Supporting Information

Thermally-Induced Agglomeration Tailors the Stability of Pt SAs on TiO_2 and Use in Photocatalytic H_2 Generation

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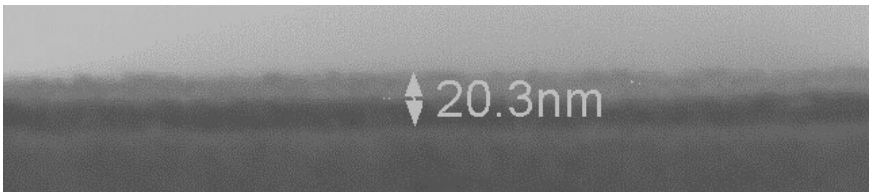

Figure S1. SEM cross-sectional image of a 20 nm thick as-deposited TiO_2 layer on SiO_2 with identical deposition parameters as for the gas cell experiments.

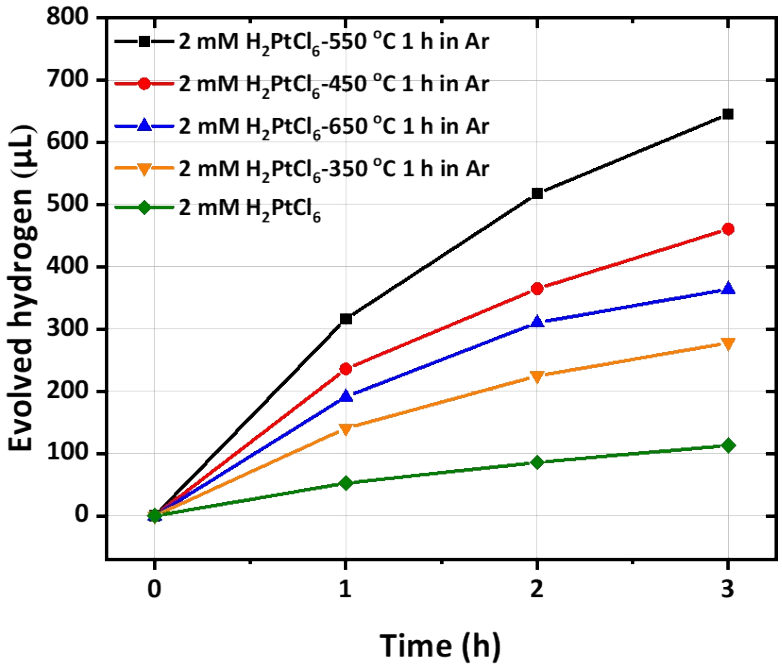

Figure S2. Time resolved hydrogen evolution data of samples with different thermal pre-annealing treatments in Ar atmosphere as compared to the non-treated sample.

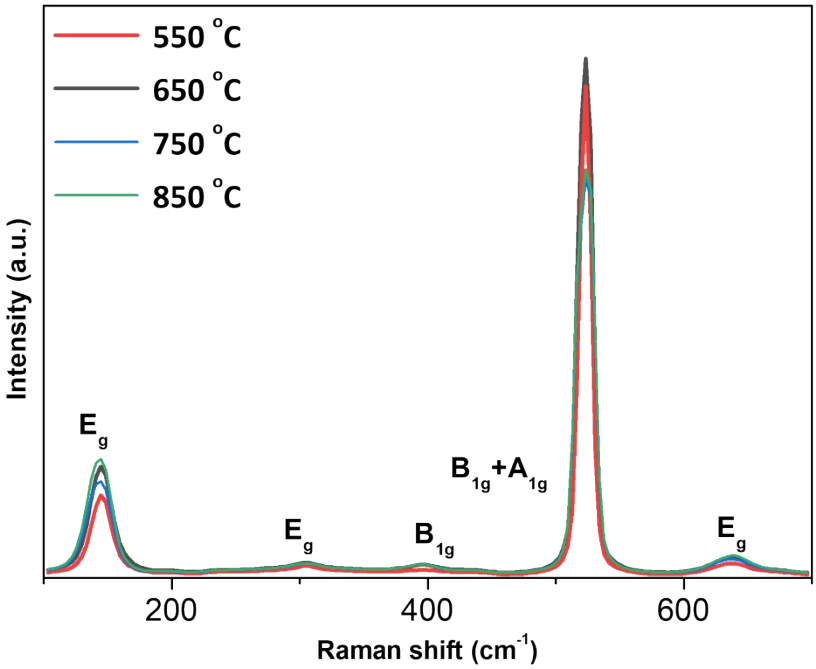

Figure S3. Raman spectra of the TiO_2 thin-films (deposited in a 2 mM H_2PtCl_6 solution) annealed at different temperatures.

