Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information (ESI)

Hierarchical N-doped TiO_2 Hollow Microspheres Consisting of Nanothorns with Exposed Anatase {101} Facets

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Experimental

All chemicals were purchased from Aldrich and used as received without further purification. In a typical synthesis, TTIP (1 mL) was added into a solution containing 2-propanol (40 mL) and DETA (0.026 mL) under stirring, then a mixture of H_2O (0.031 mL) and 2-propanol (5ml) was added . After sufficient mixing for 15 min, the formed homogeneous sol solution was transferred to a Teflon-lined autoclave to conduct a solvothermal reaction at 200 ^oC for 24 h. Then the yellowish precipitates were collected by centrifugation and washed several times using dry ethanol before finally calcined at 450 °C for 2 h in a muffle furnace.

X-ray diffraction (XRD) patterns were obtained by on a Shimadzu XRD-6000 diffractometer with a monochromated high-intensity Cu Kα radiation of wavelength λ = 0.15418 nm operated at 40 KV and 30 mA under ambient condition at a step size of 5^o/min. The morphology and surface microstructure of the TiO_2 spheres were observed on a field-emission scanning electron microscope (SEM, JEOL JSM-6700F) operated at 5 kV, and a transmission electron microscope (TEM, JEOL JEM-2010) operated at 200 kV. N_2 adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) using a surface area and porosimetry analyzer (Nova 100, Quantachrome Instruments). Before measurement, the mesoporous TiO_2 samples were outgassed under vacuum for 8 h at 150 ^oC. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area from the adsorption data in the relative pressure range of P/P_0 = 0.01–0.30. The average pore diameter was estimated using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherm. Diffuse reflectance spectra for TiO_2 samples were recorded on a UV-Vis-NIR scanning spectrophotometer (Shimudzu UV-3101 PC) in the wavelength range of 250–800 nm. X-ray photoelectron spectroscopy (XPS) analyses of thin films were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 5 $\times 10^{-9}$ Torr at room temperature. Photoemission spectra

were recorded on a Sigma Probe Instrument (Thermo VG, U.K.) equipped with a standard monochromatic Al Kα excitation source ($h\nu$ = 1486.6 eV). The pass energy and step size of low-resolution XPS scan were performed at 50 and 10 eV, respectively. For the high-resolution XPS scan, the parameters above were adjusted to 20 and 0.1 eV. The binding energy (BE) scale was calibrated by measuring a C 1s peak at 284.5 eV from the surface contamination.

The photocatalytic activities of TiO_2 photocatalysts were evaluated by measuring the degradation rate of methylene blue (MB) and orange II under visible light irradiation. An aqueous solution containing 100 mL 5 ppm dye and 0.1 g TiO_2 was magnetically stirred in the dark for 1 h, and then exposed to a 350 W Xenon lamp equipped with a 420 nm cut-off filter. UV/Vis absorption spectra were recorded at different time intervals to monitor the absorption and photocatalytic degradation of dye, and the concentration of dye left in the aqueous system was measured by a UV-visible spectrophotometer (UV-1601, Shimadzu). Before measurement, the suspension was centrifuged and filtered with Millex Millipore filter (0.1 μm) to remove the powered photocatalysts.

