

Supporting information

Anomalous electrochemical capacitance in Mott-insulator titanium sesquioxide

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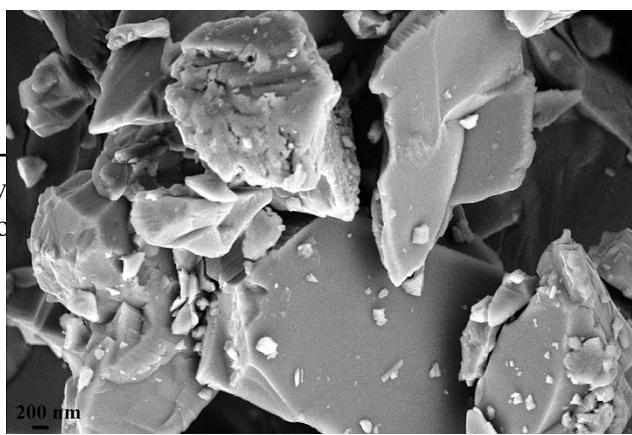


Figure S1. SEM image of as - purchased granular powder of Ti_2O_3 .

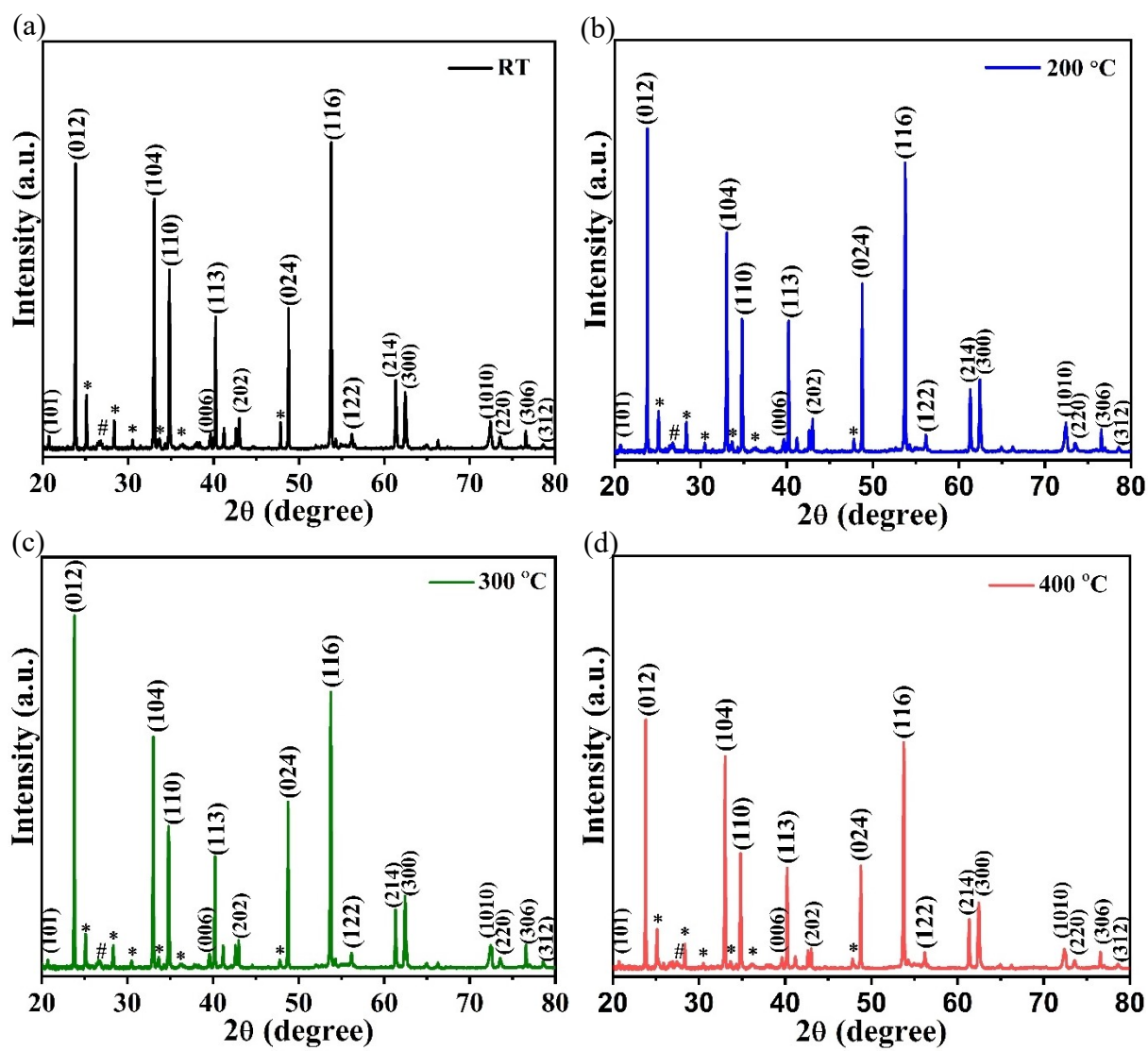


Figure S2. XRD spectra of (a) pristine Ti_2O_3 and after annealing at (b) 200 °C, (c) 300 °C and (d) 400 °C.

