

Electronic Supplementary Information for:

h-BN nanosheets as simple and effective additives to largely enhance the activity of Au/TiO₂ plasmonic photocatalysts

Experimental

Materials. P25 and TS-1 (BET surface areas are 50 and 262 m² g⁻¹, respectively) were supplied by Nippon Aerosil and Catalysis Society of Japan, respectively. Au/P25 was prepared according to the literature^{11c} as follows: P25 (1.0 g) was added to water (50 mL) containing HAuCl₄·3H₂O (44.4 mg, 2 wt% of loaded Au). The solution pH was adjusted to ca. 7 with NaOH, and the solution was stirred at 353 K for 3 h. The particles were recovered by centrifugation, washed thoroughly with water and dried at 353 K for 12 h. The powders were calcined under air at 673 K for 2 h (a heating rate of 2 K min⁻¹).^{11c} h-BN nanosheets were prepared as follows.^{21c} Commercially available micrometer size BN particles (1 g, Aldrich) were dispersed in a DMF solution using a high power (7000-8000 W) ultrasonic cleaner for 20 h and then centrifuged at 10000 rpm for 5 h to precipitate (remove) large-size BN flakes, resulting in thin BN sheets. The obtained thin sheets were annealed at 1200 °C for 4 h under N₂ flow to improve their crystallinity. The obtained h-BN nanosheets has a lateral size of up to 2 μm, thickness of up to 20 nm, and BET surface area of 15 m² g⁻¹. MPTNF was prepared according to the reported procedures and the BET surface area was 236 m² g⁻¹.¹⁶

Photocatalytic activity tests. Au/P25 (15 mg) and the additive (0–3 mg) were mixed in a O₂-saturated aqueous solution of formic acid (5 vol%) in a stainless-steel container (75 mL) equipped with Pyrex window by ultrasonication (1 min) and the subsequent stirring (5 min) under dark. The dispersion was photoirradiated at λ > 420 nm by a solar simulator (San-Ei Electric, 1000 W m⁻²) through UV cutting filter, under stirring. The gas in the container was withdrawn with a gas-tight syringe and quantified using a BID gas chromatograph (Shimadzu BID-2010 plus) equipped with a Micropacked ST column.

ESR analysis. The ESR spectra were recorded on a JEOL JES RE-1X spectrometer (X-band). The magnetic field was calibrated and radical yields were determined using Mn²⁺/MgO as a standard marker. Au/P25 (15 mg) and the additive (1.5 mg) were mixed in a mortar and a portion (10 mg) of the mixture was placed in a quartz ESR tube, which was evacuated at 423 K for 1 h and cooled to room temperature. O₂ (20 Torr) was introduced into the tube and kept for 10 min. The tube was photoirradiated at room temperature using the 500 W-Xe lamp at λ > 420 nm for 5 min. The tube was then evacuated for 10 min to remove excess O₂ and analysed at 77 K.