

Oriented Attachment and Nanorod Formation in Atomic Layer Deposition of TiO₂ on Graphene Nanoplatelets

Fabio Grillo,^{*,†,‡} Damiano La Zara,^{†,‡} Paul Mulder,[†] Michiel T. Kreutzer,[†] and J.
Ruud van Ommen[†]

[†]*Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The
Netherlands*

[‡]*These authors contributed equally to this work*

E-mail: f.grillo@tudelft.nl

Supporting Information

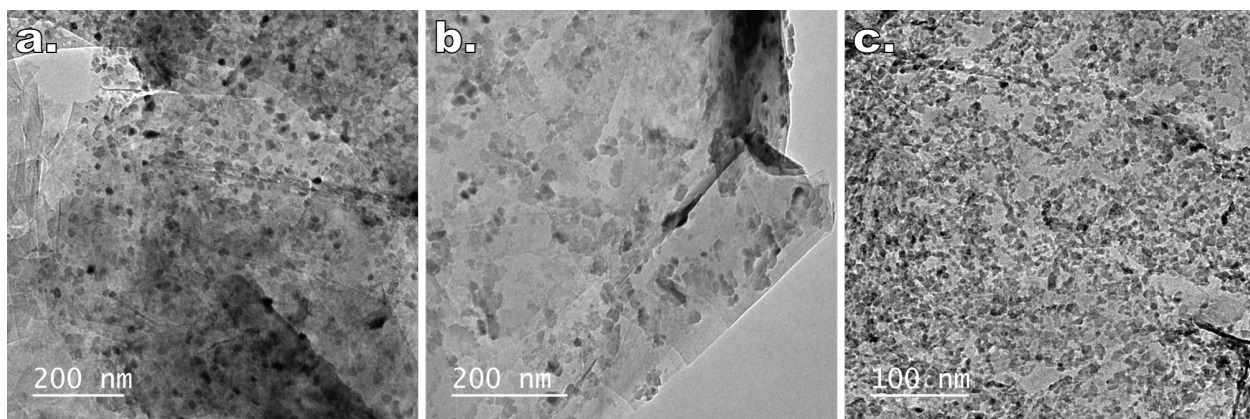


Figure S1: Effect of 2 hours of annealing at 300 °C in $N_2 + H_2O$ (a and b) and synthetic air (c) on the morphology of the TiO_2 /graphene composites obtained after 10 ALD cycles carried out at 200 °C (a and b) and 100 °C (c). The ALD cycles were carried out by following the pulsing sequence: 30 s $TiCl_4$ - 5 min N_2 purge - 30 s H_2O - 5 min N_2 purge.