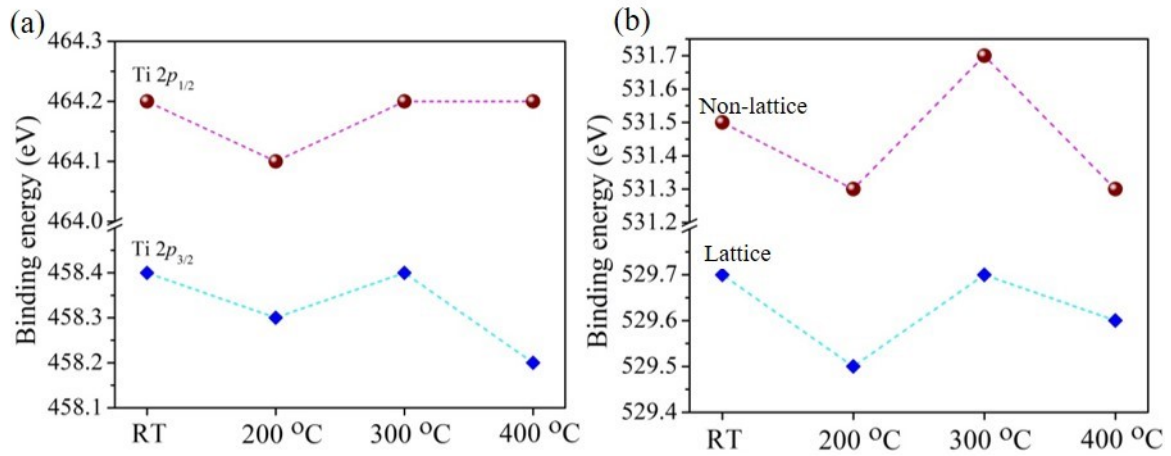


Figure S3. The change of binding energy for (a) Ti and (b) O as a function of the annealing temperature.

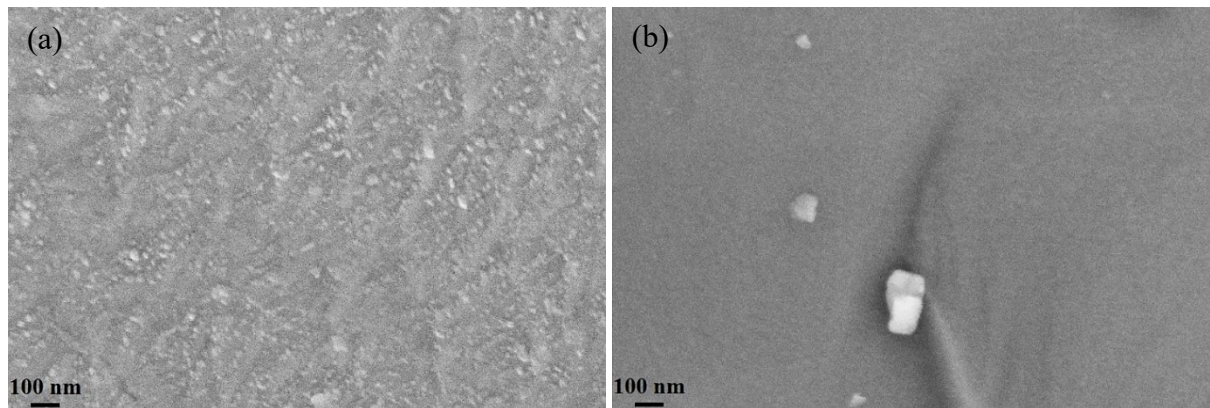


Figure S4. Surface morphology of Ti_2O_3 annealed at (a) 200 °C and (b) 300 °C.

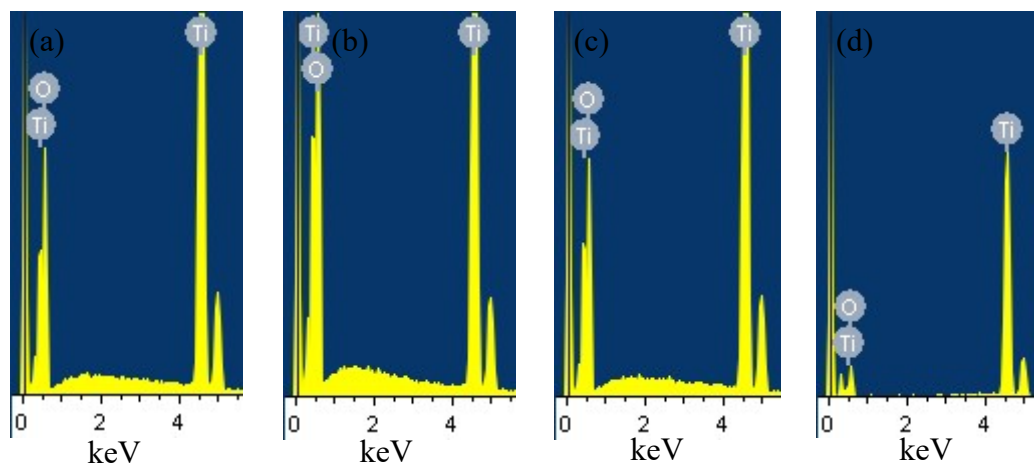


Figure S5. Energy dispersive X - ray analysis for the samples at (a) RT, annealed at (b) 200 °C, (c) 300 °C, and (d) 400 °C.