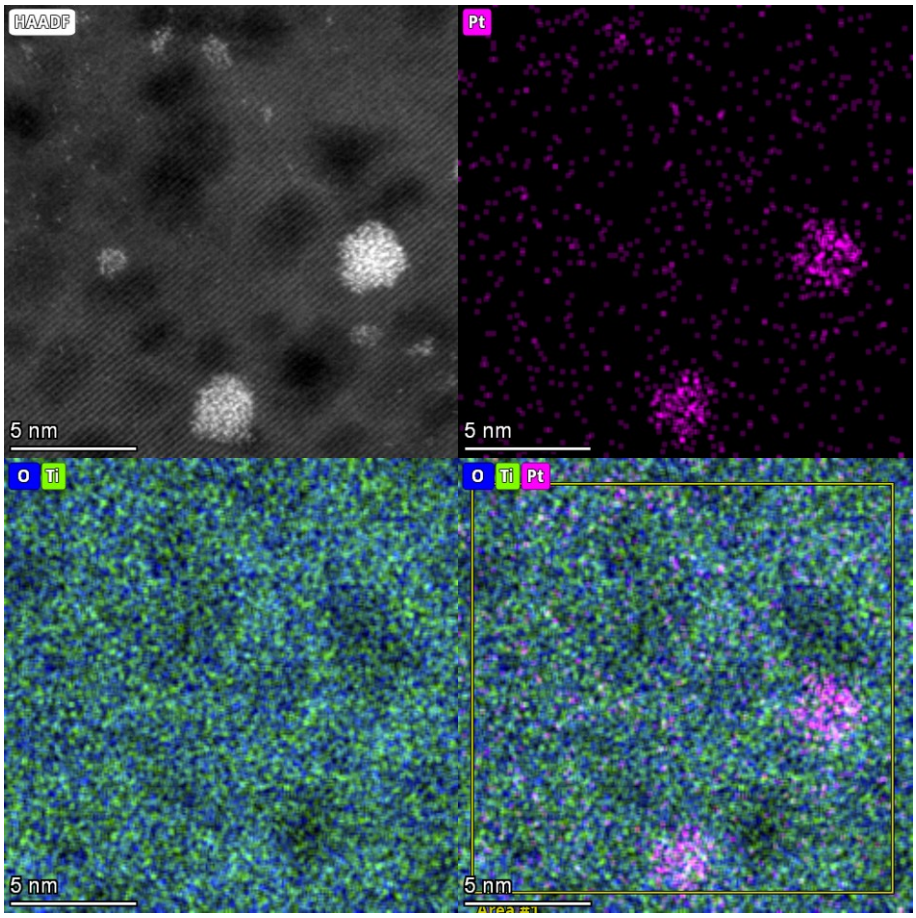

Figure S4. EDXS mapping of a TiO_2 thin film loaded with Pt after annealing at 550 °C for 1h. The TiO_2 composition of the area indicated on the bottom right yields a composition of 70 at% O and 30 at% Ti.