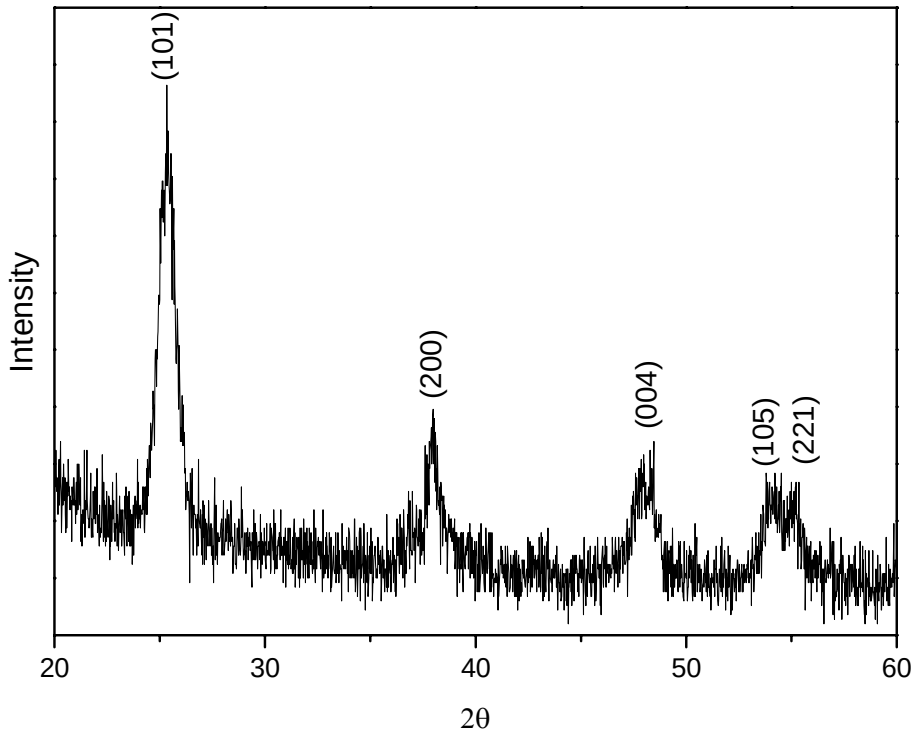

Fig. S1: XRD pattern for a N-TiO_2 HMS sample.

