

**Figure 1 a)** In situ GISAXS patterns of Pd NPs grown by the ALD processes with  $H_2^*$  and  $H_2^*+O_2^*$  as co-reactant on Al<sub>2</sub>O<sub>3</sub>. **b**) The evolution in NP morphology (average center-to-center distance, height and width of Pd particles) with Pd loading, extracted from in situ GISAXS patterns. A faster increase in average center-to-center distance is shown for the  $H_2^*+O_2^*$  process. **c**) SEM images for Pd NPs deposited by the  $H_2^*$  and  $H_2^*+O_2^*$  processes at higher loadings. A clear difference in the morphology is shown: worm-like structure vs. isolated particles. **d**) In situ GISAXS patterns and **e**) SEM images of Pd NPs grown by the ALD process with and without TMA exposures during the first 10 ALD cycles. **f**) ALD based tuning strategy for Pd NPs' size (number of Pd atoms per particle) and coverage (particle distance). This figure shows that the morphology of ALD Pd NPs can be precisely tailored by tuning TMA exposures and applied cycles (Pd loading). Red (black) dots refer to the in situ measurement with (without) TMA pulses in the first 10 ALD cycles and blue dots refer to the ex situ measurement on Pd NPs samples with the same Pd loading, grown by ALD processes with a different number of TMA pulses.