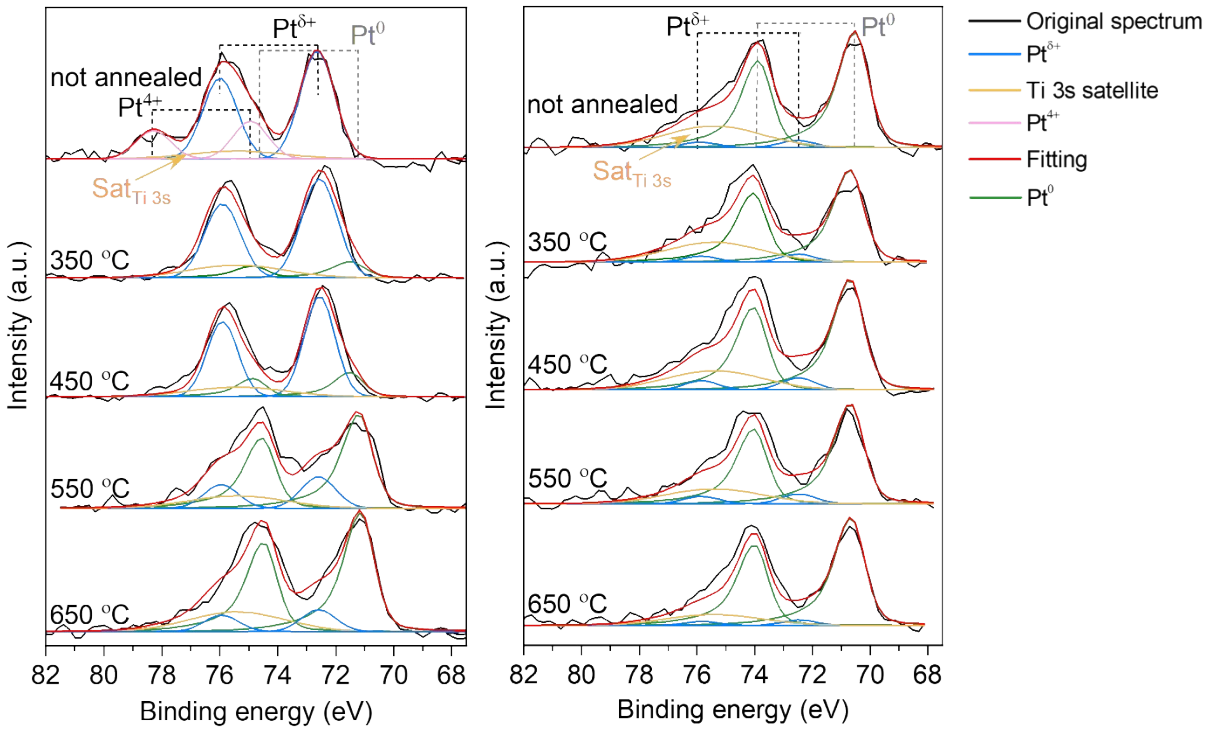

Figure S5. Pt 4f XPS spectra of Pt on TiO2 after different thermal pre-treatments before (left) and after (right) photocatalysis for 3h illumination (275 nm, 30 mW).

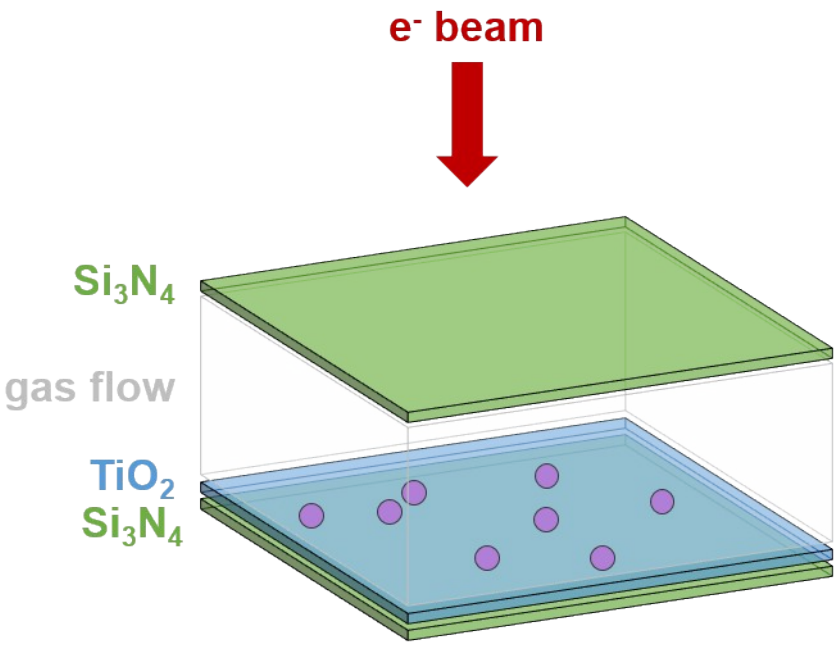

Figure S6. Scheme of the experimental setup. The electron beam is focused on the Pt containing TiO_2 surface, which is exposed to an Ar gas flow. The gas flow is constrained within the gas cell, while observations are enabled by several ten nanometer thick Si_3N_4 windows.

