SUPPORTING INFORMATION TO

Substrate Grain-Dependent Chemistry of Carburized Planar Anodic TiO_2 on Polycrystalline Ti

Celine Rüdiger[a*], *Marco Favaro*[b†], *Carlos Valero-Vidal*[c‡], *Laura Calvillo*[b], *Nathalie Bozzolo*[d], *Suzanne Jacomet*[d], *Jennifer Hein*[e#], *Luca Gregoratti*[f], *Stefano Agnoli*[b], *Gaetano Granozzi*[b], *Julia Kunze-Liebhäuser*[c*]

[a] Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany.

[b] Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy.

[c] Institut für Physikalische Chemie, Leopold-Franzens-Universität Innsbruck, Innrain 52c, 6020 Innsbruck, Austria.

[d] MINES ParisTech, PSL - Research University, CEMEF - Centre de Mise en Forme des Matériaux, CNRS UMR 7635, CS 10207 Rue Claude Daunesse 06904 Sophia Antipolis Cedex, France.

[e] Lehrstuhl für Technische Chemie II, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany.

[f] Elettra – Sincrotrone Trieste SCpA, SS14-Km163.5 in Area Science Park, 34149 Trieste, Italy.

[*]Corresponding authors: celine.ruediger@tum.de, Julia.Kunze@uibk.ac.at

Present Addresses

[†] Helmholtz-Zentrum Berlin (HZB), Institute for Solar Fuels, Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

[‡] Advanced Light Source (ALS) and Joint Center for Energy Storage Research (JCESR), Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720, USA.

[#] Shell Global Solutions International B.V., PO Box 38000, 1030 BN Amsterdam, The Netherlands.

Additional information on SPEM

The Ti $2p_{3/2}$ chemical maps of $TiOC_{650}$, $TiOC_{750}$ and $TiOC_{850}$, (TiC/TiO_2 or TiO_x/TiO_2) were generated by dividing the integrated map obtained in the energy range 456 - 452.15 eV by the integrated map obtained in the energy range 459.85 - 456 eV. The Ti $2p_{3/2}$ chemical maps of $TiOC_{550}$ (TiO_2/BG) were generated by dividing the integrated map obtained in the energy range 459.85 - 456 eV by the integrated map obtained in the energy range 456 - 452.15 eV. The C 1*s* chemical maps of all TiOC (C/BG) were generated by dividing the integrated map obtained in the energy range 286.85 - 283 eV by the integrated map obtained in the energy range 283 - 279.15 eV.

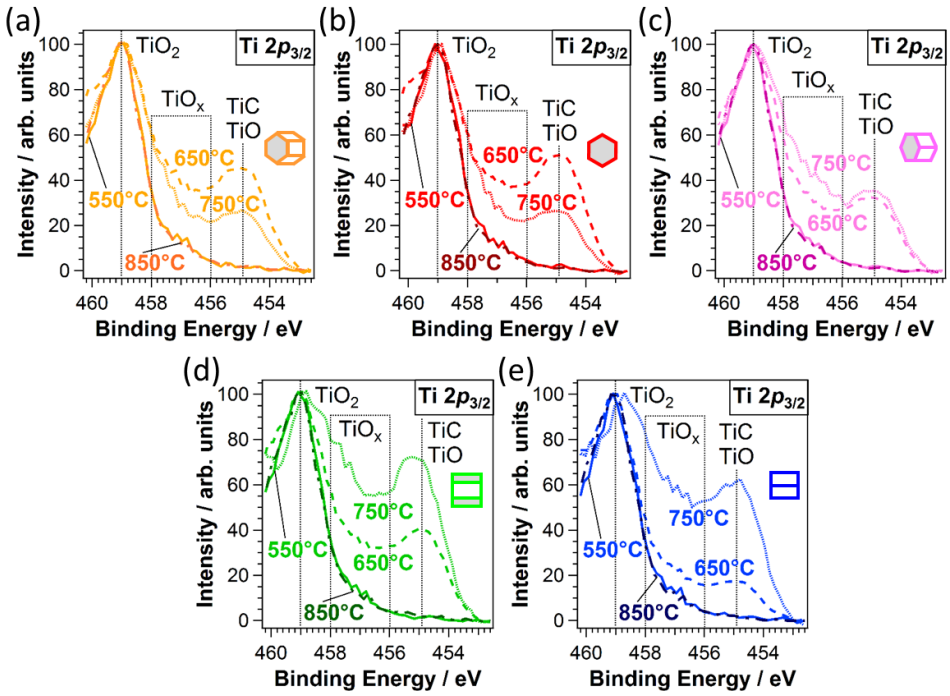

Figure S1. XP spectra from Ti $2p_{3/2}$ photoelectron micrographs taken of TiOC on top of five differently oriented substrate grains for the four annealing temperatures. The substrate orientations are (a) $15° \leq \Phi \leq 40°$, $0° \leq \varphi_2 \leq 30°$, (b) $0° \leq \Phi \leq 15°$, $0° \leq \varphi_2 \leq 30°$ (c) $40° \leq \Phi \leq 50°$, $0° \leq \varphi_2 \leq 30°$, (d) $50° \leq \Phi \leq 90°$, $15° \leq \varphi_2 \leq 30°$ (e) $50° \leq \Phi \leq 90°$, $0° \leq \varphi_2 \leq 15°$.

