Electronic Supplementary Information

Experimental

For the Scherrer analysis, XRD peaks were fitted with a Lorentzian peak shape using fitting software (Fityk, version 0.9.2). In the case of the (004) diffraction peak, the neighbouring signals of the two satellite peaks at 2Θ= 37.2° and 2Θ=38.8° for the (103) and (112) crystal domains, respectively, were included in the fit, since the overlap of the three peaks is significant for the small particles sizes in the current study (for an example see Figure S1). Although, the large degree of overlap between the three peaks and the low intensity of the two satellites render reliable fitting challenging, the resulting FWHM of the fitted (004) diffraction peak can be used for Scherrer analysis and hence semi-quantitative comparison between samples.

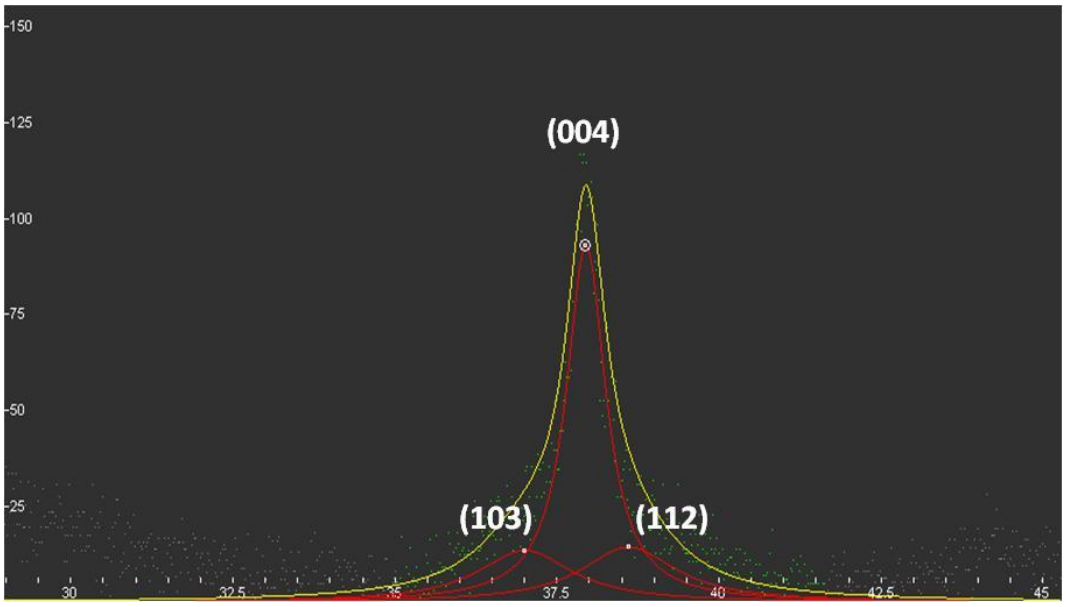

Figure S1. Fit of the (004) XRD peak and its two satellite peaks for the product of the standard reaction (Reaction 3). The peaks were fitted with Lorentzians and the FWHM of the (004) peak used to calculate the corresponding crystal domain size discussed in the main text.

Results and discussion

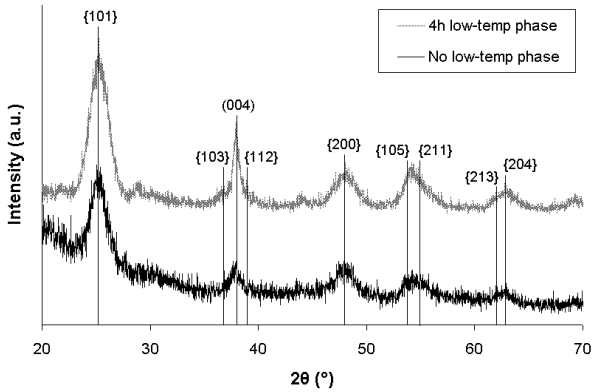

Figure S2. XRD spectra of products after reaction with the initial low-temperature phase lasting 0 and 4 hours, respectively, and the high-temperature stage lasting 4 h (Reactions 4 and 3, respectively)

The XRD spectra of the two limiting samples ('zero-hour' sample, i.e. Reaction 4, and 'four-hour' sample, i.e. Reaction 3) indicate the presence of anatase TiO_2 in both materials. However, the broad background peak in the XRD spectrum of the 'zero hour sample' is consistent with a significant fraction of amorphous TiO_2, as observed by TEM. From the width of the (004) and (200) peaks of the XRD spectra, crystallite domain sizes were calculated to be 10 nm and 4 nm, respectively, for the 'zero-hour' sample, and correspondingly, 21 nm and 4 nm for the 'four-hour' sample.

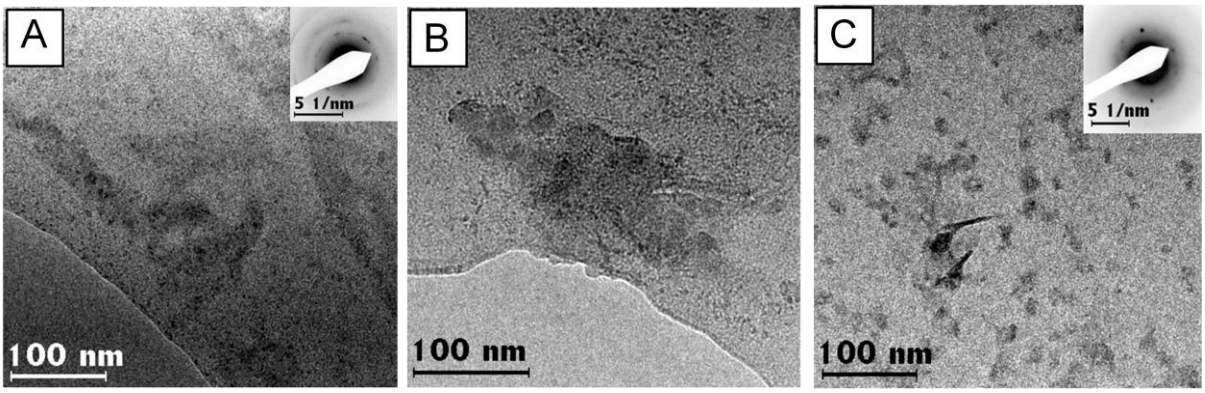

Figure S3. TEM images showing the variation in the TiO_2 products depending on the temperature of the high-temperature phase of the reaction: reaction products for high-temperature phases at (a) 200°C, (b) 250°C, and (c) 275°C (Reactions 10-12). The insets display the corresponding SAED patterns.