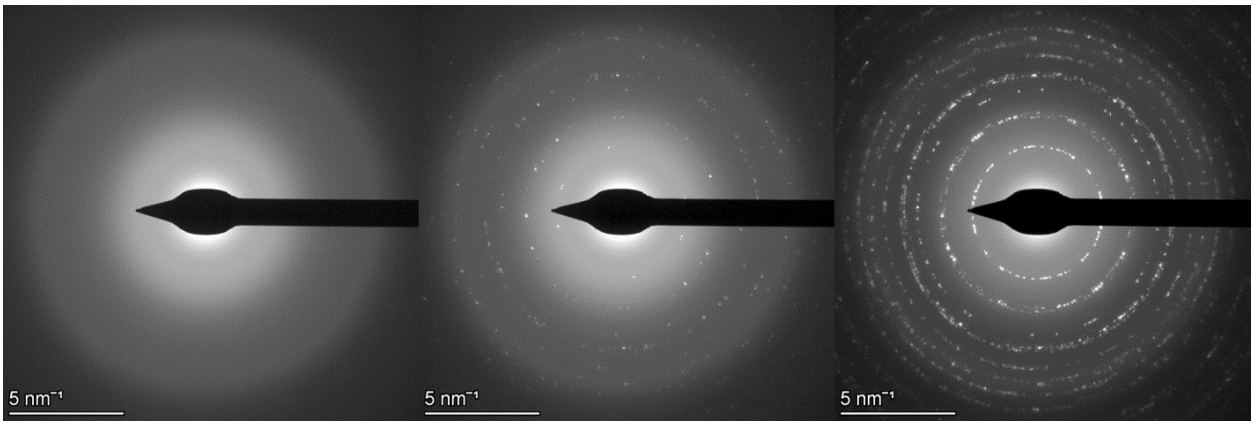

Figure S7. *In situ* SAED patterns of an amorphous TiO_2 film (left image) heated to 400 °C (heating rate 100°C s^{-1}) in Ar atmosphere. The film starts to crystallize within 20 s (center image) and already exhibits its final polycrystalline nature after 2 min (right image). The pattern does not further change after 30 min at 400 °C.

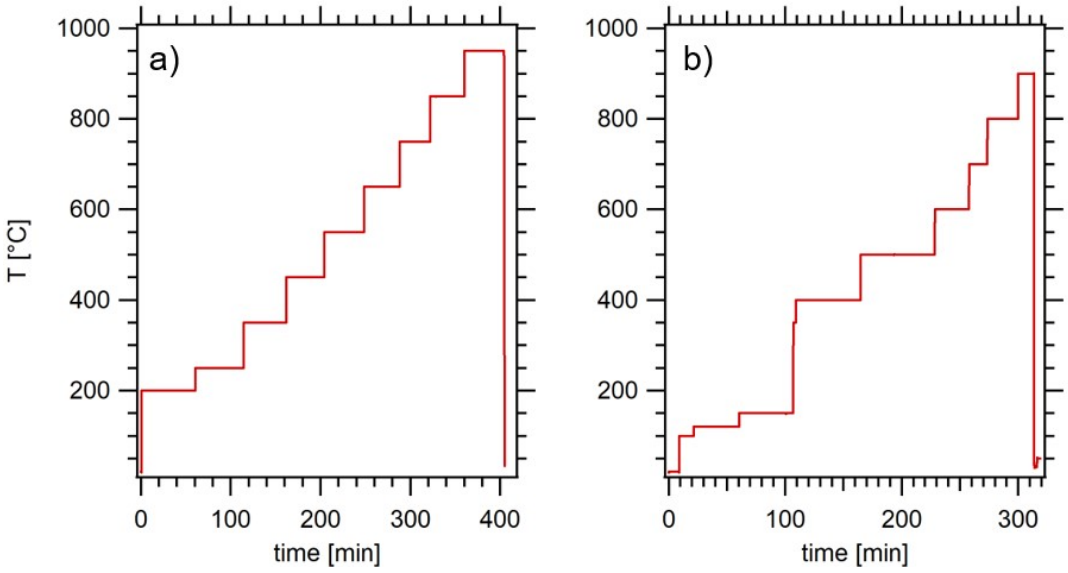

Figure S8. Measured temperature profiles of the heating experiments in Ar atmosphere for the samples produced at different H_2PtCl_6 concentrations: a) 0.05 mM; b) 0.005 mM.

