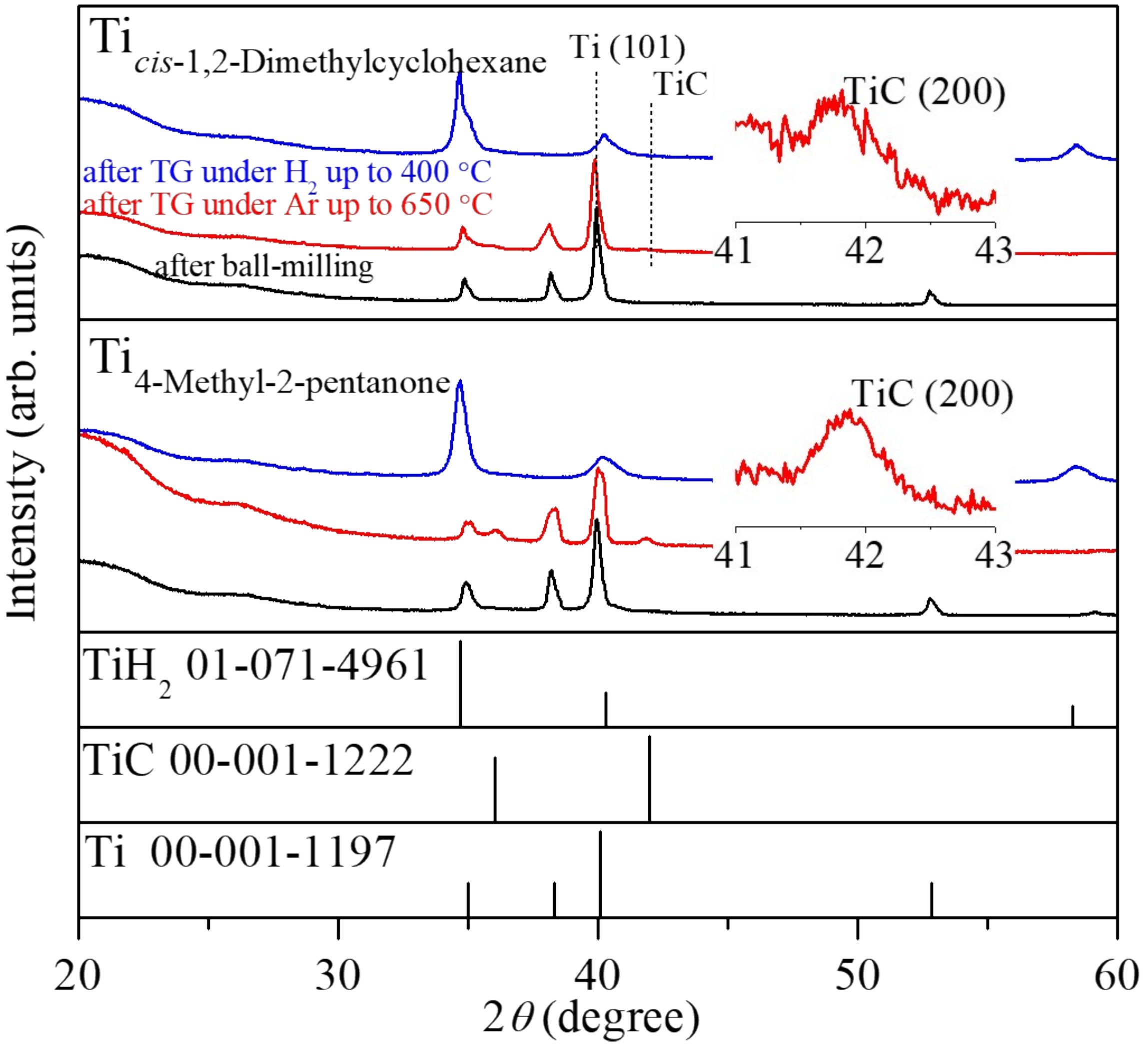

Fig. S3 XRD results of $Ti_{cis\text{-}1,2\text{-}Dimethylcyclohexane}$ and $Ti_{4\text{-}Methyl\text{-}2\text{-}pentanone}$ before and after TG. TG measurements were performed under $H_2$ and Ar atmosphere up to 400 °C and 650 °C, respectively.