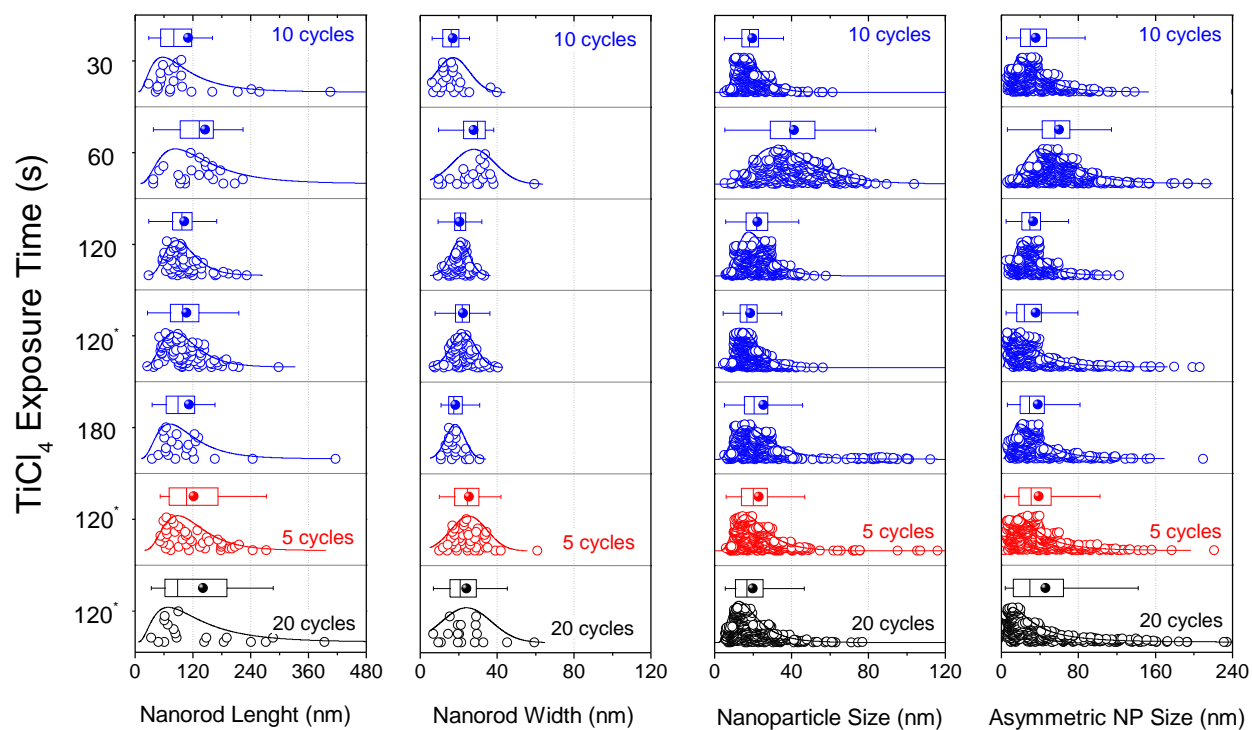


Figure S2: From left to right: distributions of the nanorod length, nanorod width, nanoparticle size, and size of the asymmetric nanoparticles. The experiments were carried out at 300°C (c). Unless otherwise specified the pulsing sequence was: 30 s TiCl₄ - 5 min N₂ purge - 30 s H₂O - 5 min N₂ purge.

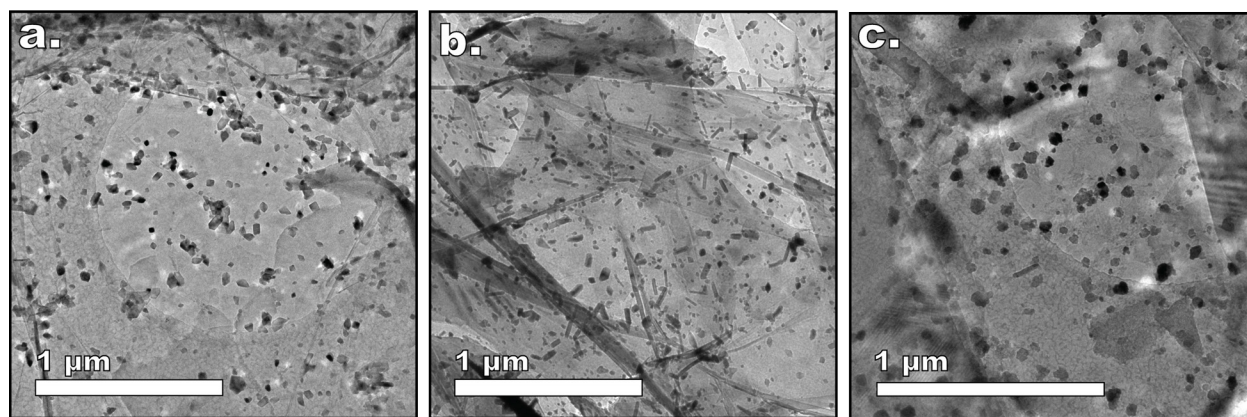


Figure S3: Effect of the water exposure on the morphology of the ALD-grown TiO₂ at 300 °C. Representative TEM images of the TiO₂/Graphene composites obtained after 10 cycles using a water exposure time of 15 s (a), 30 s (b), and 2 min (c).