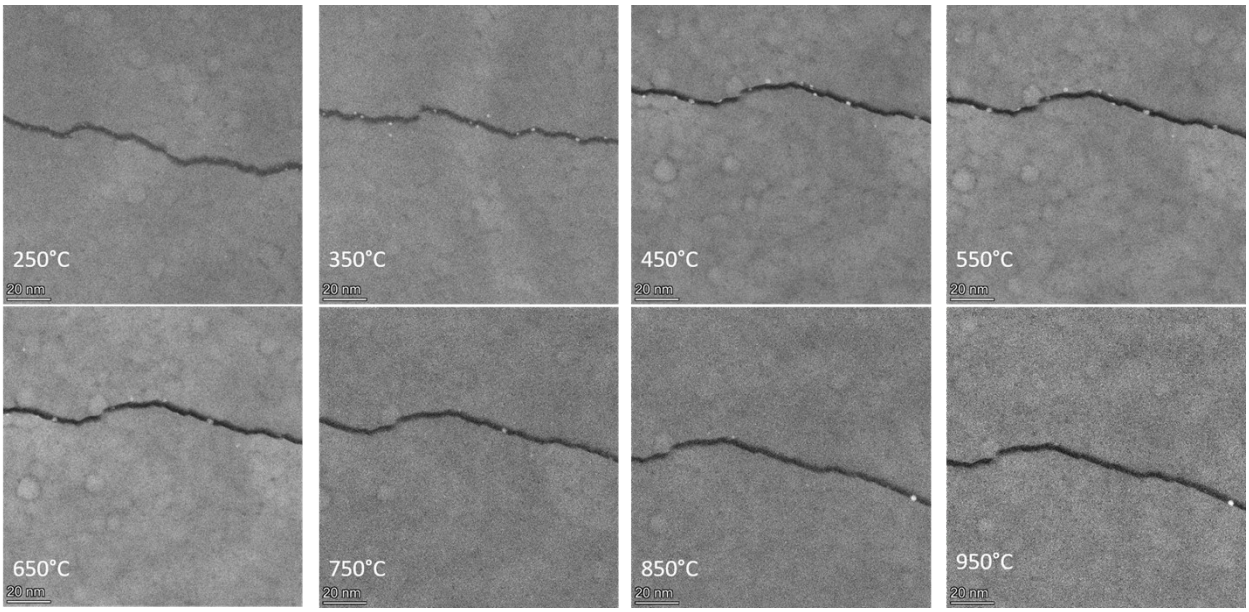

Figure S9. HAADF-STEM characterization at lower magnification in the same area, as in Figure 4.