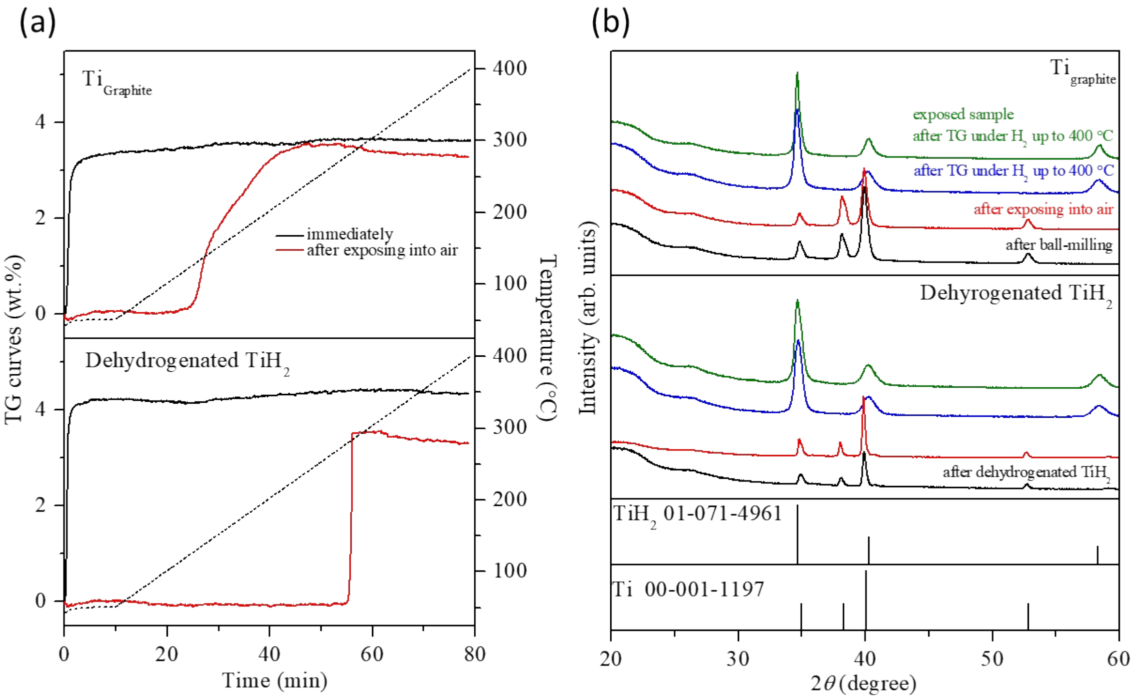

Fig. S4 (a) TG curves and (b) XRD results of $Ti_{Graphite}$ and dehydrogenated $TiH_2$ before and after exposing into air for 1 day. Dehydrogenated $TiH_2$ was prepared from pristine $TiH_2$ (98%, 325 mesh, Sigma Aldrich) by heating up to 650 °C under high purity Ar flow using TG apparatus.

