

Supporting Information

Thermal and Photocatalytic Reactions of Methanol and Acetaldehyde on Pt-Modified Brookite TiO₂ Nanorods

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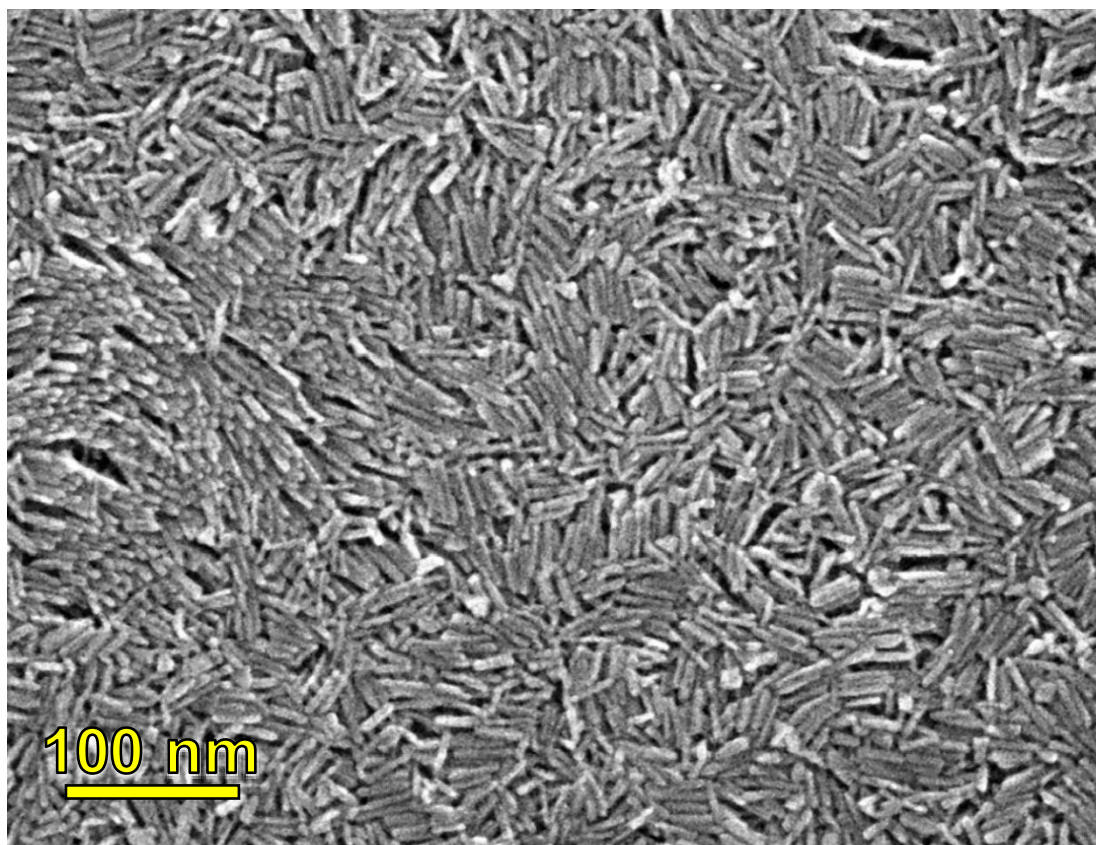


Figure S1. SEM micrograph of a thin film of the B-TiO₂ nanorods on an oxidized Si substrate.