Theoretical Details:

All the calculations have been performed within the framework of plane - wave density functional theory (PW - DFT), implemented in the Vienna ab - initio simulation package (VASP).[1,2] A very popular and reliable hybrid functional (i.e. Heyd - Scuseria - Ernzerhof (HSE06)) has been used in the present work, thereby making our results on the bandgap and other electronic properties quite accurate.[3] In these calculations mixing parameter (α) of 25% and a screening parameter of 0.2 \AA^{-1} have been used. To obtain the total charge density for orthorhombic Ti_2O_3 , a Monkhorst - Pack scheme has been adopted for self - consistent - field (SCF) calculations employing a coarse grid composed of a $7 \times 7 \times 7$ k - point mesh. All the calculations have been done with the experimental value of lattice constants.

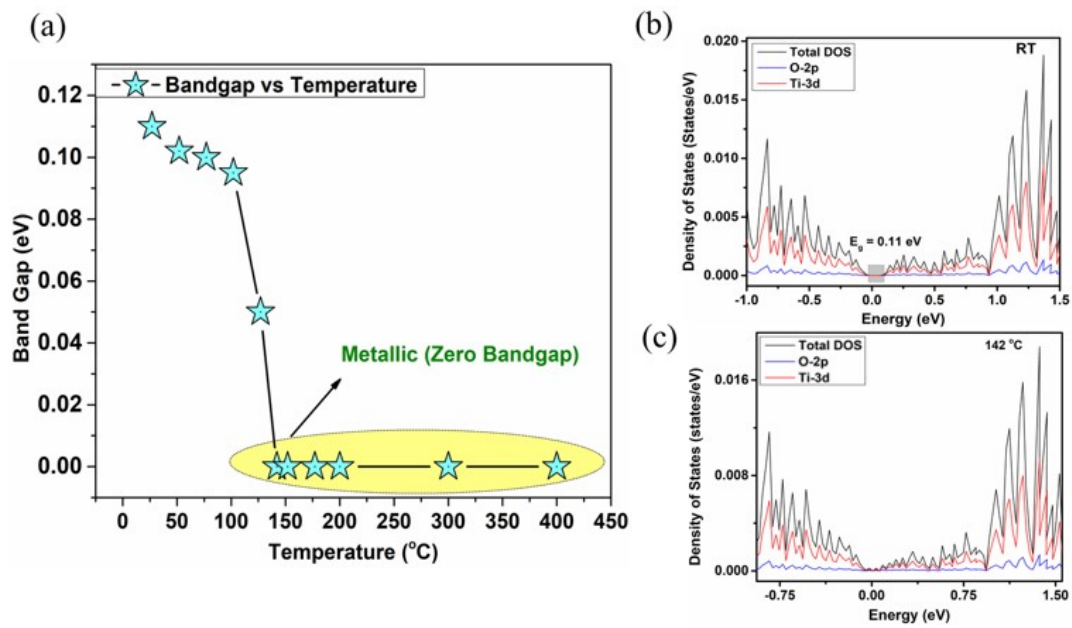


Figure S6. (a) Calculated band gap as a function of temperature exhibits a metallic-to-insulator transition around 142 °C. DOS of Ti and O along with TDOS at (b) RT and at (c) 142 °C

Table- S1: Bader charge calculations of Ti atoms in Ti₂O₃

Atoms	RT	152 °C	77 °C	102 °C	127 °C	142 °C	152 °C	177 °C	200 °C	300 °C	400 °C
Ti1	3.001	3.002	3.006	3.026	3.076	3.1	3.113	3.212	3.245	3.259	3.296
Ti2	3.002	3.004	3.008	3.008	3.088	3.131	3.167	3.234	3.267	3.302	3.375
Ti3	3.001	3.006	3.011	3.011	3.112	3.116	3.167	3.271	3.298	3.312	3.412
Ti4	3.001	3.002	3.012	3.052	3.125	3.265	3.298	3.321	3.356	3.378	3.432
Ti5	3.003	3.003	3.045	3.085	3.155	3.378	3.388	3.412	3.423	3.444	3.464
Ti6	3.001	3.004	3.01	3.01	3.01	3.003	3.001	3.002	3.004	3.005	3.001
Ti7	3.002	3.006	3.009	3.009	3.001	3.002	3.001	3.004	3.003	3.005	3.002
Ti8	3.001	3.005	3.002	3.012	3.011	3.006	3.004	3.005	3.006	3.002	3.001
Ti9	3.003	3.009	3.005	3.015	3.009	3.005	3.005	3.007	3.005	3.004	3.003
Ti10	3.001	3.003	3.007	3.017	3.005	3.005	3.006	3.002	3.001	3.004	3.004
Ti11	3.002	3.003	3.006	3.016	3.003	3.001	3.001	3.005	3.002	3.005	3.006
Ti12	3.004	3.004	3.01	3.01	3.01	3.004	3.006	3.008	3.007	3.006	3.007
Ti13	3.001	3.008	3.004	3.014	3.014	3.006	3.011	3.012	3.011	3.01	3.003
Ti14	3.002	3.006	3.003	3.013	3.013	3.014	3.013	3.025	3.02	3.019	3.014
Ti15	3.001	3.008	3.005	3.015	3.015	3.009	3.012	3.014	3.016	3.012	3.017
Ti16	3.004	3.004	3.007	3.017	3.017	3.004	3.009	3.011	3.008	3.005	3.012
Ti17	3	3.002	3.048	3.098	3.118	3.153	3.184	3.21	3.234	3.312	3.351
Ti18	3.001	3.001	3.012	3.012	3.112	3.125	3.198	3.32	3.334	3.342	3.41
Ti19	3.001	3.002	3.017	3.017	3.127	3.156	3.178	3.195	3.199	3.226	3.237
Ti20	3.001	3.004	3.053	3.103	3.123	3.217	3.231	3.421	3.434	3.448	3.456
Ti21	3.004	3.004	3.025	3.125	3.145	3.156	3.167	3.256	3.278	3.298	3.378
Ti22	3.001	3.001	3.002	3.001	3.002	3.01	3.004	3.003	3.001	3.004	3.005
Ti23	3.005	3.004	3.009	3.003	3.006	3.004	3.005	3.004	3.002	3.007	3.008
Ti24	3.001	3.001	3.004	3.006	3.004	3.006	3.005	3.003	3.005	3.006	3.005
Ti25	3.003	3.007	3.001	3.01	3.001	3.003	3.002	3.005	3.001	3.004	3.007
Ti26	3.001	3.003	3.011	3.008	3.005	3.007	3.004	3.002	3.002	3.005	3.009
Ti27	3.002	3.002	3.007	3.011	3.005	3.005	3.004	3.001	3.006	3.005	3.005
Ti28	3.003	3.003	3.002	3.011	3.01	3.001	3.006	3.009	3.004	3.003	3.012
Ti29	3.001	3.001	3.003	3.017	3.017	3.003	3.008	3.011	3.001	3.002	3.015
Ti30	3.002	3.007	3.009	3.007	3.009	3.006	3.008	3.005	3.006	3.005	3.018
Ti31	3.001	3.005	3.011	3.01	3.005	3.004	3.016	3.014	3.017	3.018	3.019
Ti32	3.002	3.007	3.013	3.013	3.006	3.012	3.013	3.014	3.019	3.022	3.023