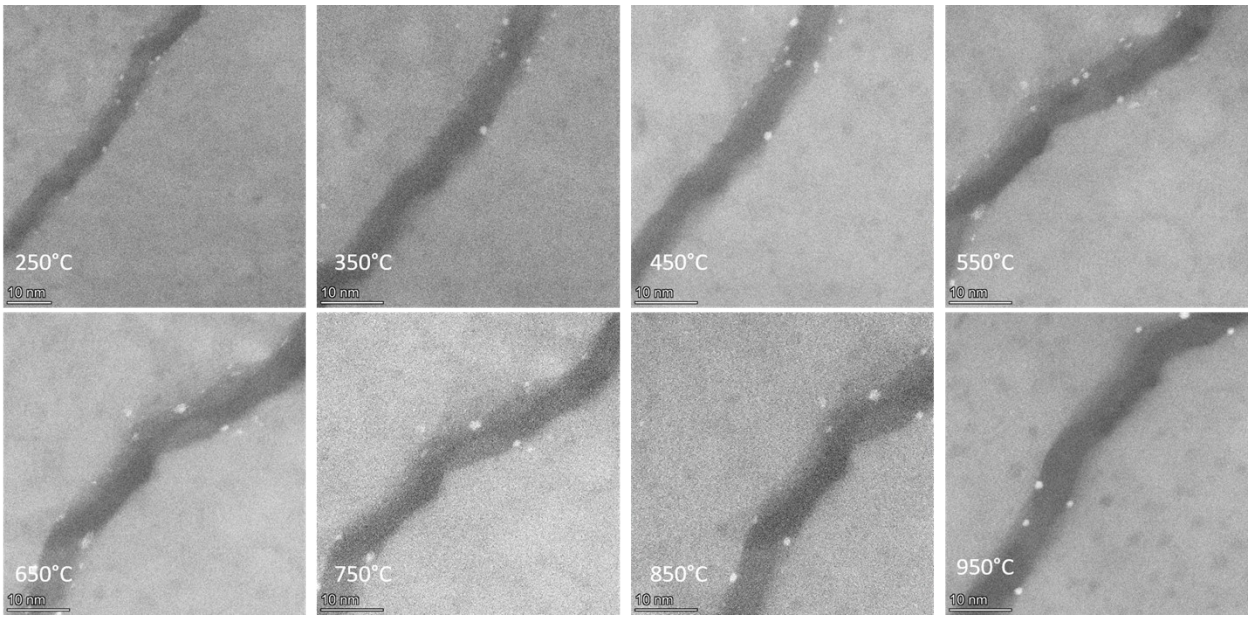

Figure S10. Identical-location HAADF-STEM images of the Pt SA decorated TiO_2 layer (using 0.05 mM H_2PtCl_6) heated in Ar atmosphere (700 mbar) to different temperatures (250–950 °C). The images are taken at a different site from that in the main text.

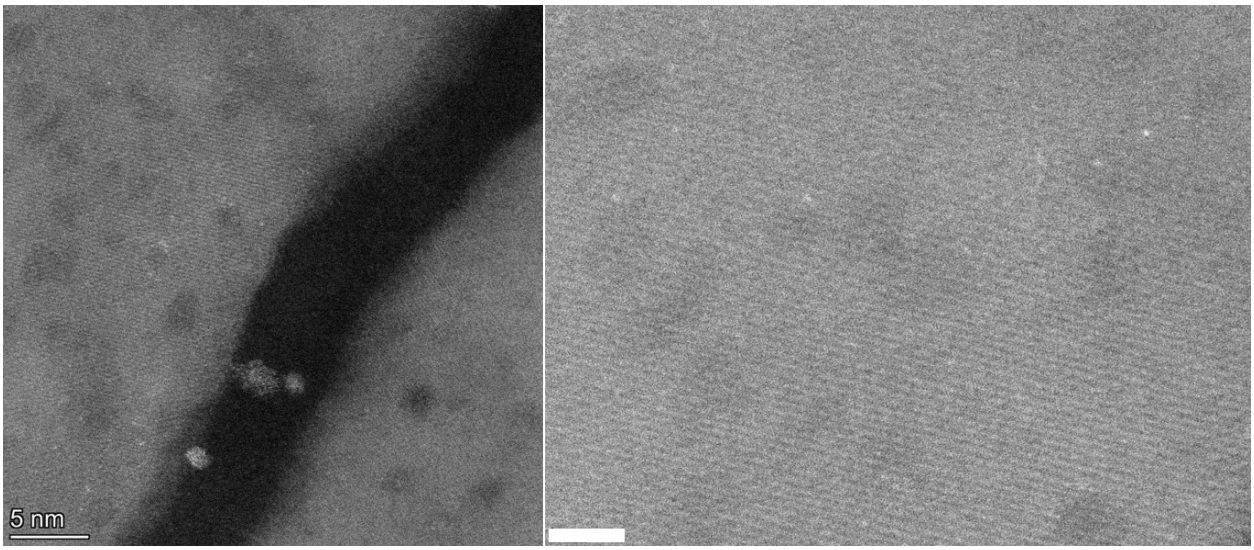

Figure S11. High magnification *ex situ* HAADF-STEM images of the Pt SA decorated TiO_2 layer (thermally treated following the procedure in Figure 4) after cooling down to room temperature. Remaining Pt agglomerates coexist with Pt SAs homogeneously distributed over the TiO_2 surface (the white bar corresponds to 2 nm).