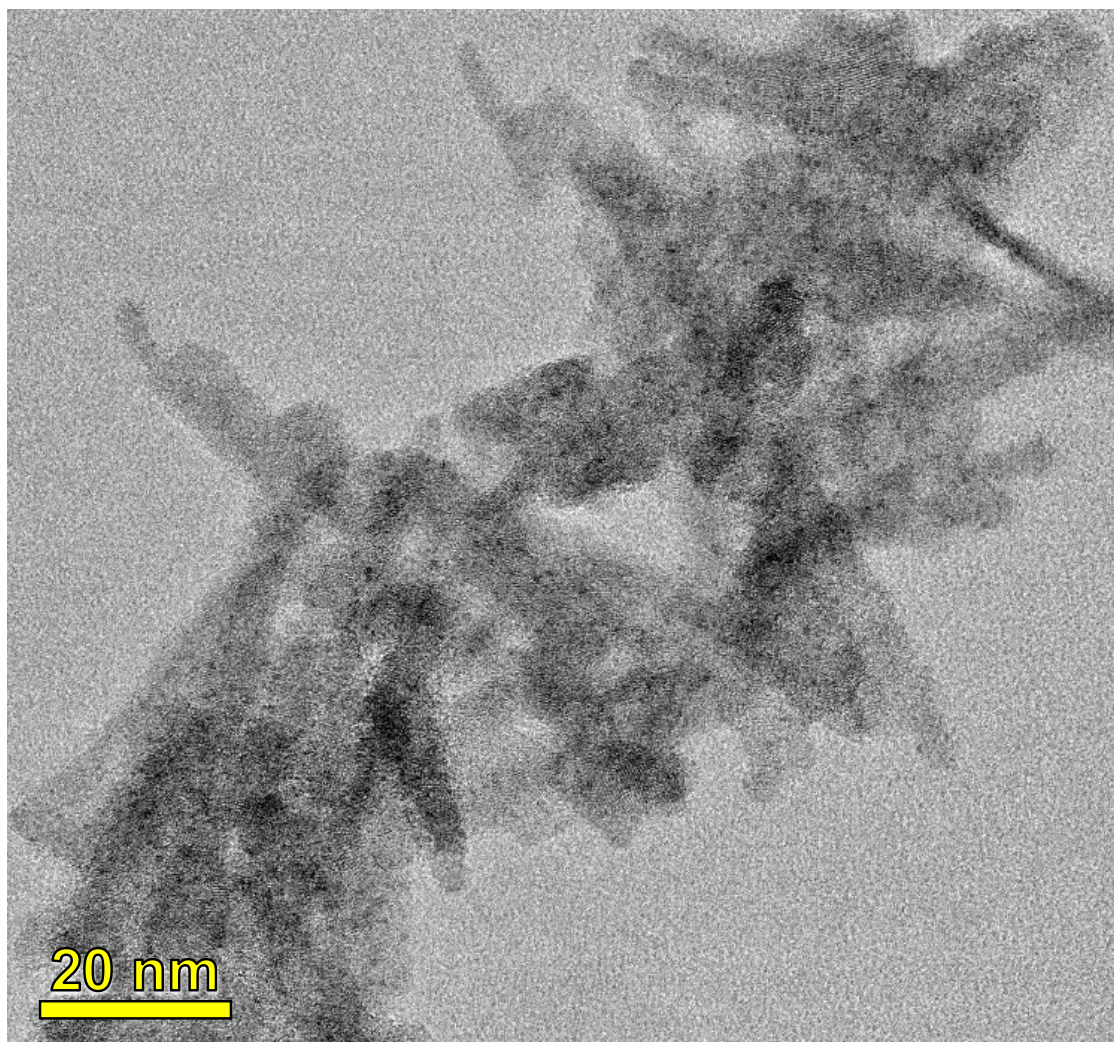


Figure S2. STEM Image of platinized nanorod powder sample. The small Pt particles, ~ 1 nm in size, are readily evident.