Bold letter with black colour represents the value of charge density of surface Ti – atoms, while bold letter with red colour represents the sharp increase in the value of charge density of surface Ti – atoms.

Table- S2: Bader charge calculations of O atoms in Ti₂O₃

Atoms	RT	152 °C	77 °C	102 °C	127 °C	142 °C	152 °C	177 °C	200 °C	300 °C	400 °C
O1	2.001	2.002	2.001	2.003	2.003	2.001	2.002	2.003	2.003	2.002	2.004
O2	2.003	2.007	2.006	2.005	2.009	2.002	2.007	2.003	2.005	2.003	2.003
O3	2.005	2.003	2.001	2.002	2.003	2.005	2.003	2.004	2.005	2.003	2.005
O4	2.001	2.001	2.002	2.001	2.002	2.005	2.001	2.011	2.001	2.002	2.01
O5	2.001	2.001	2.004	2.004	2.007	2.003	2.001	2.003	2.007	2.001	2.002
O6	2.001	2.004	2.003	2.005	2.003	2.006	2.004	2.003	2.005	2.003	2.013
O7	2.001	2.001	2.002	2.004	2.006	2.004	2.001	2.002	2.009	2.001	2.008
O8	2.001	2.003	2.001	2.004	2.008	2.003	2.003	2.005	2.004	2.003	2.008
O9	2.002	2.002	2.003	2.006	2.003	2.003	2.002	2.001	2.001	2.002	2.005
O10	2.002	2.006	2.005	2.003	2.007	2.005	2.006	2.004	2.003	2.005	2.006
O11	2.001	2.001	2.003	2.001	2.005	2.002	2.001	2.006	2.006	2.001	2.004
O12	2.001	2.008	2.006	2.002	2.004	2.002	2.008	2.003	2.002	2.008	2.003
O13	2.001	2.002	2.003	2.006	2.007	2.005	2.002	2.003	2.006	2.002	2.001
O14	2.002	2.003	2.004	2.005	2.004	2.004	2.003	2.004	2.004	2.003	2.004
O15	2.001	2.003	2.005	2.002	2.007	2.002	2.003	2.006	2.006	2.006	2.008
O16	2.002	2.003	2.006	2.004	2.004	2.004	2.003	2.002	2.007	2.003	2.002
O17	2	2.002	2.003	2.006	2.008	2.005	2.002	2.001	2.009	2.002	2.002
O18	2.001	2.003	2.002	2.006	2.004	2.004	2.003	2.002	2.003	2.007	2.002
O19	2.003	2.004	2.003	2.004	2.005	2.005	2.004	2.003	2.002	2.004	2.006
O20	2.001	2.002	2	2.003	2.003	2.001	2.002	2.004	2.003	2.002	2.004
O21	2	2.002	2.003	2.005	2.008	2.006	2.002	2.003	2.006	2.002	2.005
O22	2.002	2.004	2.005	2.006	2.003	2.008	2.004	2.001	2.006	2.004	2.001
O23	2.001	2.005	2.003	2.005	2.007	2.004	2.005	2.004	2.004	2.005	2.005
O24	2.001	2.005	2.002	2.007	2.008	2.005	2.005	2.003	2.006	2.005	2.003
O25	2.002	2.003	2.006	2.002	2.004	2.003	2.003	2.005	2.002	2.003	2.005
O26	2.002	2.004	2.003	2.006	2.007	2.006	2.004	2.003	2.005	2.005	2.004
O27	2.001	2.005	2.003	2.005	2.006	2.005	2.005	2.003	2.005	2.005	2.01
O28	2.002	2.001	2.005	2.005	2.004	2.004	2.001	2.001	2.008	2.001	2.001
O29	2.001	2.003	2.002	2.002	2.004	2.008	2.003	2.005	2.002	2.001	2.016
O30	2.003	2.004	2.005	2.008	2.007	2.005	2.004	2.003	2.005	2.004	2.003
O31	2.001	2.006	2.003	2.005	2.009	2.002	2.006	2.002	2.005	2.006	2.011

