Formation Mechanisms of the Interfaces between Different Ti_nO_{2n-1} Phases Prepared by Carbothermal Reduction Reaction

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Supplementary Materials

1. XRD and TEM characterization results of anatase precursor, carbon black and the ball-milled samples.

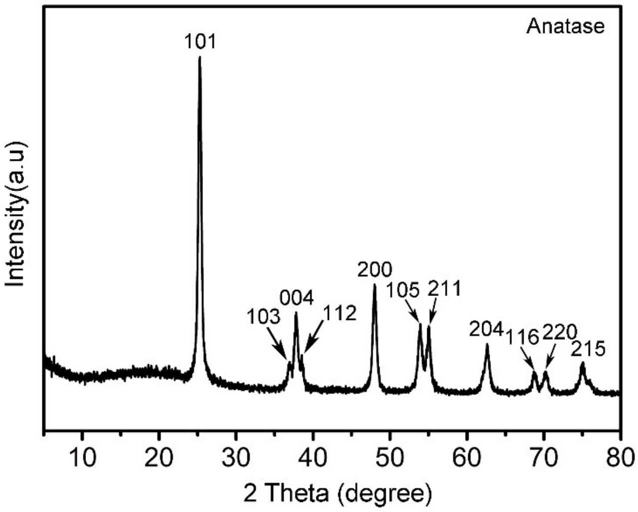

Fig. S1 The XRD spectrum of anatase precursor.

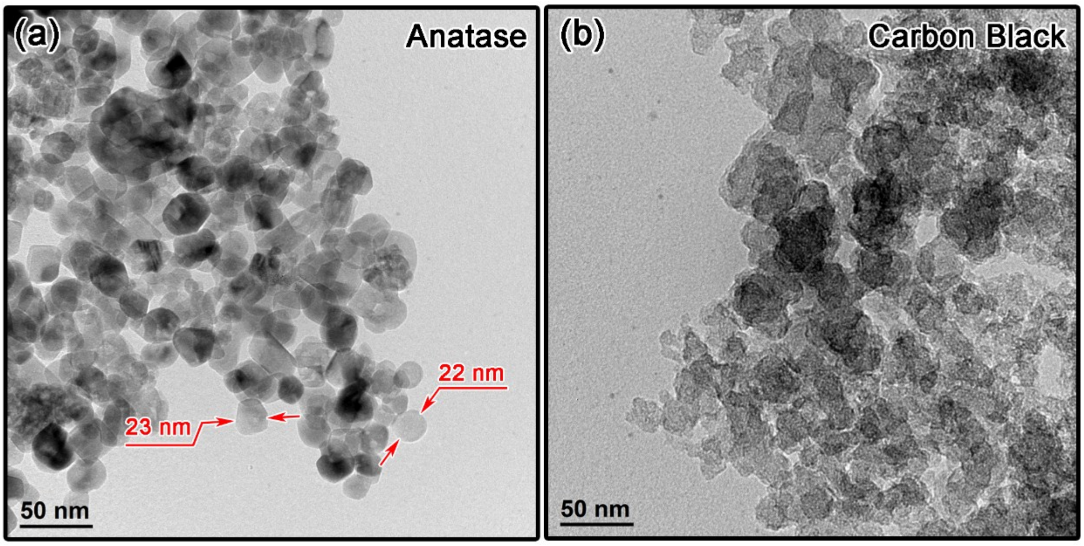

Fig. S2 The TEM BF images of anatase precursor and carbon black particles.