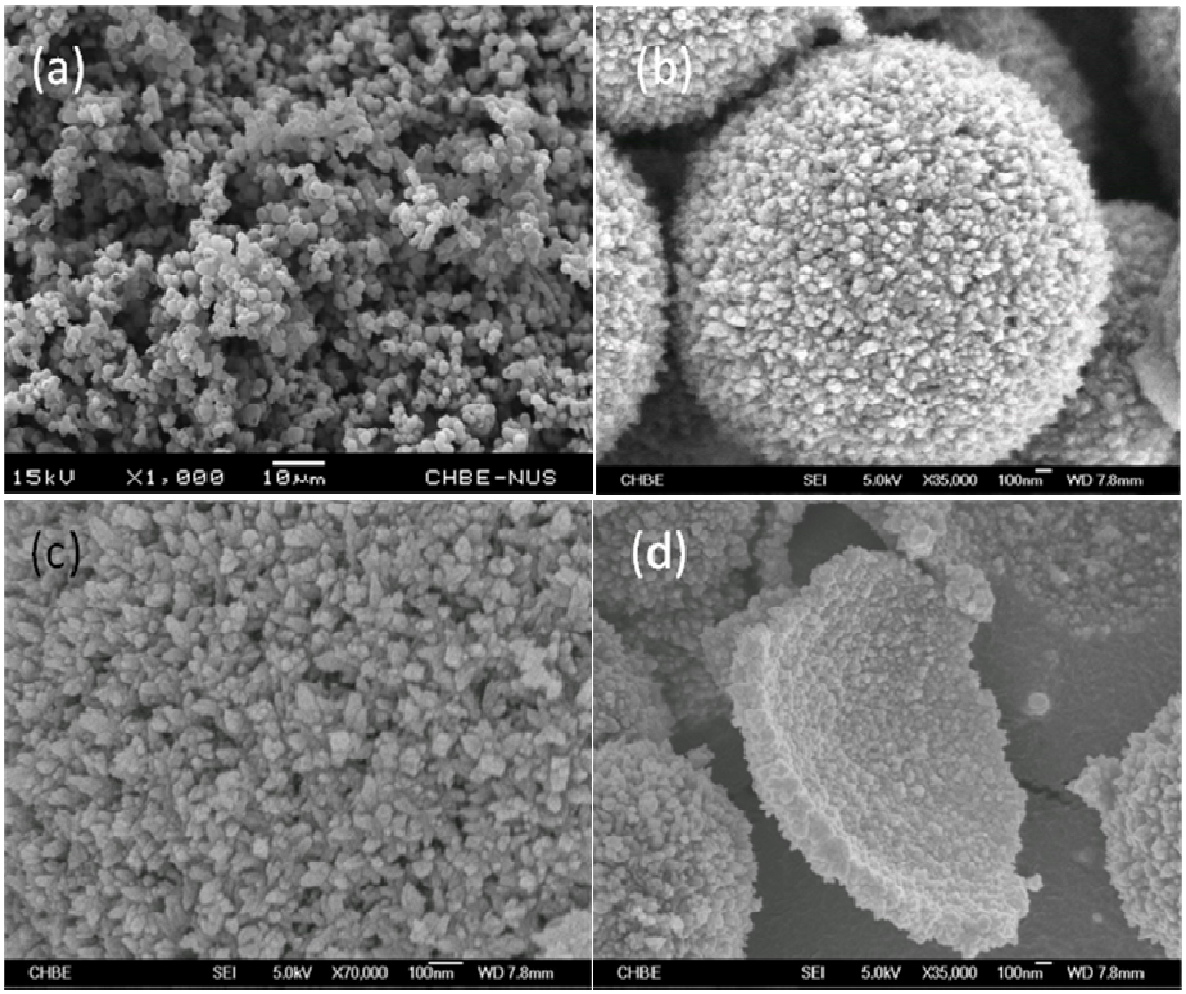

Fig. S2: SEM images for N-TiO_2 HMS: (a) a low-magnification view; (b) a high-magnification view showing the rough surface consisting of nanothorns; (c) a closer view for the arrangement of nanothorns on the spherical surface; and (d) a broken shell of the hollow microspheres.