O32	2.002	2.004	2.007	2.002	2.003	2.002	2.004	2.003	2.003	2.007	2.003
O33	2.002	2.003	2.004	2.009	2.002	2.003	2.003	2.004	2.007	2.003	2.012
O34	2.001	2.002	2.001	2.008	2.008	2.007	2.002	2.005	2.005	2.002	2.005
O35	2.002	2.003	2.007	2.007	2.001	2.007	2.003	2.002	2.007	2.006	2.003
O36	2.001	2.001	2.004	2.002	2.009	2.003	2.001	2.004	2.002	2.001	2.004
O37	2.003	2.005	2.002	2.004	2.004	2.003	2.005	2.001	2.005	2.001	2.005
O38	2.001	2.003	2.005	2.001	2.006	2.004	2.003	2.005	2.001	2.003	2.005
O39	2.001	2.005	2.006	2.002	2.004	2.001	2.005	2.004	2.002	2.002	2.005
O40	2.004	2.005	2.003	2.004	2.007	2.009	2.005	2.003	2.007	2.005	2.003
O41	2.005	2.002	2.001	2.005	2.001	2.006	2.002	2.003	2.005	2.002	2.006
O42	2.001	2.003	2.007	2.007	2.005	2.006	2.003	2.002	2.003	2.001	2.002
O43	2.006	2.007	2.004	2.008	2.008	2.008	2.007	2.002	2.003	2.007	2.002
O44	2.001	2.002	2.006	2.006	2.006	2.008	2.002	2.003	2.005	2.012	2.003
O45	2.001	2.003	2.005	2.002	2.005	2.001	2.003	2.001	2.002	2.003	2.008
O46	2.002	2.004	2.002	2.007	2.003	2.008	2.004	2.001	2.004	2.001	2.001
O47	2.004	2.005	2.003	2.006	2.006	2.005	2.005	2.005	2.008	2.015	2.004
O48	2.006	2.007	2.002	2.008	2.009	2.006	2.006	2.003	2.006	2.007	2.005