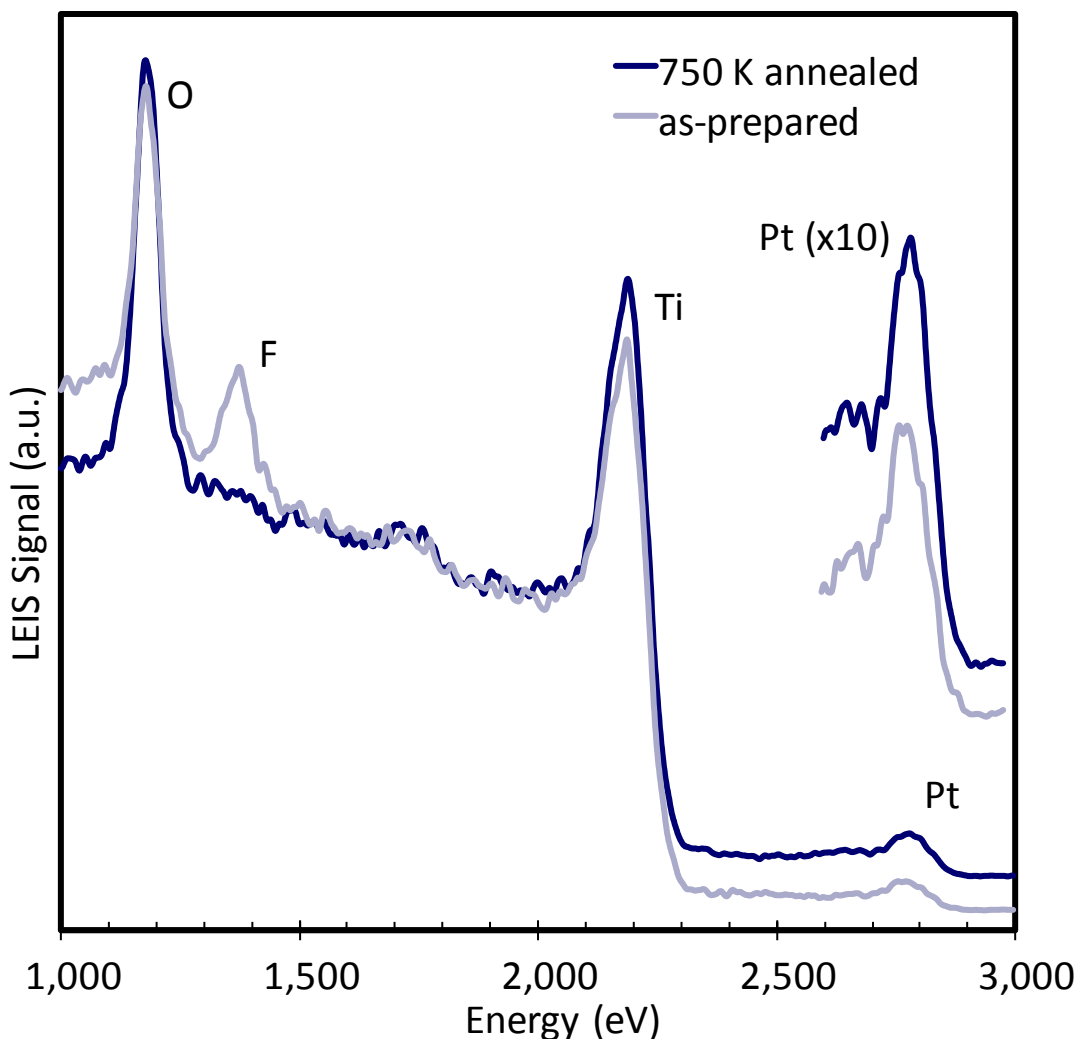


Figure S3. LEIS spectra for the 5m-Pt/TiO₂ nanorod thin film sample, before and after annealing in vacuum at 750 K. The spectra are offset to facilitate comparison of the Pt peaks.

As noted in the results section, these spectra indicate that a large fraction of the nanorod surface is still exposed for this sample. Upon annealing the sample, other than the removal of the F impurity, there is no obvious change in the spectra following annealing, indicating that an encapsulating TiO_x layer over the Pt deposits has not formed to any appreciable extent.