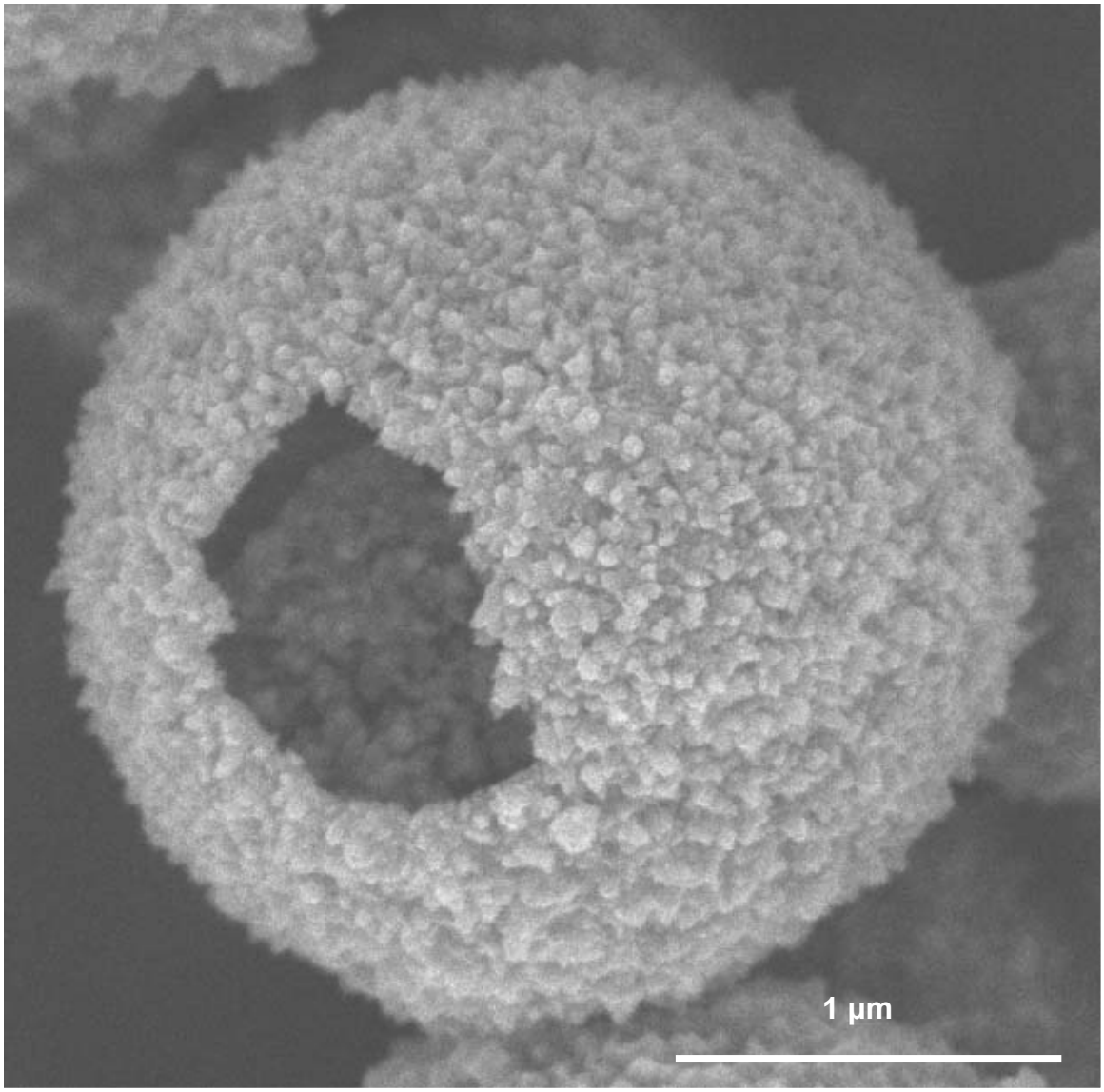

Fig. S3: An enlarged image for N-TiO_2-HMS shown in the inset of Fig. 1b.

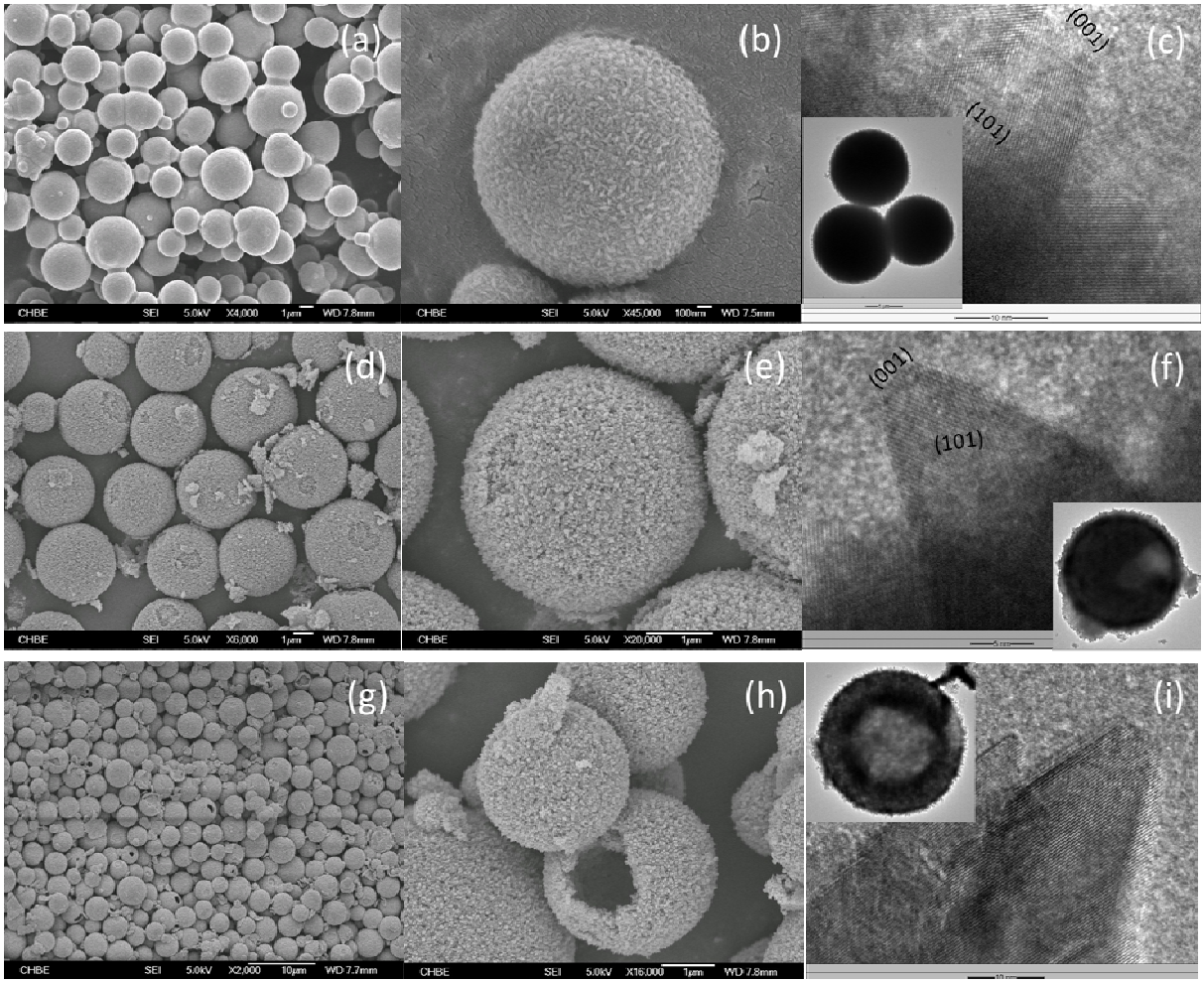

Fig. S4: SEM (a, b, d, e, g, h), TEM (insets of c, f, i) and high-resolution TEM (c, f, i) images for N-doped TiO_2 microspheres synthesized under controlled solvothermal conditions with molar ratios of H_2O/Ti = 0 (a-c), 0.3 (d-f), and 1.0 (g-i).