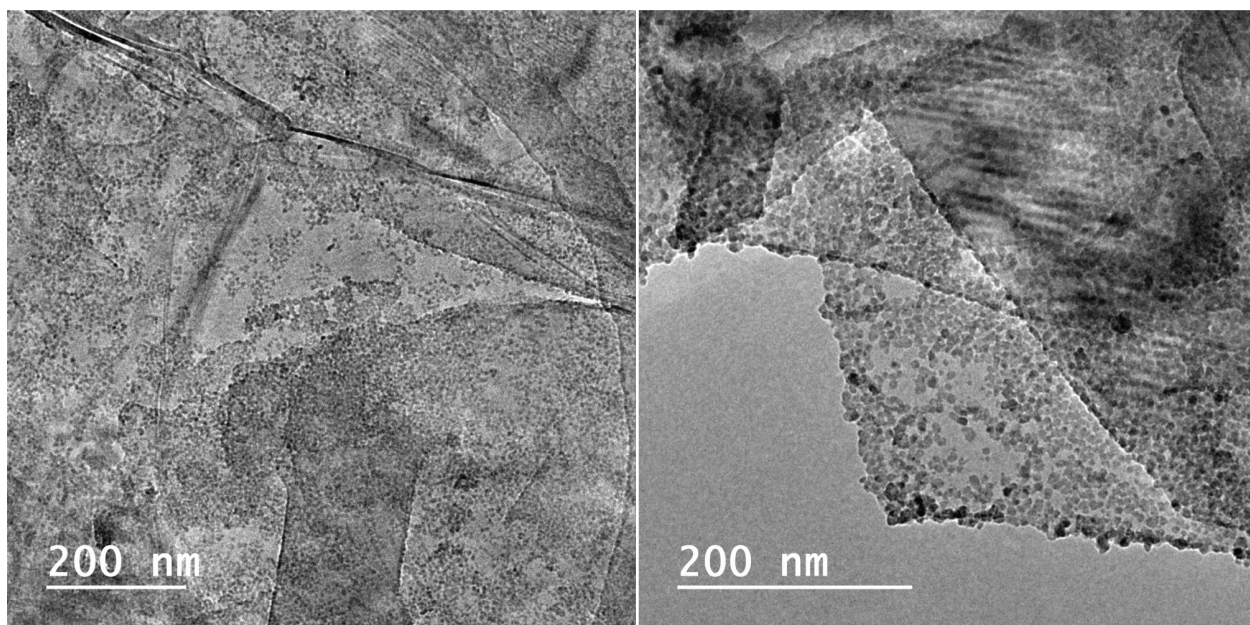


Figure S4: Representative TEM images of the TiO₂/Graphene composite obtained after 10 ALD cycles carried out at 300 °C using titanium tetraisopropoxide (TTIP) instead of TiCl₄ as the titanium precursor. The ALD experiment was carried out by following the pulsing sequence: 2 min TTIP / 5 min N₂ purge / 30 s H₂O / 5 min N₂ purge.