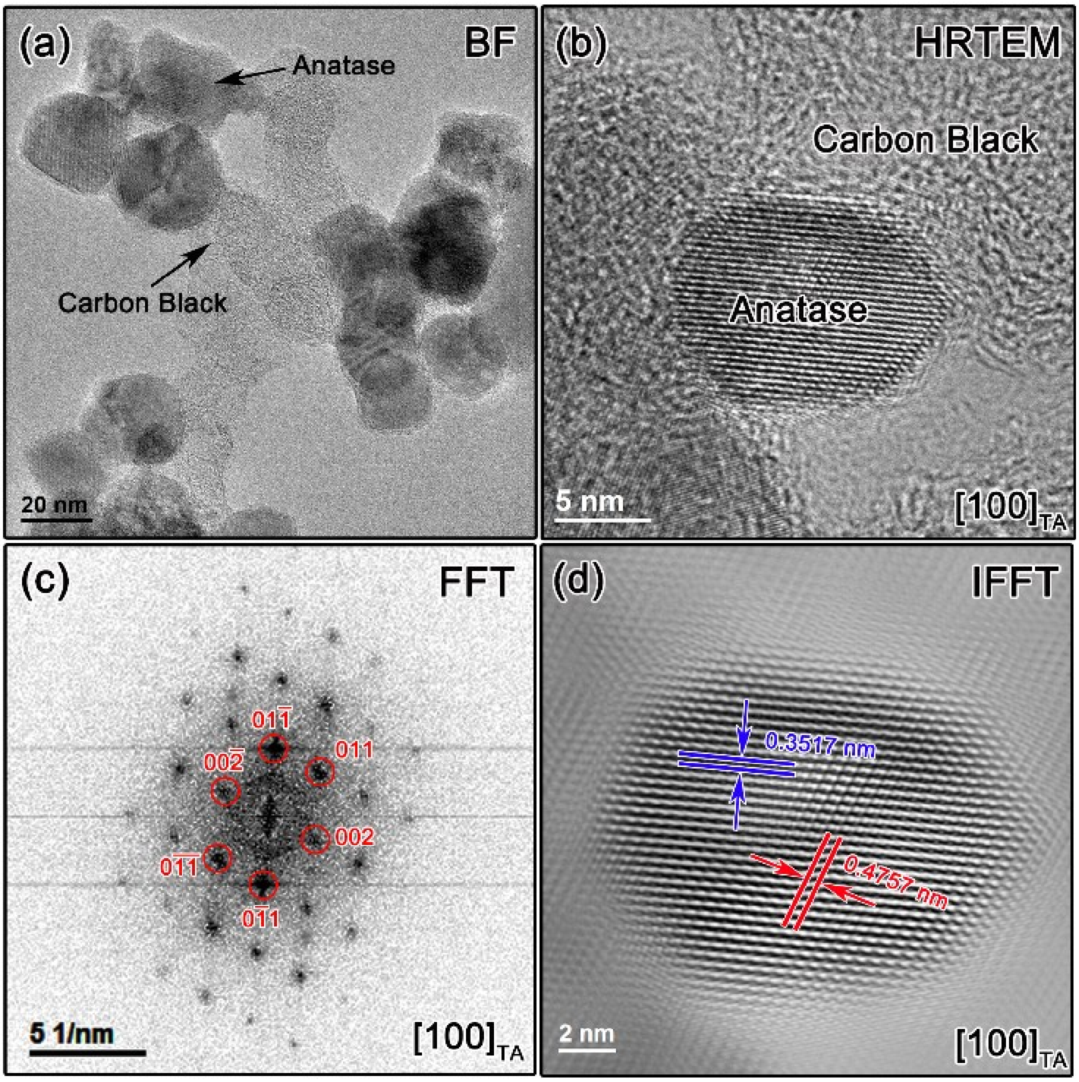

Fig. S3 TEM BF (a) and HRTEM images (b) of the ball-milled samples. The corresponding FFT (c) and IFFT image (d) show excellent crystalline status of the anatase nanoparticles.

2. The thermodynamic calculation methods of the Gibbs free energies

The calculation of chemical equilibrium by using the standard reaction heat effect is normally based on the Gibbs-Helmholtz equation:

$$d\left(\frac{\Delta G_T^{\ominus}}{T}\right) = -\frac{\Delta H_T^{\ominus}}{T^2}dT \tag{S1}$$

In order to use Eq. S1, Kirchhoff equation need to be applied to obtain the relationship between the standard reaction heat effect and the temperature:

$$d\Delta H_T^{\ominus} = \Delta C_p dT \tag{S2}$$

Here, ΔC_p represents the difference between the molar heat capacity of the product and that of the reactant at constant pressure:

$$\Delta C_p = \Sigma(n_i C_{p,i})_{Product} - \Sigma(n_i C_{p,i})_{Reactant} \tag{S3}$$

The relationship between molar heat capacity and the temperature can be approximately expressed by the following equations:

$$C_p = A_1 + A_2 \times 10^{-3}T + A_3 \times 10^5 T^{-2} + A_4 \times 10^{-6}T^2 + A_5 \times 10^8 T^{-3} + A_6 \times T^{-0.5} \tag{S4}$$

Based on Eq. S3, ΔC_p can be expressed as follows:

$$\Delta C_p = \Delta A_1 + \Delta A_2 \times 10^{-3}T + \Delta A_3 \times 10^5 T^{-2} + \Delta A_4 \times 10^{-6}T^2 + \Delta A_5 \times 10^8 T^{-3} + \Delta A_6 \times T^{-0.5} \tag{S5}$$

By substituting Eq. S5 to Eq. S2 and make integral, $\Delta H_T^{\ominus}$ can be calculated accordingly:

$$\Delta H_T^{\ominus} = \Delta A_1 T + \frac{1}{2}\Delta A_2 \times 10^{-3}T^2 - \Delta A_3 \times 10^5 T^{-1} + \frac{1}{3}\Delta A_4 \times 10^{-6}T^3 + \frac{1}{2}\Delta A_5 \times 10^8 T^{-2} + 2\Delta A_6 \times T^{0.5} + A_7 \tag{S6}$$