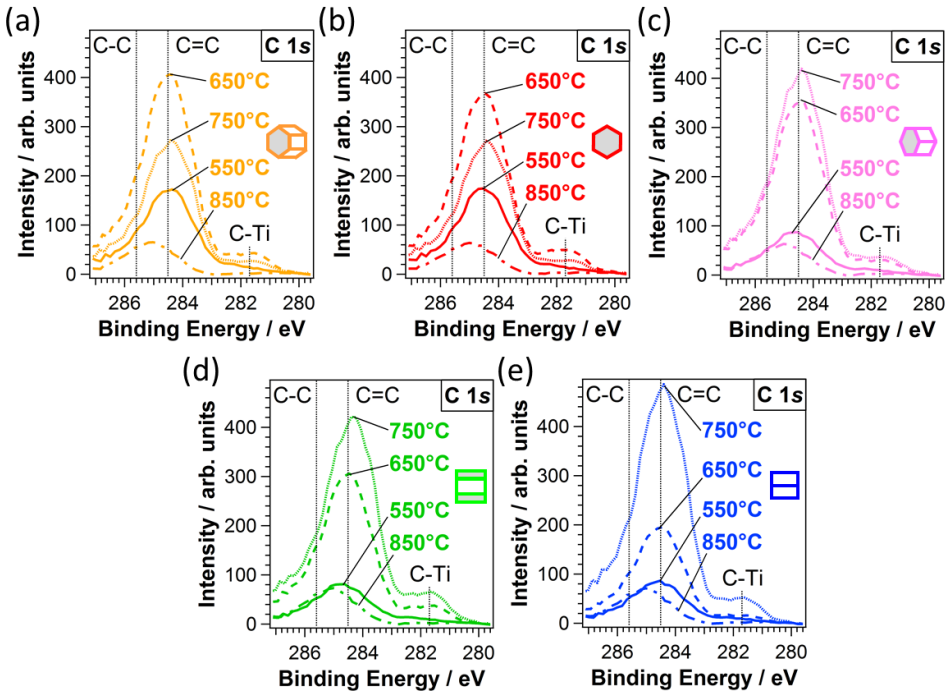

Figure S2. XP spectra from C 1*s* photoelectron micrographs taken of TiOC on top of five differently oriented substrate grains for the four annealing temperatures. The substrate orientations are (a) $15° \leq \Phi \leq 40°$, $0° \leq \varphi_2 \leq 30°$, (b) $0° \leq \Phi \leq 15°$, $0° \leq \varphi_2 \leq 30°$ (c) $40° \leq \Phi \leq 50°$, $0° \leq \varphi_2 \leq 30°$, (d) $50° \leq \Phi \leq 90°$, $15° \leq \varphi_2 \leq 30°$ (e) $50° \leq \Phi \leq 90°$, $0° \leq \varphi_2 \leq 15°$.

Additional information on micro-Raman spectroscopy

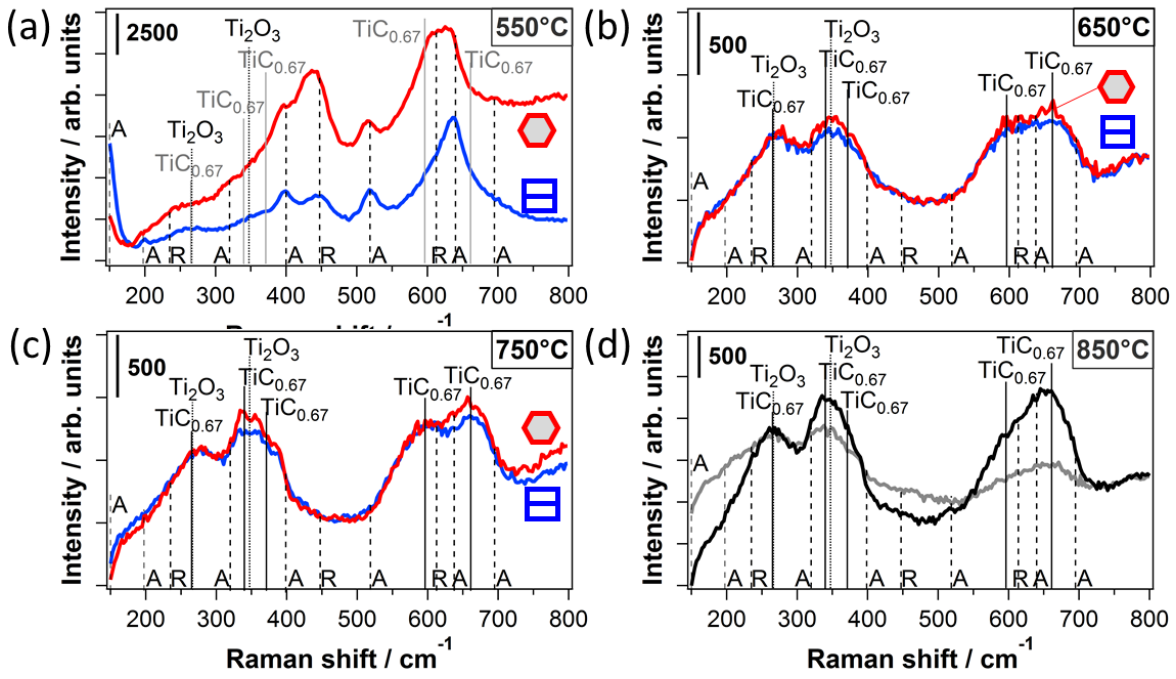

Figure S3. Micro-Raman spectra of (a) $TiOC_{550}$, (b) $TiOC_{650}$ and (c) $TiOC_{750}$ on top of ~Ti{10$\bar{1}$0} and ~Ti(0001). (d) Micro-Raman spectra of two spots on $TiOC_{850}$ with different optical appearance. Baseline correction: constant shift to a common level.