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Electronic Supporting Information

# A Kinetic Model for Two-Step Phase Transformation of Hydrothermally Treated Nanocrystalline Anatase

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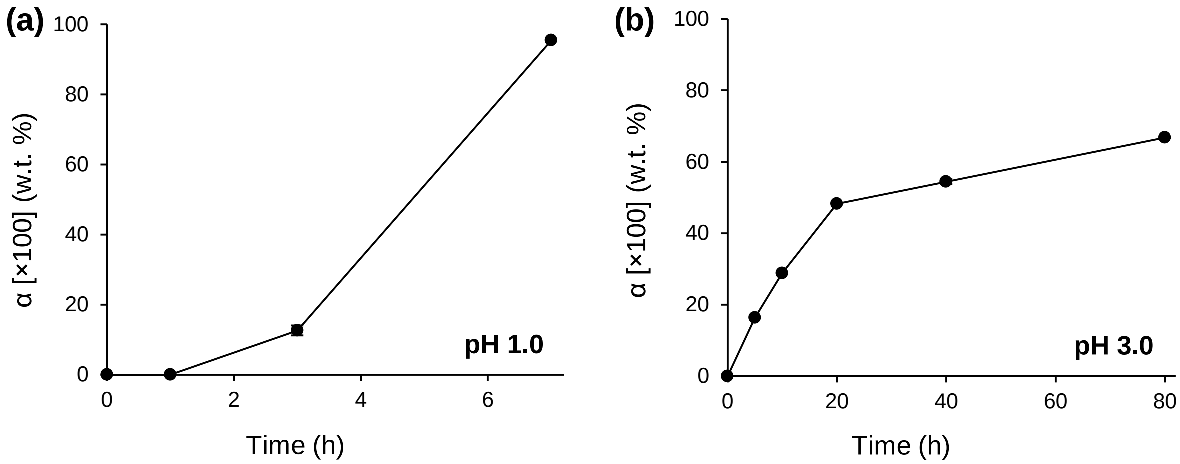


**Fig. S1** Weight percentage transformation as a function of aging time at pH 1.0 (a) and 3.0 (b).

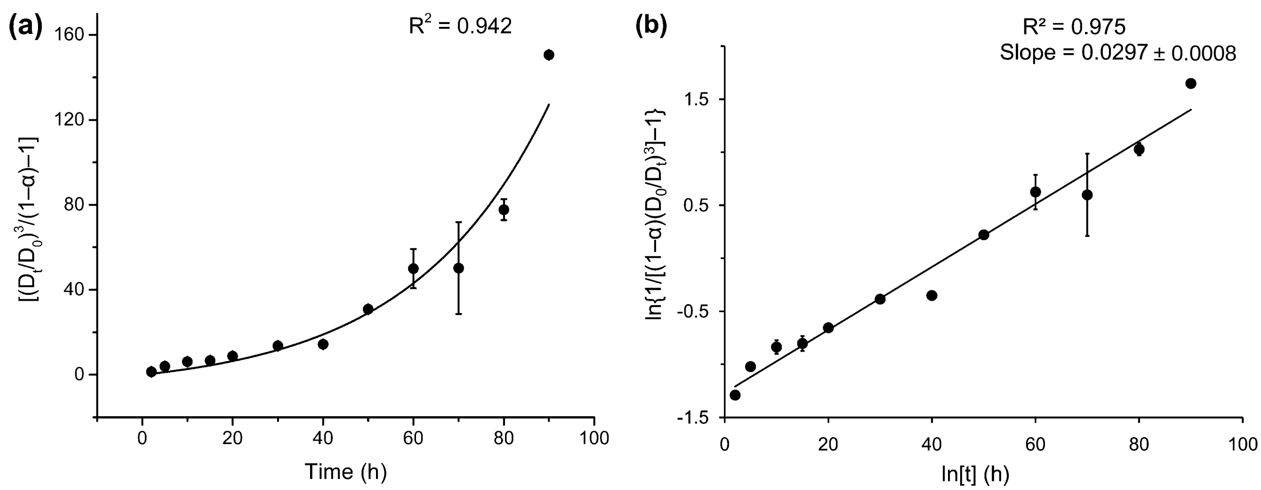


**Fig. S2** Plots presenting the application of combined kinetic model on anatase to rutile phase transformation at 200 °C and pH 1.0. Non-linear (a) and linear (b) regression curve fit performed on the experimental data using eqn 5 and 4, respectively. $R^2$ values are shown to indicate how well the data points fitted the equations.