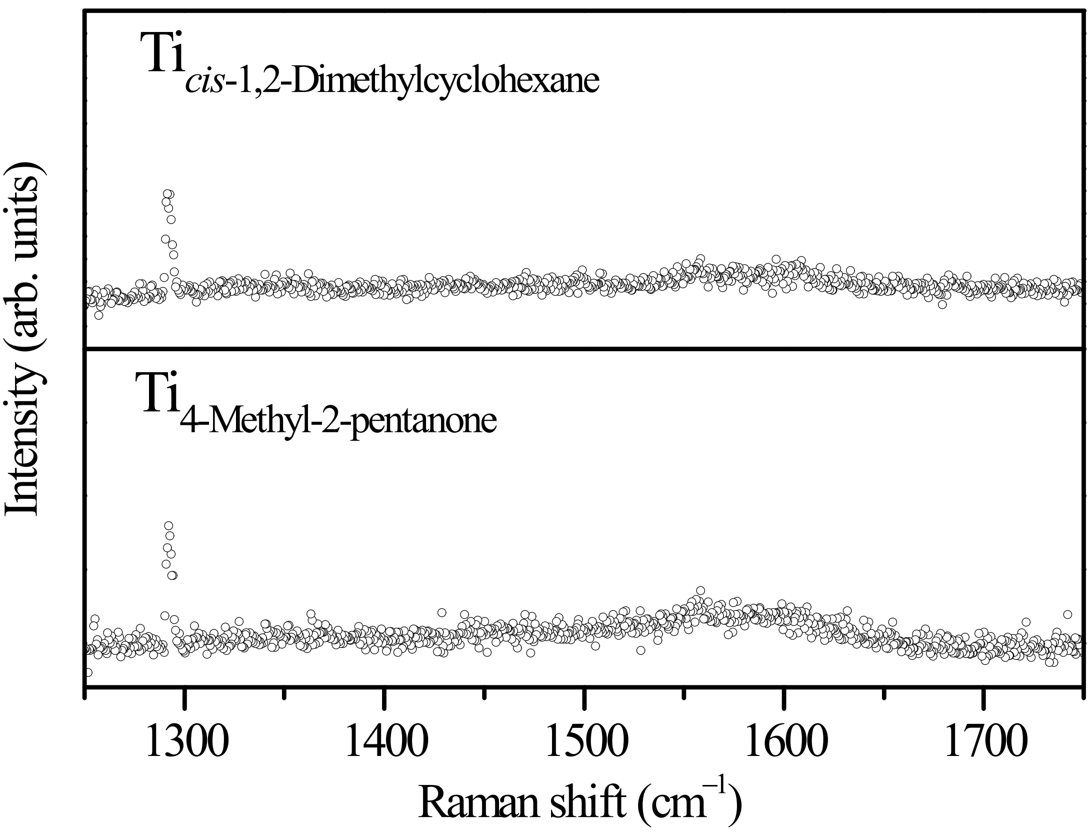

Fig. S5 Raman spectra of $Ti_{cis\text{-}1,2\text{-Dimethylcyclohexaone}}$ and $Ti_{4\text{-Methyl-2-pentanone}}$ measured just after the sample preparation.