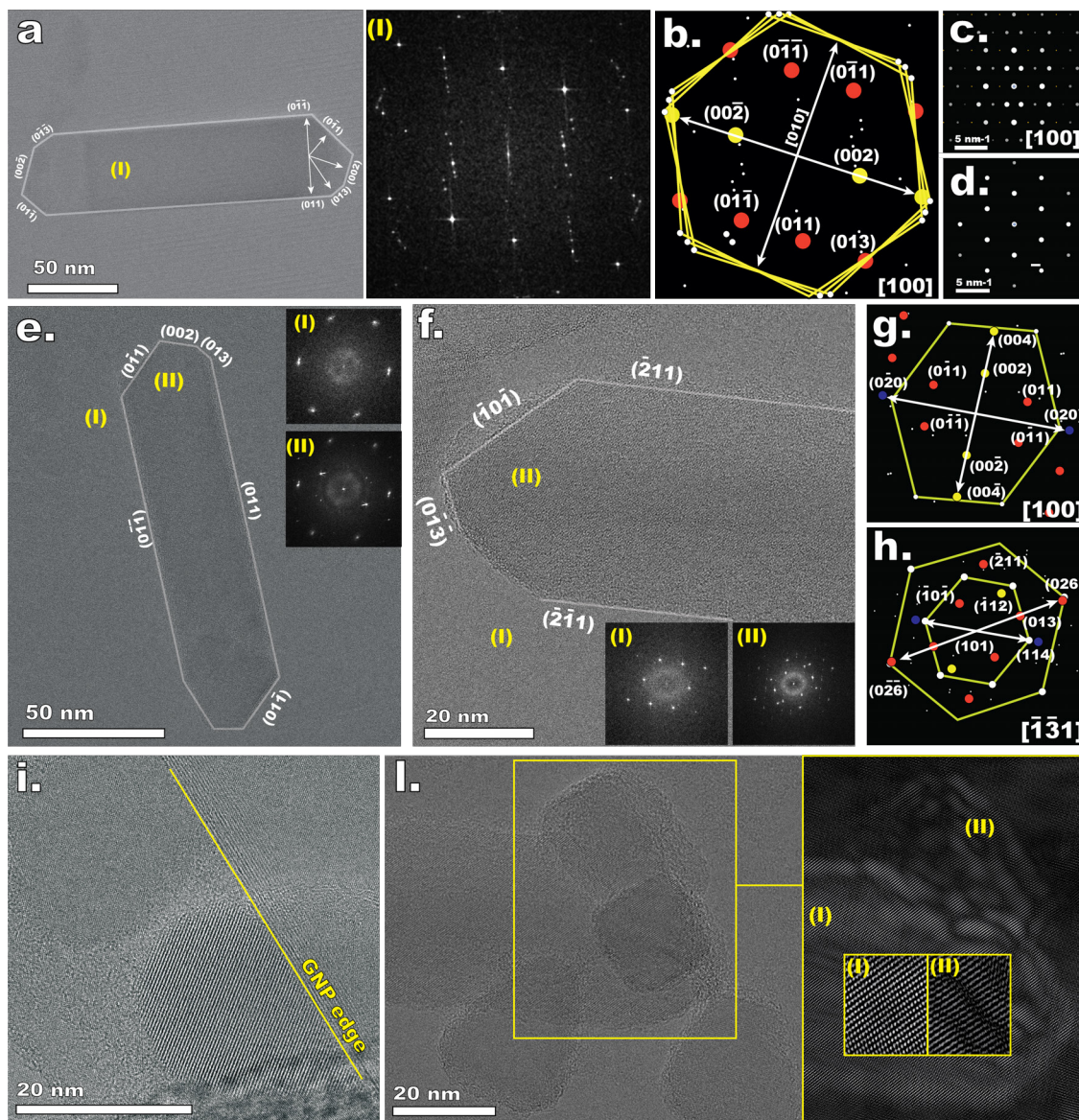


Figure S5: High resolution transmission electron microscopy (HRTEM) analysis of TiO_2 nanostructures deposited after 10 cycles at 300°C . HRTEM image of a nanorod and its Fast-Fourier-Transform (a). Analysis of the FFT of the HRTEM image shown in (a), highlighting the alignment between the TiO_2 lattice and the one of the underlying graphene nanoplatforms (b). Simulated electron diffraction patterns of anatase TiO_2 (c) and graphene (d). HRTEM images of nanorods (e and f) and FFT images of selected areas of the graphene surface (I) and of the (II) nanorods. (g) and (h) show the analysis of the FFT spectra of images (e) and (f), respectively. HRTEM image of a TiO_2 crystal pinned on the edge of a graphene nanoplatform (i). HRTEM image of the back of a nanorod and few TiO_2 nanoparticles (l). The insert highlights the oriented attachment of one nanoparticle to the nanorod. The insert was obtained by inverting the FFT of image (l) after singling out the pattern associated with the TiO_2 lattice. All the experiments were carried out by following the pulsing sequence: 2 min TiCl_4 / 5 min N_2 purge / 30 s H_2O / 5 min N_2 purge.