**Derivation of combined kinetic model (eqn 4)**

It has been demonstrated that the kinetics of dissolution-precipitation (DP) and interface-nucleation (IN) are first and second order with respect to number of anatase nanoparticles ($N$),[1, 2] respectively. Subsequently, the combination of these two models can be expressed by the kinetic equation (eqn 3):

$$-\frac{dN}{dt} = k_{\mathrm{DP}}N + k_{\mathrm{IN}}N^2 \tag{3}$$

where $k_{\mathrm{DP}}$ and $k_{\mathrm{IN}}$ are rate constants for DP and IN, respectively. After rearranging the equation, eqn S1 is obtained:

$$-\frac{dN}{N} = k_{\mathrm{DP}}dt + k_{\mathrm{IN}}Ndt \tag{S1}$$

As $dt$ can be expressed in terms of $N$ according to the relation:

$$dt = -\frac{dN}{k_{\mathrm{DP}}N + k_{\mathrm{IN}}N^2} \tag{S2}$$

substituting $dt$ into the second term ($k_{\mathrm{IN}}Ndt$) of the eqn S1 and rearranging the equation lead to the following expression:

$$\frac{k_{\mathrm{IN}}dN}{k_{\mathrm{DP}} + k_{\mathrm{IN}}N} - \frac{dN}{N} = k_{\mathrm{DP}}dt \tag{S3}$$

Eqn S4 can be derived by integrating eqn S3 from $N_0$ to $N_t$ and from $t = 0$ to $t$ and rearranging it:

$$\ln\left[k_{\mathrm{DP}}\frac{N_0}{N_t} + k_{\mathrm{IN}}N_0\right] = k_{\mathrm{DP}}t + \ln(k_{\mathrm{DP}} + k_{\mathrm{IN}}N_0) \tag{S4}$$

Finally, the combined kinetic model (eqn 4) is derived by substituting $N_0/N_t$ of eqn S4 with right-hand-side of eqn S5 (the derivation of eqn S5 is presented in the reference article):[2]

$$\frac{N_0}{N_t} = \frac{(D_t / D_0)^3}{(1-\alpha)} \tag{S5}$$

**Derivation of percent ratio of $R_{\mathrm{IN}}$ to $R_{\mathrm{TOT}}$ (eqn 6)**

The percent ratio of the rate by IN ($R_{\mathrm{IN}}$) to the total rate ($R_{\mathrm{TOT}}$) can be expressed in terms of the following expression:

$$\frac{R_{\mathrm{IN}}}{R_{\mathrm{TOT}}} \cdot 100 = \frac{k_{\mathrm{IN}}N_t^{\,2}}{k_{\mathrm{DP}}N_t + k_{\mathrm{IN}}N_t^{\,2}} \cdot 100 \tag{S6}$$

Then, the final form of the percent ratio (eqn 6) can be derived from eqn S6 using eqn S5 and eqn 5 as follows:

$$\frac{R_{\mathrm{IN}}}{R_{\mathrm{TOT}}}\cdot 100=\frac{k_{\mathrm{IN}}}{\frac{k_{\mathrm{DP}}}{N_t}+k_{\mathrm{IN}}}\cdot 100=\frac{k_{\mathrm{IN}}}{\frac{k_{\mathrm{DP}}}{N_0}\left[\frac{N_0}{N_t}\right]+k_{\mathrm{IN}}}\cdot 100=\frac{k_{\mathrm{IN}}}{\frac{k_{\mathrm{DP}}}{N_0}\left[\frac{(D_t/D_0)^3}{1-\alpha}\right]+k_{\mathrm{IN}}}\cdot 100=$$

$$=\frac{k_{\mathrm{IN}}}{\frac{k_{\mathrm{DP}}}{N_0}\left[\left(1+\frac{k_{\mathrm{IN}}N_0}{k_{\mathrm{DP}}}\right)(e^{k_{\mathrm{DP}}t}-1)+1\right]+k_{\mathrm{IN}}}\cdot 100=\frac{k_{\mathrm{IN}}}{\left[\frac{k_{\mathrm{DP}}\cdot e^{k_{\mathrm{DP}}t}}{N_0}+k_{\mathrm{IN}}\cdot e^{k_{\mathrm{DP}}t}\right]}\cdot 100=\frac{k_{\mathrm{IN}}N_0\cdot e^{-k_{\mathrm{DP}}t}}{(k_{\mathrm{DP}}+k_{\mathrm{IN}}N_0)}\cdot 100$$

**References**


1 K. Sabyrov, N. D. Burrows and R. L. Penn, *Chem. Mater.*, 2012, **25**, 1408-1415.

2 H. Zhang and J. F. Banfield, *Am. Mineral.*, 1999, **84**, 528-535.