Supplementary information

Short-Range Plasmonic Nanofocusing Within Submicron Regimes Facilitates In Situ Probing and Promoting of Interfacial Reactions

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Additional discussion on the aggregation of TiO_2 NPs:

The aggregation of dielectric NPs might influence the results in a few ways. It has been reported that the Raman signals would be enhanced in the arrays of dielectric nanostructures [1, 2]. Herein, the aggregation of NPs might enhance the Raman signals as well. It is worth mentioning that the electric field intensity would be enhanced on the bottom NPs that contact with the Au surface. The upper NPs (not contact with the Au surface) would still contribute to the enhanced electric field intensity. However, according the experiment (Figure 5a and 5b) and simulation result (Figure 5c and 5d), the excess aggregation of NPs would reduce the nanofocusing intensity instead. From the experiment results, the enhanced Raman intensity was much higher on the sample decorating with 0.1 wt% TiO_2 NPs (Figure 5a and 5b) than that of higher concentration samples. Moreover, it is apparent the electric field intensities of hot spots are much weaker in the sample decorating with higher density of TiO_2 NPs (Figure 5d) than that decorating with lower density of TiO_2 NPs (Figure 5c). We suppose that the excess aggregations of NPs might cause an interference and scattering of incoming light, and disturb the coupling efficiency of incoming photons transferred to SPPs. And this phenomenon might reduce the nanofocusing intensity.

Additional discussion on the photocatalysis test:

We observed an interesting phenomenon in that the reaction rate on the nanofocusing configuration dropped suddenly after 10 min, whereas that on the P25/flat Al film dropped after approximately 20–30 min. We suspected that this phenomenon might have been attributable to the two distinct MB degradation periods (Periods I and II, Fig. S1). In Period I, the degradation of MB was dominant near the P25 surface. During this period, the MB molecules on the P25 surface were degraded much faster than those on the Al surface (no contact with the P25). Therefore, the Raman signals of MB decreased rapidly, as a result of photocatalysis, during this period. As indicated in Fig. 8d, the reaction rate on the P25/plasmonic rod arrays decreased suddenly after 10 min, indicating that the MB molecules on the P25 surface had degraded completely within this period of time. On the other hand, the reaction rate on the P25/flat Al film decreased significantly after 20–30 min, indicating that this system required a much longer period of time for complete degradation of MB on the P25 surface. These results prove, once again, that the nanofocusing of submicron-short-range SPPs could facilitate the photocatalysis reaction. Moreover, after the MB molecules on the P25 surface had degraded almost completely, the MB molecules on the Al surface dominated the degradation rate

(Period II, Fig. S1). Because the MB molecules on the Al surface (no contact with P25) were degraded mainly through photoinduced decomposition (without P25 TiO2 NPs), as characterized by the MB molecules on the reference Al film (no P25 NPs), the rate of degradation was much slower, becoming similar to that on the reference Al film during Period II for both of the P25 systems. Note that the photocatalysis reaction could be performed practically for a solution-based pollutant; every pollutant molecule would, thereby, contact the P25 surface, leading to a sustainable reaction rate induced by the nanofocusing structures.

Reference:

[1] D. Qi, L. Lu, L. Wang, and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 9886-9889.

[2] D. Qi, X. Yan, L. Wang, J. Zhang, *Chem. Commun.*, 2015,**51**, 8813-8816.

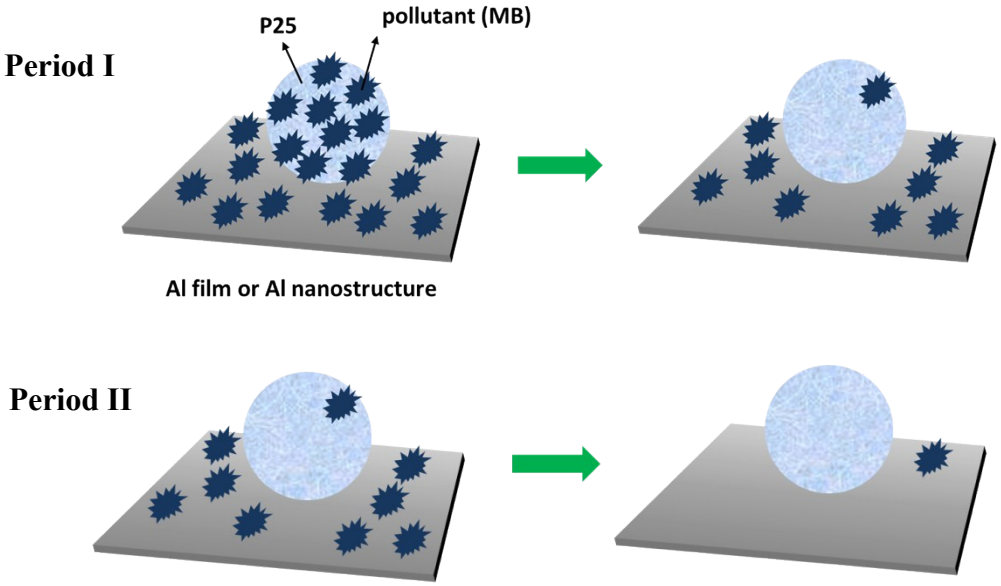

Fig. S1 Schematic representation of the dominant mechanisms during the different periods of the photocatalysis process. In Period I, the degradation of MB was performed predominantly on the surfaces of the P25 TiO2 NPs (photocatalysis). On the other hand, during Period II, the degradation of MB was performed predominantly on the Al surface (photoinduced decomposition), because there were almost no MB molecules left on the P25 surface. The MB molecules on the reference Al film were all degraded through photoinduced decomposition.