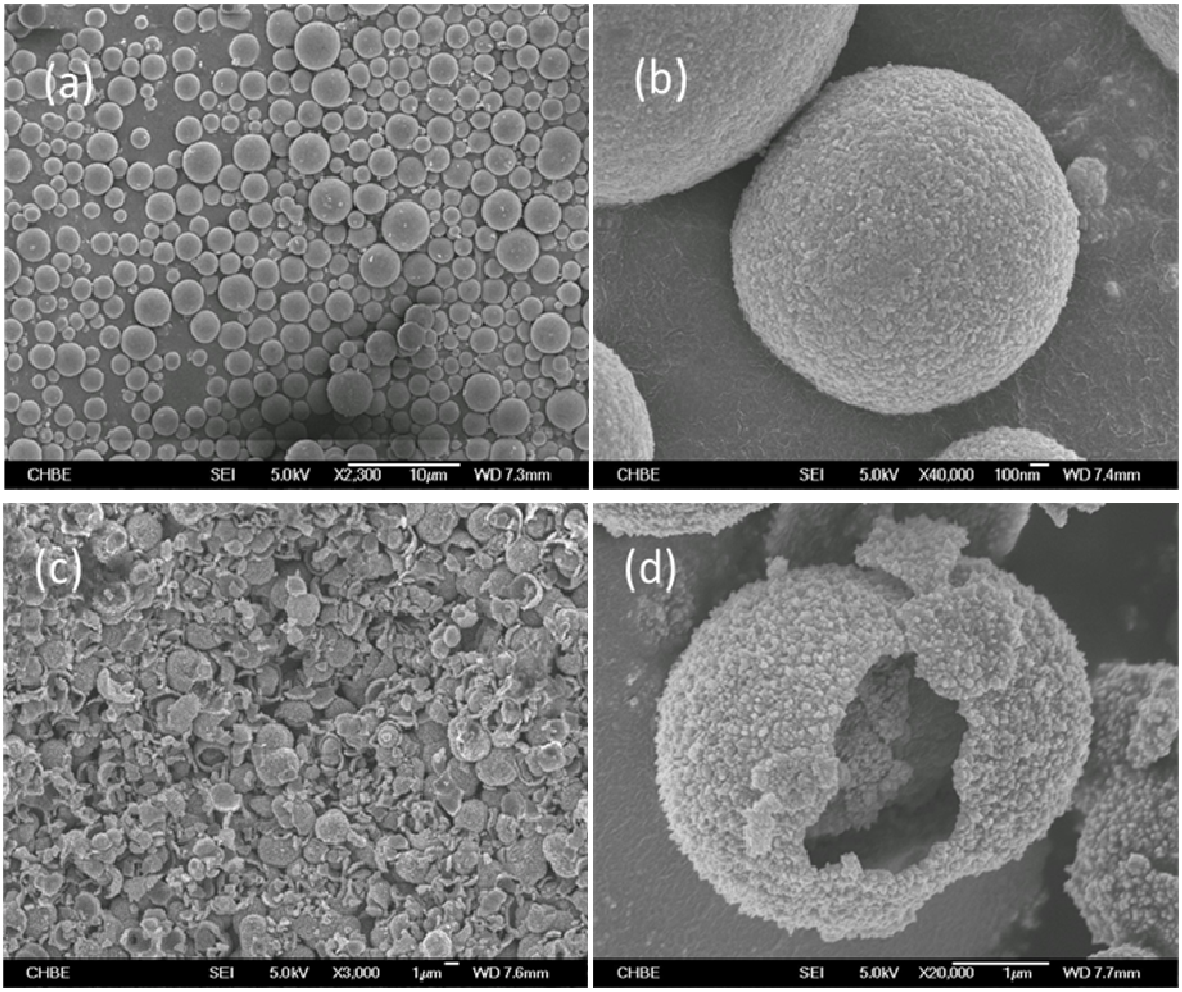

Fig. S5: SEM images showing the morphologies of the products obtained after 6 h (a, b) and 12 h (c, d) of solvothermal reaction.