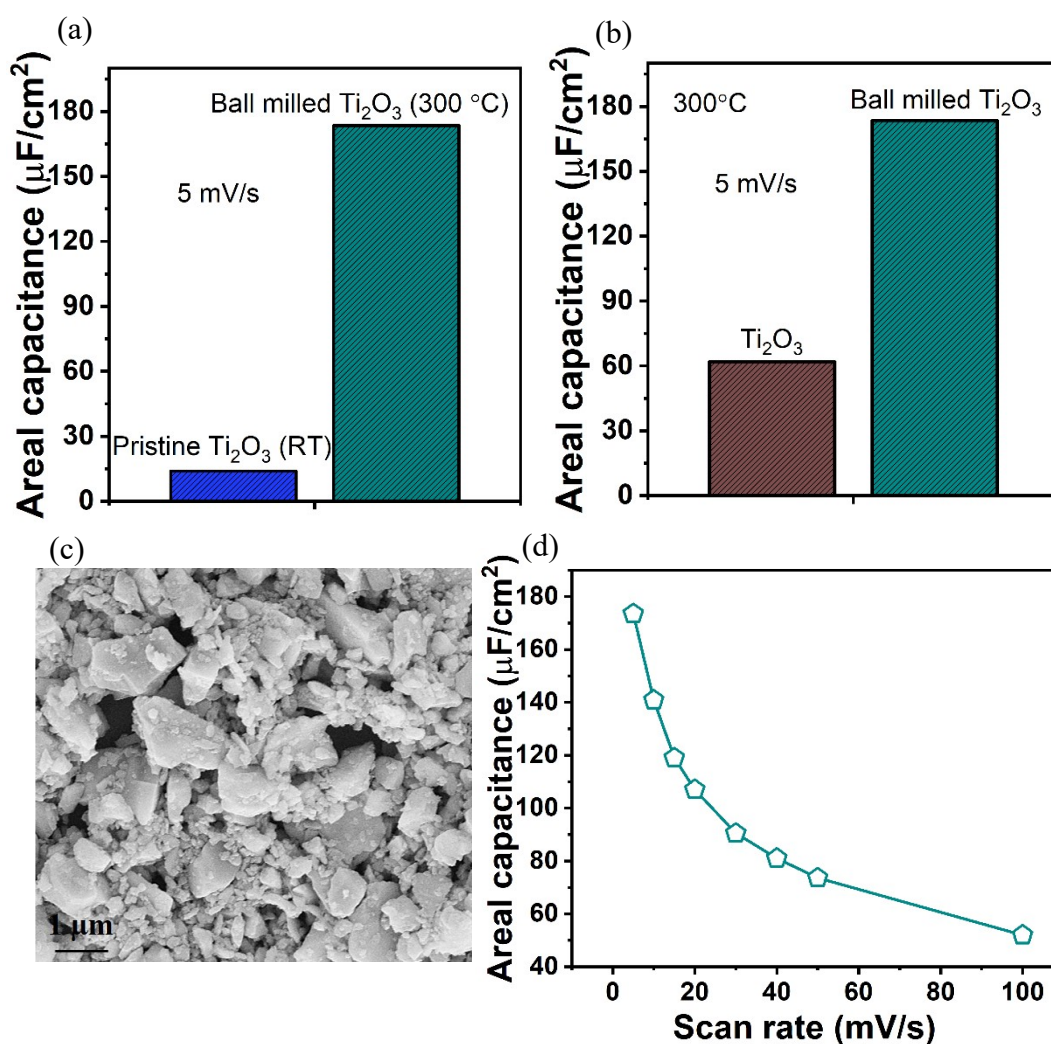


Figure S7. (a) Areal capacitance comparison between pristine Ti_2O_3 and ball - milled Ti_2O_3 devices annealed at 300°C at 5 mV/s scan rate extracted from CV curve. (b) Areal capacitance comparison between Ti_2O_3 and ball - milled Ti_2O_3 devices, both annealed at 300°C at 5 mV/s scan rate extracted from CV curve. (c) SEM image of ball-milled Ti_2O_3 . (d) Areal capacitance plotted against scan rates of the ball - milled Ti_2O_3 device annealed at 300°C .

Ball-milling condition: Bill-milling of granular Ti_2O_3 performed at 300 rpm for 12 h in the ethanol solution.