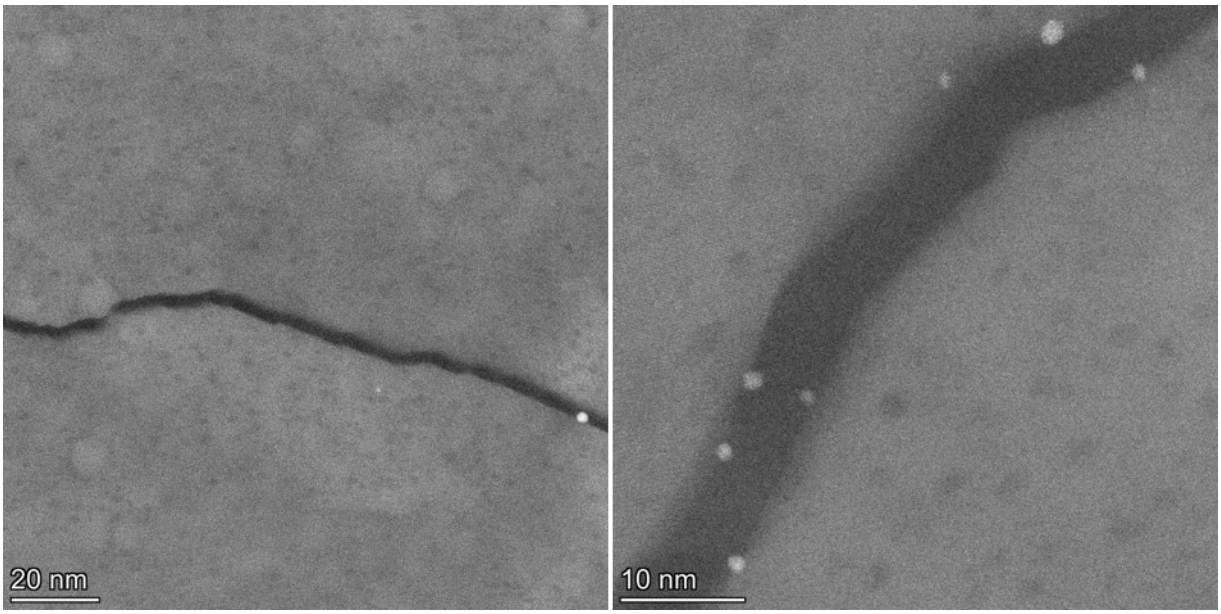

Figure S12. Identical-location HAADF-STEM images of the Pt SA decorated TiO_2 surface taken *in situ* at 950 °C (thermally treated following the procedure in Figure 4) and *ex situ* upon cooling down to room temperature. The left and right images taken at room temperature can be compared to Figure 4 (950 °C) and Figure S8 (950 °C), respectively.

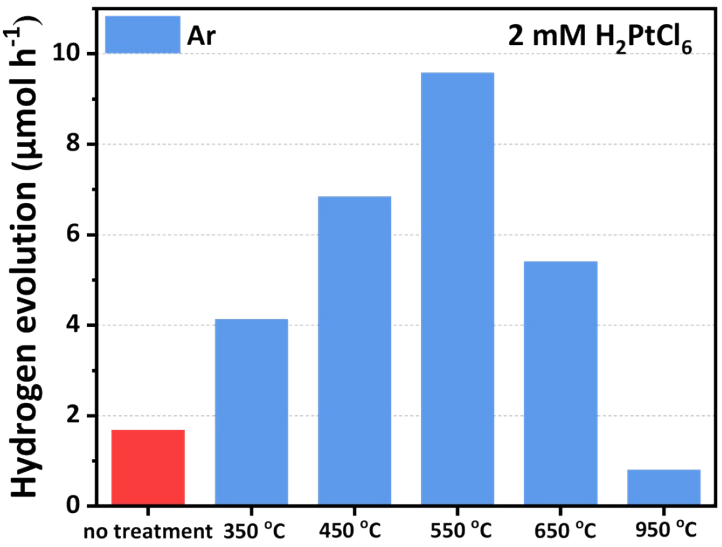

Figure S13. Hydrogen evolution data of the sample annealed at 950 °C as compared to the other samples.