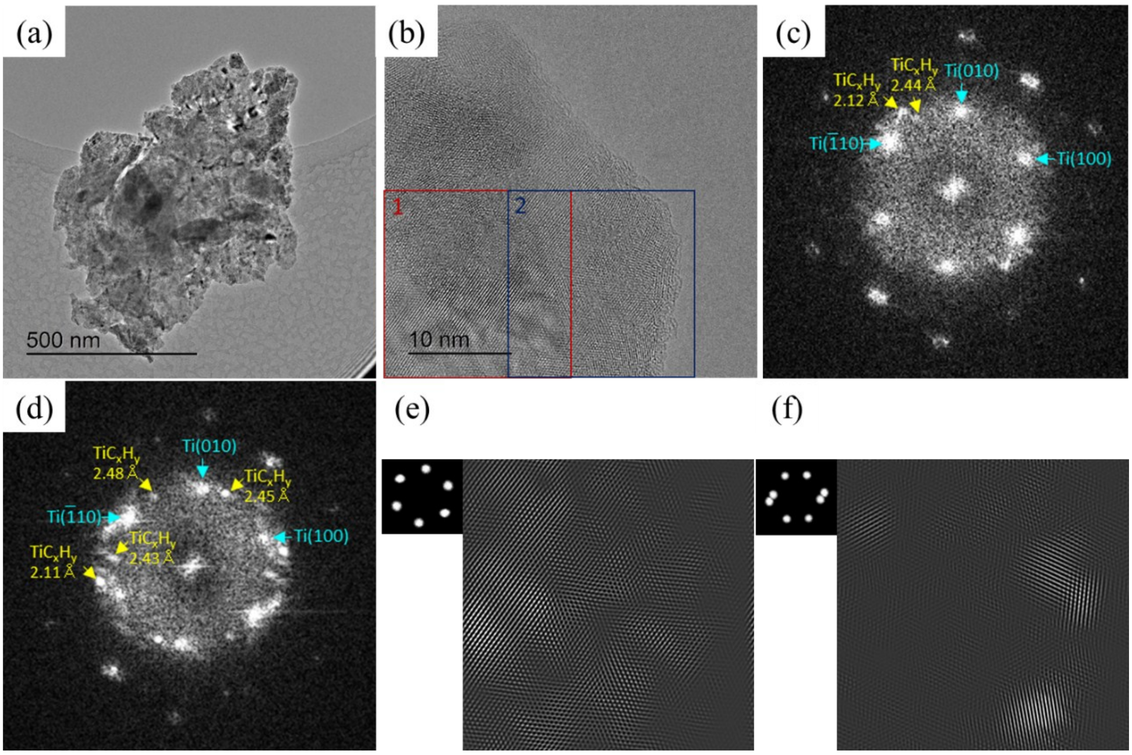

Fig. S6 TEM observation results of $Ti_{Acetone}$. (a) TEM bright-field and (b) high resolution TEM (HRTEM) images. The Fast Fourier Transform (FFT) patterns were acquired from (c) area 1 and (d) area 2. Inverse FFT images from (e) blue spots and (f) yellow spots in area 2. The yellow spots are assigned to $TiC_xH_y$ such as $TiC_{0.5}H_{0.21}$ and $TiC_{0.47}H_{0.18}$. The IFFT image revealed that $TiC_xH_y$ exists in the outside of the particle.