If the standard molar enthalpy of formation for both products and reactants can be known, the standard heat effect of the reaction can be calculated:

$$\Delta H_{298}^{\ominus} = \Sigma(n_i \Delta H_{i,f,298}^{\ominus})_{Product} - \Sigma(n_i \Delta H_{i,f,298}^{\ominus})_{Reactant} \tag{S7}$$

By substituting the calculated $\Delta H_{298}^{\ominus}$ and T=298 K to Eq. S6, the integral constant A_7 can be calculated:

$$A_7 = \Delta H_{298}^{\ominus} - \Delta A_1 T - \frac{1}{2}\Delta A_2 \times 10^{-3}T^2 + \Delta A_3 \times 10^5 T^{-1} - \frac{1}{3}\Delta A_4 \times 10^{-6}T^3 + \frac{1}{2}\Delta A_5 \times 10^8 T^{-2}$$
$$- 2\Delta A_6 \times T^{0.5} \qquad \text{(S8)}$$

Then, Eq. S6 can be substituted to Eq. S1 followed by integral, the following equations can be obtained:

$$\frac{\Delta G_T^{\ominus}}{T} = -\int \frac{\Delta H_T^{\ominus}}{T^2} dT \qquad \text{(S9)}$$

$$\Delta G_T^{\ominus}$$
$$= -\Delta A_1 T lnT - \frac{1}{2}\Delta A_2 \times 10^{-3}T^2 - \frac{1}{2}\Delta A_3 \times 10^5 T^{-1} - \frac{1}{6}\Delta A_4 \times 10^{-6}T^3 - \frac{1}{6}\Delta A_5 \times 10^8 T^{-2} + 4\Delta$$
$$\times T^{0.5} + A_7 + TA_8$$

(S10)

Here, A_8 is defined to be the integral constant of Gibbs- Helmholtz equation. As the standard reaction heat effect and the standard reaction entropy at 298 K can be found from the database, the Gibbs free energy of reaction at 298 K can also be calculated through:

$$\Delta G_{298}^{\ominus} = \Delta H_{298}^{\ominus} - 298\Delta S_{298}^{\ominus} \qquad \text{(S11)}$$

By substituting $\Delta G_{298}^{\ominus}$ and T=298 K to Eq. S10, the integral constant A_8 can be calculated by the following equation:

$$A_8$$
$$= \frac{\Delta G_T^{\ominus}}{T} + \Delta A_1 lnT + \frac{1}{2}\Delta A_2 \times 10^{-3}T + \frac{1}{2}\Delta A_3 \times 10^5 T^{-2} + \frac{1}{6}\Delta A_4 \times 10^{-6}T^2 + \frac{1}{6}\Delta A_5 \times 10^8 T^{-}$$
$$A_6 \times T^{-0.5} - A_7 T^{-1}$$

(S12)

In this case, the Gibbs free energies under different temperatures can be calculated by using Eq. S10. Table S1 summarized the constant from A_1 to A_6 for the phases involved in the main text.

Table S1 Constants during the calculation of Gibbs free energies during the CRR

Phase	A_1	A_2	A_3	A_4	A_5	A_6	$\Delta_f H_{298}$ (J·mol^{-1})	ΔS_{298} (J·mol^{-1}·K^{-1})
TiO_2	75.019	0	-17.615	0	0	0	-933032	49.915
C	24.435	0.418	-31.631	0	0	0	0	5.732
CO	28.409	4.1	-0.46	0	0	0	-110541	197.527
CO_2	44.141	9.037	-8.535	0	0	0	-393505	213.635
$Ti_{10}O_{19}$	831.39283	0	-227.26564	0	22.730958	-2110.8923	-9085912.9	505.1
Ti_9O_{17}	753.55521	0	-193.58722	0	18.701551	-2110.8923	-8141241.7	453.8
Ti_8O_{15}	675.71769	0	-159.90881	0	14.672144	-2110.8923	-7196482.4	402.35
Ti_7O_{13}	597.87977	0	-126.2304	0	10.642738	-2110.8923	-6251589	350.6
Ti_6O_{11}	520.04235	0	-92.55199	0	6.613331	-2110.8923	-5306800	298.3
Ti_5O_9	442.20473	0	-58.87358	0	2.583924	-2110.8923	-4361900	245.7
Ti_4O_7	364.36711	0	-25.19517	0	-1.445482	-2110.8923	-3412700	195
Ti_3O_5	158.99208	50.20795	0	0	0	0	-2448268	155.4
Ti_2O_3	147.674	3.47423	-47.9085	0.0009203	0	0	-1510000	85.2
TiO	41.9948	17.8	-6.5403	-0.0658277	0	0	-540660	28