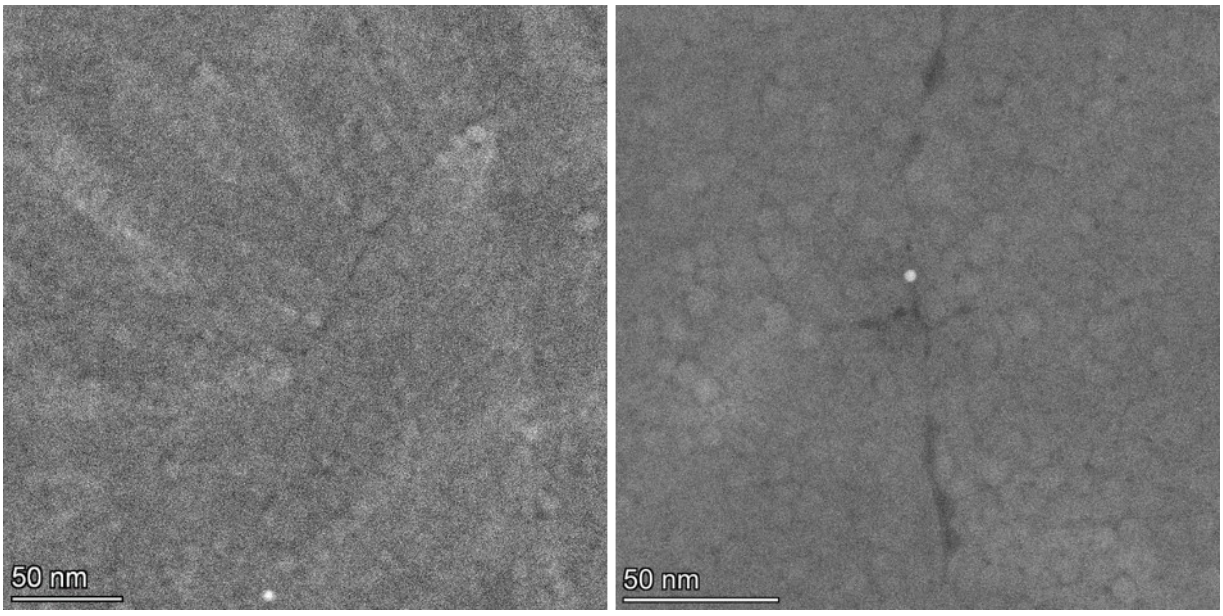

Figure S14. Low magnification *in situ* HAADF-STEM images of the Pt SA decorated (using 0.005 mM H_2PtCl_6) amorphous TiO_2 layer heated in Ar atmosphere (700 mbar) to 400 °C (left) and 900 °C (right). The images reveal an overall low degree of agglomeration.

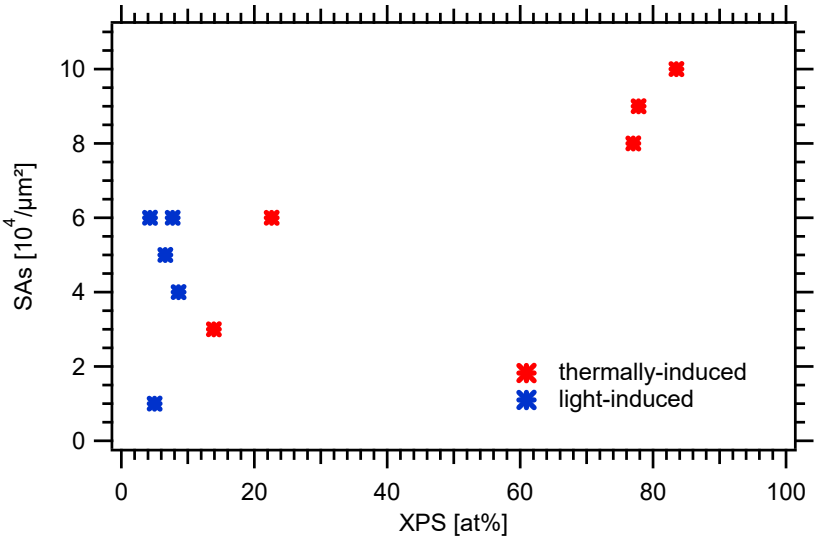

Figure S15. Relationship of the structural SA density as determined by STEM with the $Pt^{\delta+}$ fraction as determined by XPS after thermally-induced (red) and light-induced agglomeration (blue).