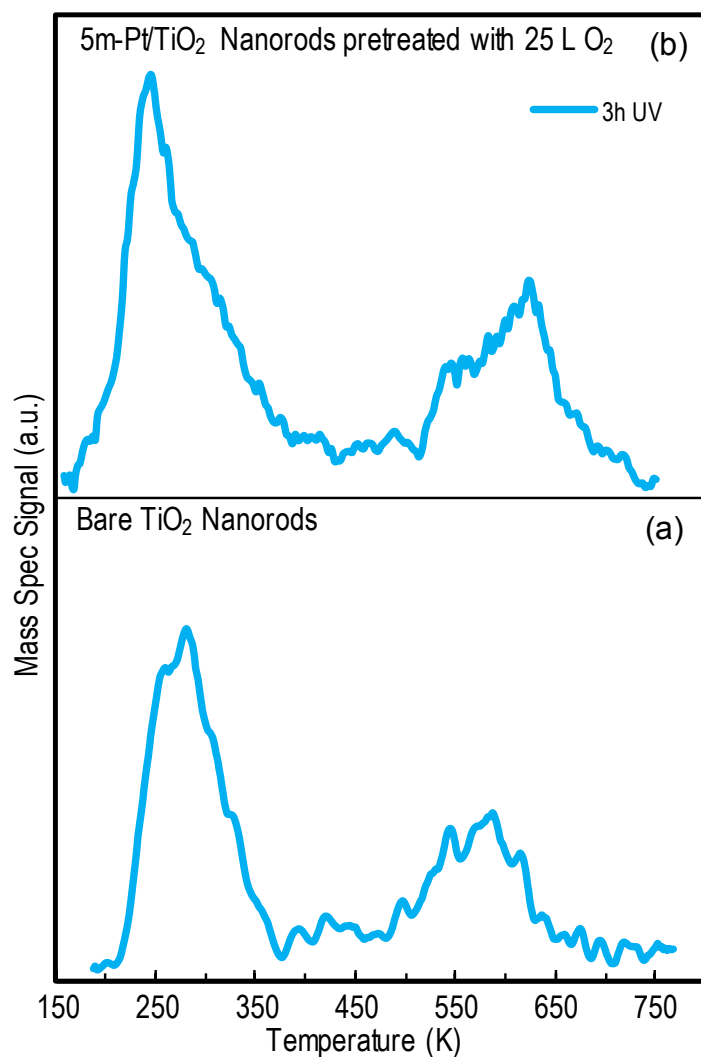


Figure S4. Normalized methyl formate yields from TPD of methanol dosed at saturation following 3 h UV exposure for the Pt-free nanorods (lower panel, a) and the O₂-pretreated 5m-Pt/TiO₂ nanorods (upper panel, b).

The similarity in both the high- and low-temperature methyl formate peaks between these two samples indicates that these two reaction pathways are not changed by the deposition of Pt. However, the surface area normalized yield of both the high- and low-temperature products from the O₂-pretreated 5m-Pt/TiO₂ sample is $\sim 33\%$ greater than from the Pt-free sample, indicating that the Pt deposits instead acts as an adsorption site for O₂, which helps facilitate these photochemical reactions that take place on the bare portions of the TiO₂ nanorod surface.

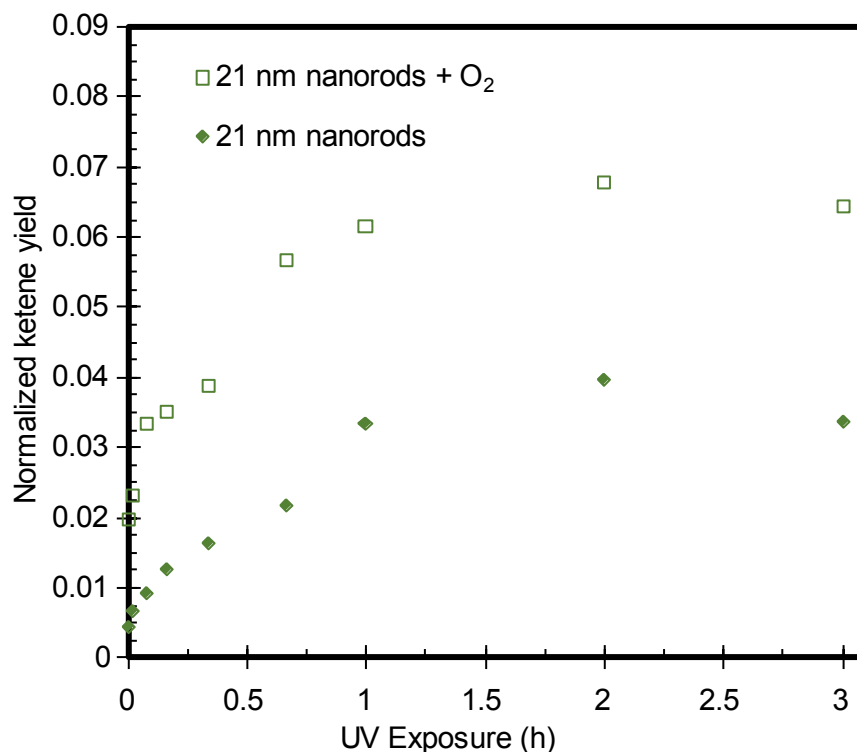


Figure S5. Ketene yields from TPD of acetaldehyde dosed at saturation on bare 21 nm nanorods, with and without oxygen pretreatment. In the O₂-pretreatment experiments the nanocrystal films were sequentially dosed with 25 L O₂ and then 5 L acetaldehyde and then exposed to UV light for a predetermined time interval, followed by TPD.

The increased ketene yield observed from O₂ pretreatment with no UV exposure ($t = 0$ h) indicates that adsorption of oxygen at vacancy sites increases the activity for the partial oxidation of acetaldehyde to acetate; however, it is apparent that this ketene increase upon O₂ pretreatment is uniform across all UV exposure intervals, suggesting that the presence of adsorbed oxygen has no impact on the rate of photo-generated adsorbed acetate. This independence of photo-activity on the presence of adsorbed oxygen, indicates that the availability of oxygen vacancies at the bare nanorod surface do not alter the dynamics of the photogenerated charge carriers, and suggests that electron trapping at these highly undercoordinated vacancy sites does not occur to any appreciable extent. Additionally, these findings indicate that acetaldehyde photo-oxidation is taking place at five-fold coordinated Ti cations on the fully oxidized planar sites and not at more highly undercoordinated Ti cations, such as at these oxygen vacancies.