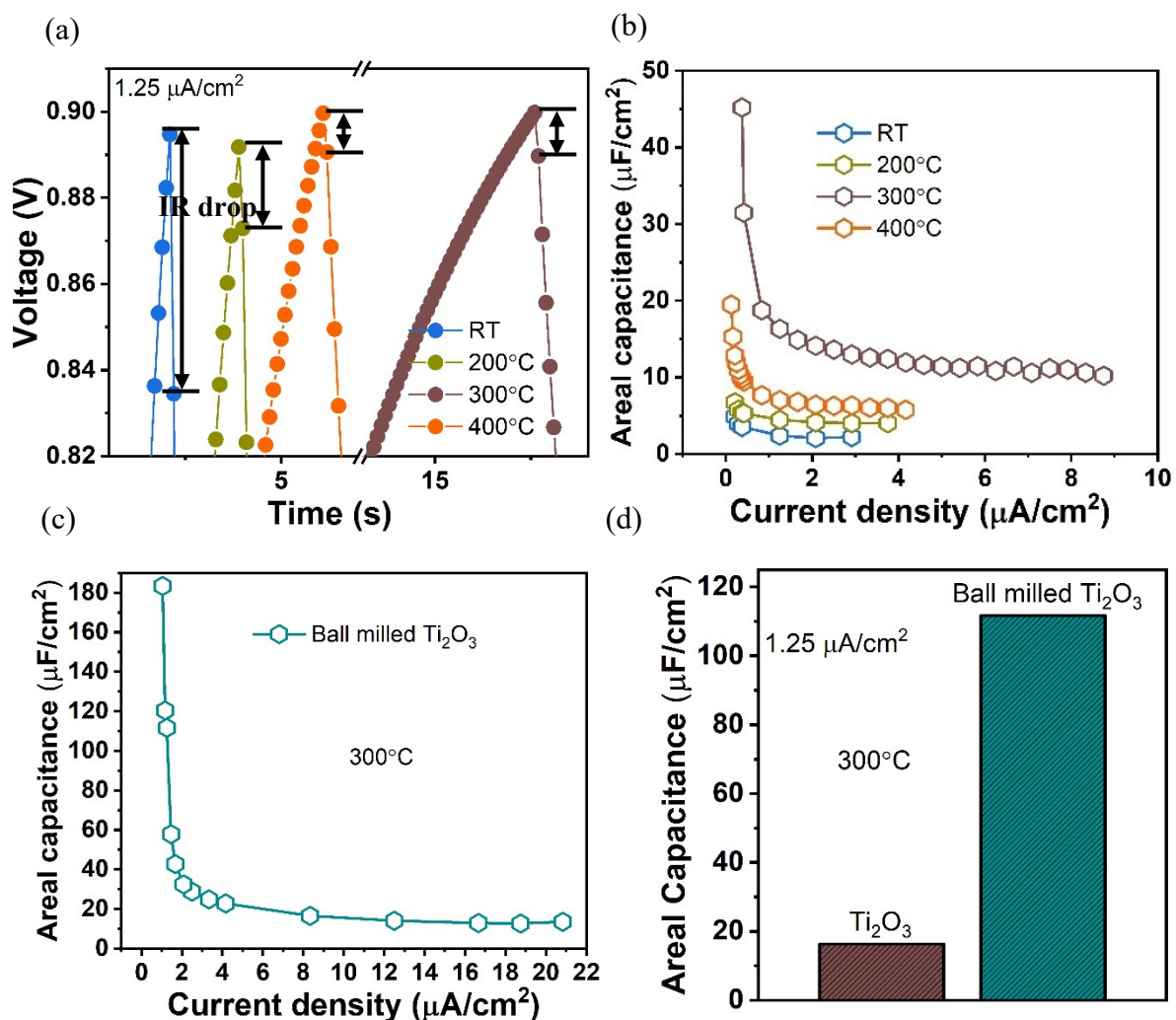


Figure S8. (a) IR drop or voltage drop at the beginning of the discharge curve at $1.25 \mu\text{A}/\text{cm}^2$ applied current density of all the Ti_2O_3 devices obtained from the charge - discharge curve. (b) Areal capacitance plotted against current densities for all the Ti_2O_3 devices extracted from the charge - discharge curve. (c) Areal capacitance plotted against current densities for ball - milled Ti_2O_3 device annealed at 300°C . (d) Areal capacitance comparison of Ti_2O_3 and ball - milled Ti_2O_3 devices both annealed at 300°C at $1.25 \mu\text{A}/\text{cm}^2$ current density.

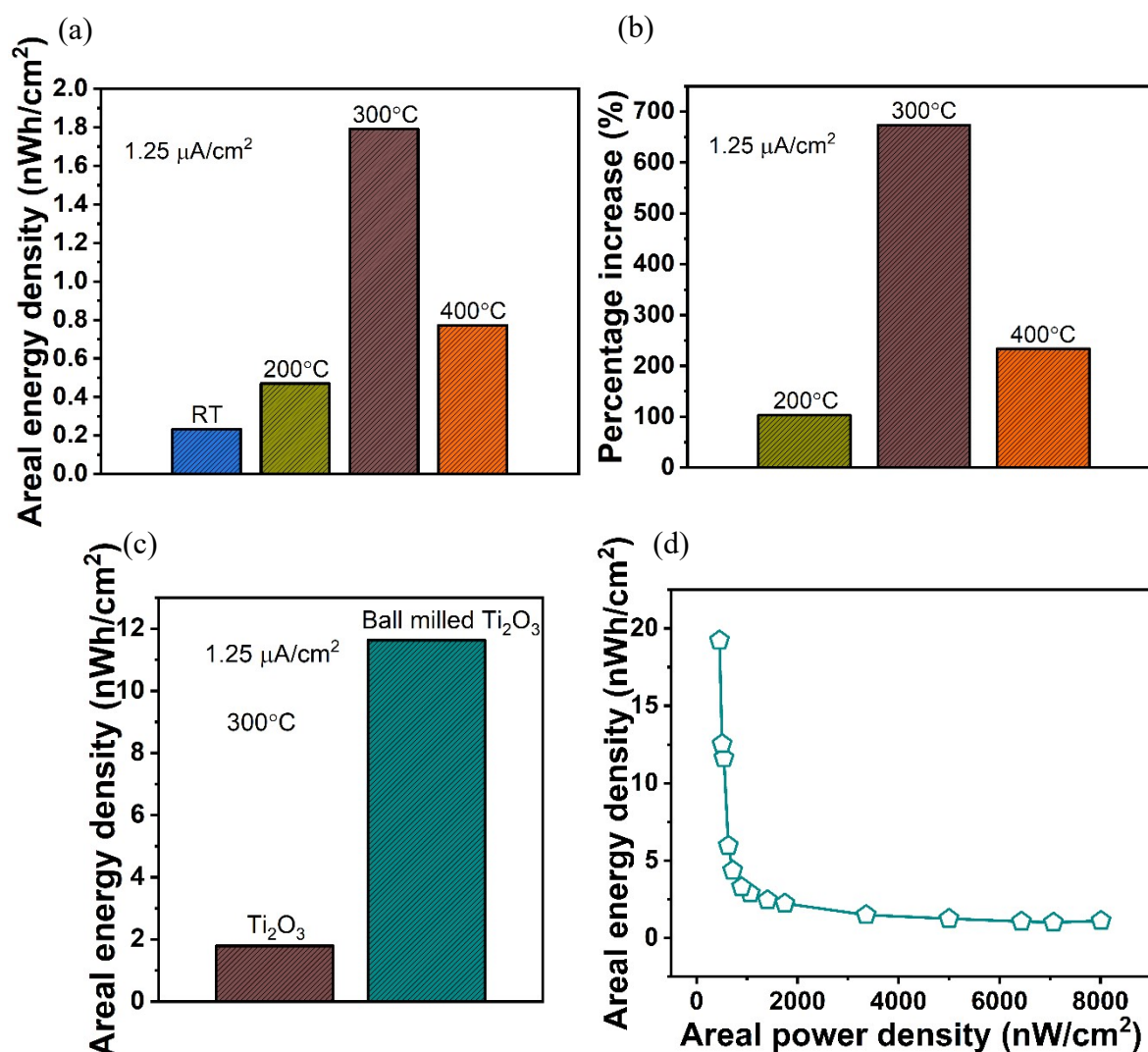


Figure S9. (a) Areal energy density of all the Ti_2O_3 devices compared at a current density of $1.25 \mu\text{A}/\text{cm}^2$. (b) Percentage increase in the energy density of the Ti_2O_3 devices annealed at

different temperatures with respect to pristine Ti_2O_3 device. (c) Areal energy density comparison of the Ti_2O_3 and ball-milled Ti_2O_3 devices both annealed at $300\text{ }^\circ\text{C}$ at a current density of $1.25\text{ }\mu\text{A}/\text{cm}^2$. (d) Areal energy density plotted against areal power density of the ball-milled Ti_2O_3 device annealed at $300\text{ }^\circ\text{C}$.