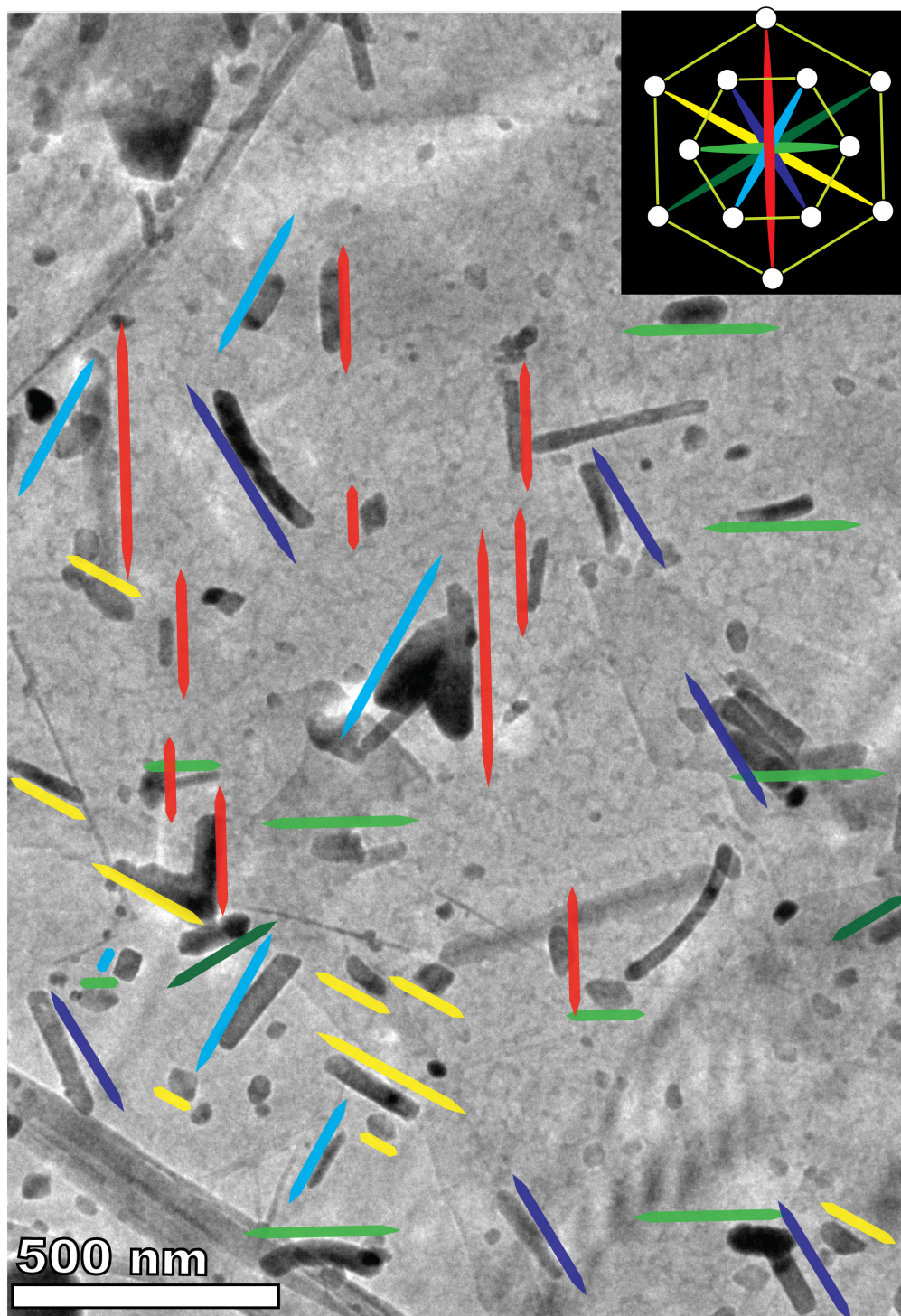


Figure S6: TEM image highlighting the preferential orientation of the nanorods according to a 12-fold symmetry.