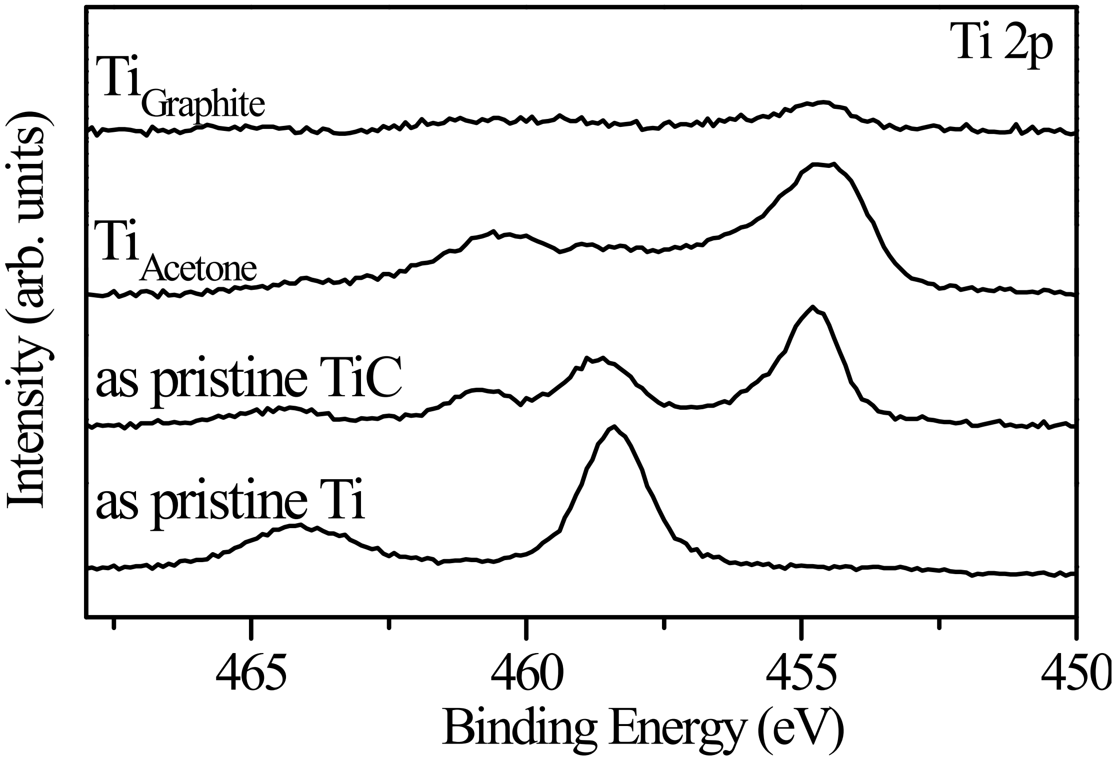

Fig. S7 Ti2p XPS spectra of $Ti_{Graphite}$, $Ti_{Acetone}$, as purchased TiC, and Ti.

X-ray photoelectron spectrometry (XPS, Japan Electro Optical Laboratory Co. Ltd., JPS-9200, Al-Kα: 1486.6 eV) was performed in order to analyze the chemical state of the Ti surface. Sample was fixed on a sample holder using carbon tape. To avoid the charge-up, electron was supplied to the sample using flood gun during XPS measurement. The binding energy was calibrated by C1s (285.0 eV) of each sample. The sample was transferred into XPS equipment from glove box using transfer vessel (Japan Electro Optical Laboratory Co. Ltd., AP-Z120042TRV). For Ti2p XPS spectrum of pristine Ti, two peaks were located at 458.4 eV and 464.2 eV. These peaks are asigned to $Ti_{3/2}$ and $Ti_{1/2}$ peaks of $TiO_2$ ($Ti^{4+}$),[1] indicating Ti without any treatment was covered by $TiO_2$ layer ($Ti^{4+}$). Considering the detectable depth of XPS, the thickness of $TiO_2$ is more than 10 nm. In the case of the pristine TiC, the low-valence Ti was detected at 454.8 eV (and 460.8 eV) with higher intensity, which is consistent to typical $Ti_{3/2}$ (and $Ti_{1/2}$) peak of TiC.[2] $TiO_2$ peak was also observed in the pristine TiC with lower intensity. The spectrum of TiC indicates that oxide layer on TiC particle is thinner than one of the pristine Ti. The spectrum of $Ti_{Acetone}$ is similar to the pristine TiC, indicating the chemical state of the surface Ti on the $Ti_{Acetone}$ is similar to TiC and the oxide layer is thin. This result agrees with previous our report.[3] $Ti_{Graphite}$ also shows peak at 454.8 eV in Ti 2p XPS spectrum, indicating TiC precursor is formed by ball-milling of Ti and graphite. Ti-C bonding was also detected by EELS spectrum of T $L_{2,3}$-edge measured at the interface between Ti and C (Figure 4). It is noteworthy that the intensity is quite low compared with one of $Ti_{Acetone}$, indicating carbon with tickness of several nm covers Ti particle. This result suggests that the local area characterized by

STEM-EDS mapping is well consistent with the average state characterized by XPS.

# Reference

1. M. Shirkhanzadeh, *Journal of Materials Science: Materials in Medicine*, 1995, **6**, 206-210.
2. A. A. El Mel, B. Angleraud, E. Gautron, A. Granier and P. Y. Tessier, *Thin Solid Films*, 2011, **519**, 3982-3985.
3. K. Shinzato, S. Hamamoto, H. Miyaoka and T. Ichikawa, *The Journal of Physical Chemistry C*, 2019, **123**, 19269-19274.