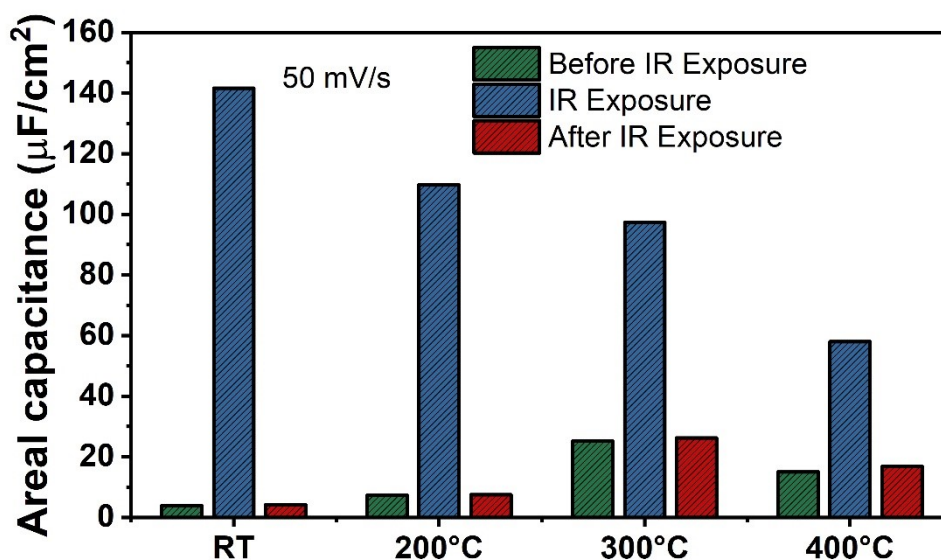


Figure S10. Areal capacitance comparison of Ti_2O_3 device annealed at different temperature including pristine one, upon IR exposure at three conditions before, at saturation and after exposure.

Electrode preparation for three-electrode measurements: The working electrode was prepared by adding 90 wt% of ball-milled Ti_2O_3 powder (annealed at $300\text{ }^\circ\text{C}$) in ethanol solvent (10 ml) followed by 4h of sonication. After that 10 wt% of Polyvinylidene fluoride (PVDF) was added to the solution and stirred for 6h. The homogeneous mixture was spray-coated on a cleaned stainless steel substrate using argon gas at $120\text{ }^\circ\text{C}$. The material-coated electrode was dried at $80\text{ }^\circ\text{C}$ for 12h and area of the electrode was $\sim 1 \times 2.5\text{ cm}^2$ with a mass loading of $1.5\text{ mg}/\text{cm}^2$. The capacitance measurements were done using $1\text{M H}_3\text{PO}_4$ aqueous solution as the electrolyte in a three-electrode cell, containing a Pt wire as a counter electrode, a saturated

Ag/AgCl electrode as a reference electrode, and the as-prepared material-coated stainless steel as the working electrode.

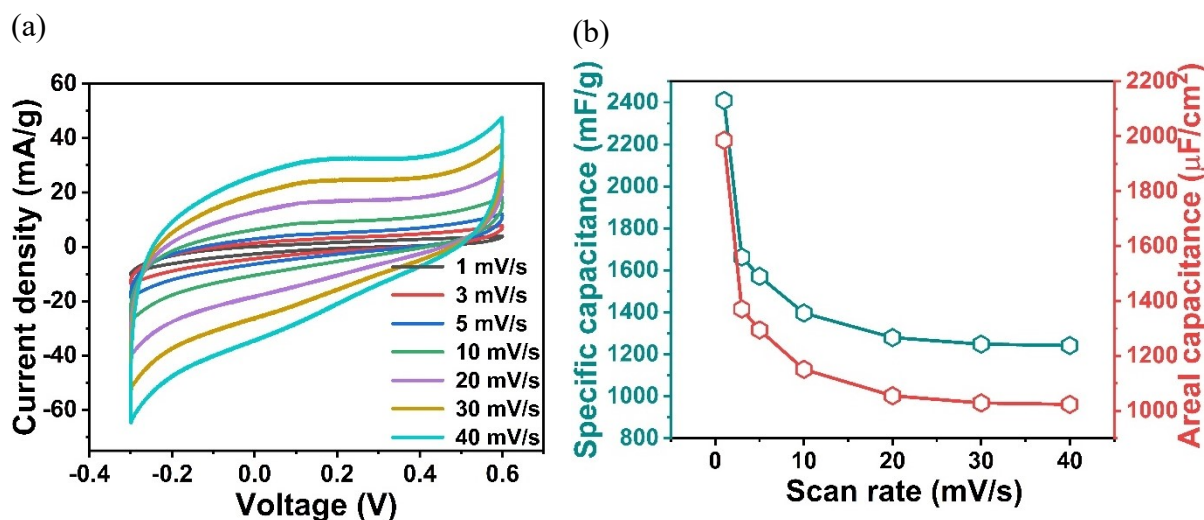


Figure S11. (a) CV curves of the ball-milled Ti_2O_3 (annealed at 300°C) electrode in three-electrode measurement using 1 M H_3PO_4 electrolyte solution. (b) Specific capacitance and areal capacitance are plotted as a function of scan rates.

References:

- [1] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15–50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
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