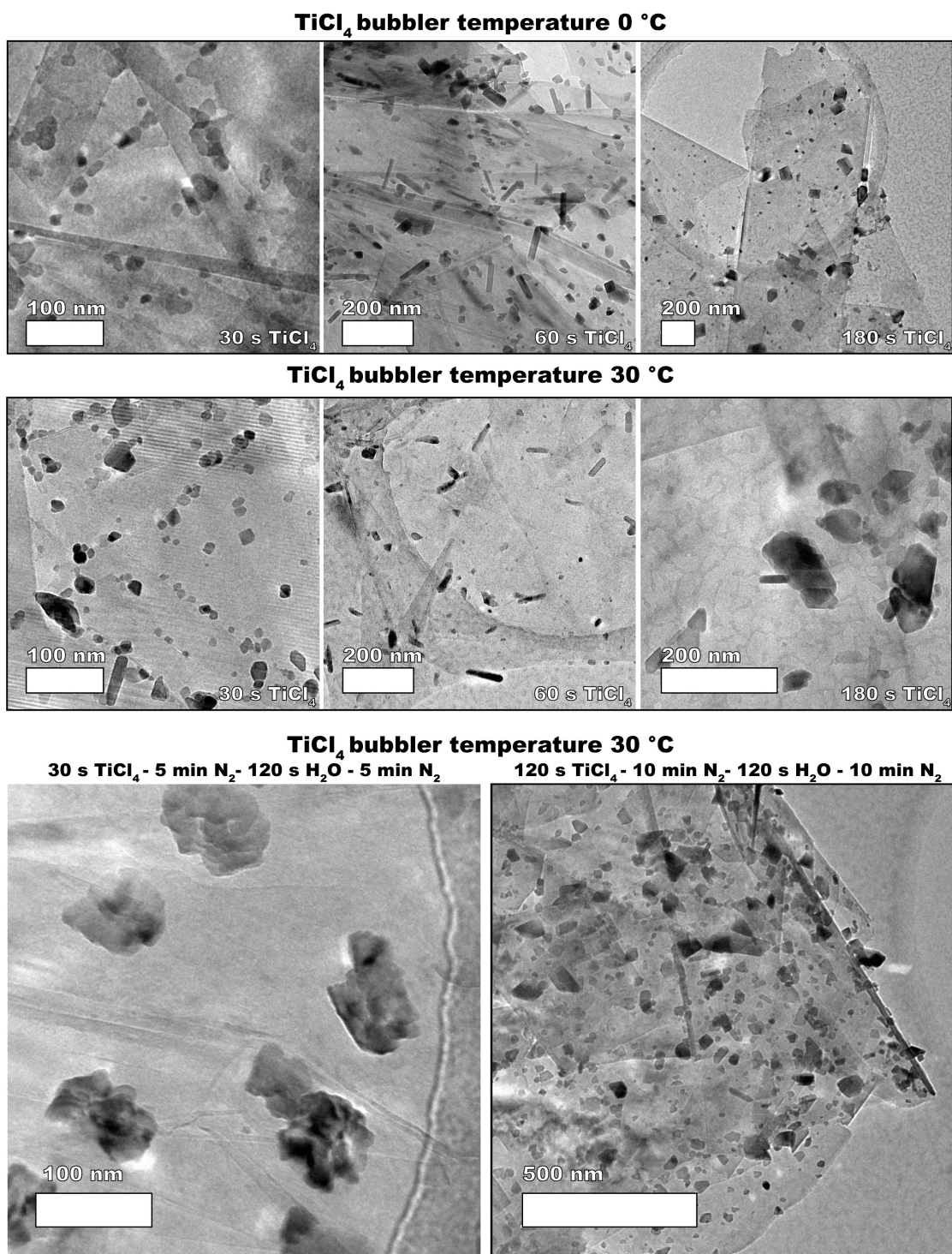


Figure S7: Supplementary TEM micrographs of TiO₂/graphene composites obtained after 10 cycles using different pulsing sequences. Unless otherwise specified the reference pulsing sequence was 30 s TiCl₄ - 5 min N₂ purge - 30 s H₂O - 5 min N₂ purge.