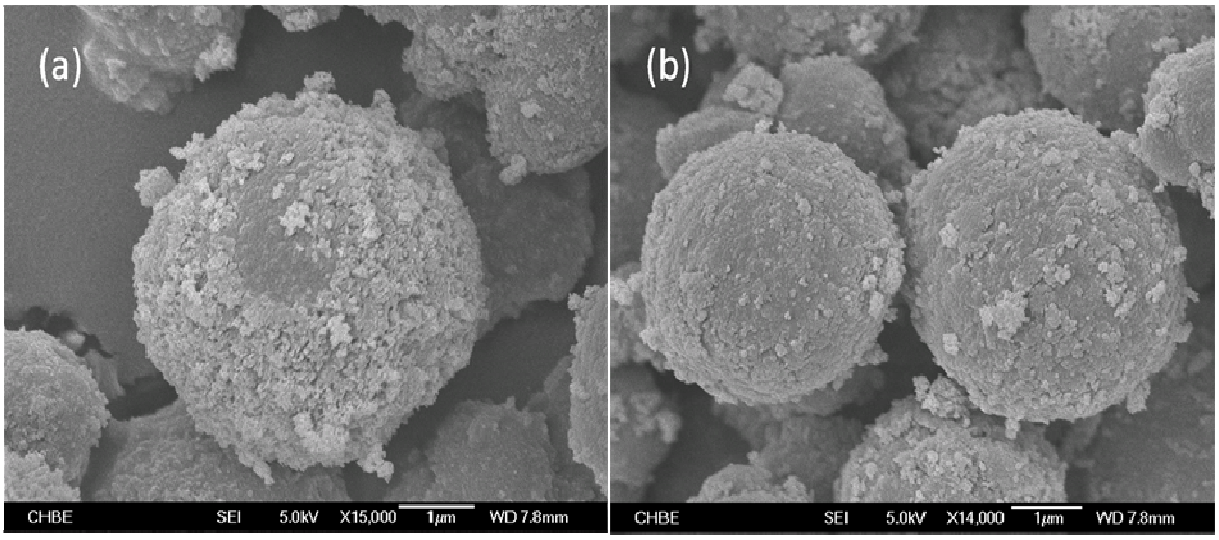

Fig. S6: SEM images for TiO_2 microspheres synthesized under controlled solvothermal conditions using ethanol (a) and butanol (b) as solvents.

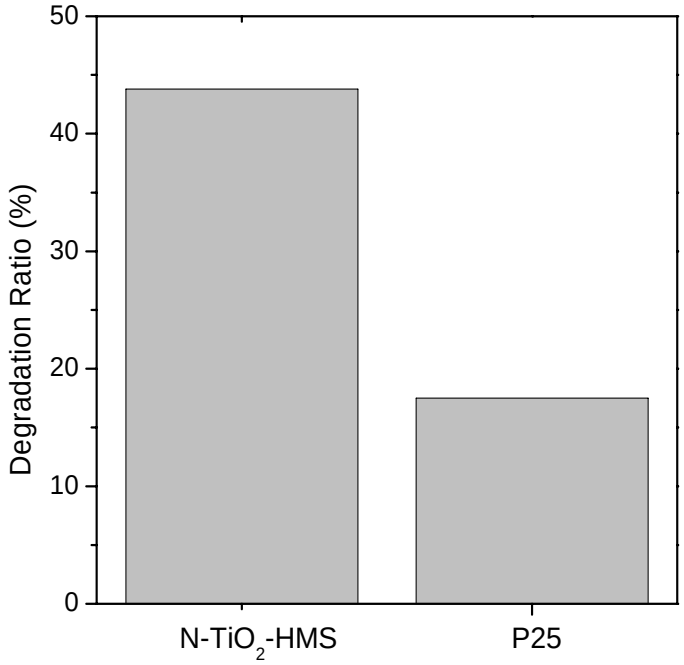

Fig. S7: Photocatalytic properties of N-TiO_2-HMS and P25 for degrading orange II. Samples were irradiated under visible light for 1.5 h. The concentrations of the photocatalytst and MB were 1 g/L and 5 ppm, respectively.