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Supplementary Information

Titanium oxynitride microspheres with the rock-salt structure for visible-light photocatalysts

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Photodegradation of methylene blue Methylene blue (MB) solution was prepared by dissolving MB in deionized water. The concentration of the MB solution is set to 10 mg/L. A 0.01 g of $TiO_2@TiO_{1-x}N_x$ was added to a 2 mL of the MB solution in a vial, which was then sealed with a screw cap. Before irradiation, the suspensions were sonicated in the dark for 5 min. The vial containing MB and $TiO_2@TiO_{1-x}N_x$ was irradiated using a 300 W xenon lamp (Newport). The light intensity of the Xe light source is 300 W. For visible-light irradiation, a 420 nm cut-off filter was used to remove UV light. The incoming light was passed through a water filter to block infrared radiation. After irradiation, the vial was unloaded and the solution was separated from the $TiO_2@TiO_{1-x}N_x$ catalyst. The solution was analyzed by measuring the characteristic absorption peak of MB at 665 nm using the UV-visible spectrometer. The percentage of degradation was calculated, based on the standard absorption curve of the MB solution.

Analysis of hydroxyl radicals Alkaline solution of terephthalic acid (TA) was first prepared in a dilute NaOH solution (2×10^{-3} M) in order to ensure complete dissolution. The TA concentration used for the measurements is fixed at 5×10^{-4} M. $TiO_2@TiO_{1-x}N_x$ (0.1g) was dispersed in a 20 mL of the TA solution. Sampling was performed at every 30 min after visible light irradiation. A fluorescence spectrometer was used to monitor the fluorescence emission at 425 nm using an excitation wavelength of 315 nm. The hydroxylation product, 2-hydroxyterephthalic acid, produced a peak at 425 nm.

Characterization A cross section TEM specimen of $TiO_2@TiO_{1-x}N_x$ microsphere was prepared by using a Quanta3D focused ion beam (FIB) equipment (FEI Co., USA) at KBSI in Daejeon. To avoid the sample damages by the Ga^+ ion, sample was located on C-coated glass substrate. After then, second C-coating & Pt deposition were carried out on $TiO_2@TiO_{1-x}N_x$ microsphere, respectively. Rough milling was performed using a 30 kV Ga ion beam with a current of 7 nA and 3 nA. Fine milling for TEM observation were carried out with a range of 0.5nA ~ 50pA at 30kV. Finally sample cleaning was performed with a current of 50 pA at 5 kV. The selected area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) images for core and shell parts of $TiO_2@TiO_{1-x}N_x$ microspheres were obtained by using a JEOL JEM-2100F microscope operating at 200 kV (JEOL, Japan). Its chemical analysis was performed using a JED-2300 system (JEOL, Japan) attached to the

TEM for energy dispersive X-ray (EDX) analysis. STEM-EELS (scanning transmission electron microscopy- electron energy loss spectroscopy) analysis was performed using the aberration corrected TEM (LIBRA 200 HT Mc Cs, Carl Zeiss). The STEM image was obtained with a spot size of 1.2 nm using the high angle annular dark field (HAADF) detector (Model 300, Fischione). The spectrum imaging (SI) from STEM image was acquired using the digital beam control system and imaging processing system (Digiscan II, Gatan Inc.). For examination of Ti, N, and O elementals, especially, SI imaging was obtained with experimental conditions of the energy loss range (385 eV ~ 565 eV), a dispersion of 0.1 eV and 50 x 50 pixels area.

Photoelectrochemical test Potentiostat/galvanostat (Model 263A, Princeton Applied Research, USA) was used for measuring the electrochemical data. Before making the working electrode, the indium tin oxide (ITO) glass was cleaned by sonication in ethanol and acetone for 30 min, respectively. The glass was then rinsed with distilled water and kept in isopropyl alcohol for 12 h.[1] The $TiO_2@TiO_{1-x}N_x$ sample (8 mg) was dispersed in a 200 µL of diluted Nafion (0.5 wt %) in methanol, which was drop-casted onto a 1.0 cm^2 of ITO glass substrate. The resulting electrode was dried in air at 100 ^oC.[2] Photoelectrochemical experiments were performed in a three-electrode cell system with Pt wire as a counter electrode, an Ag/AgCl electrode (3 M NaCl) as a reference electrode, and a $TiO_2@TiO_{1-x}N_x$ catalyst on an ITO glass as a working electrode. The three-electrode cell was immersed in a Pyrex vial with a volume of 15 mL. A 300 W xenon lamp was used as light source with a 420 nm cut-off filter to generate visible light only.[3,4] The working electrodes were illuminated from the backside.

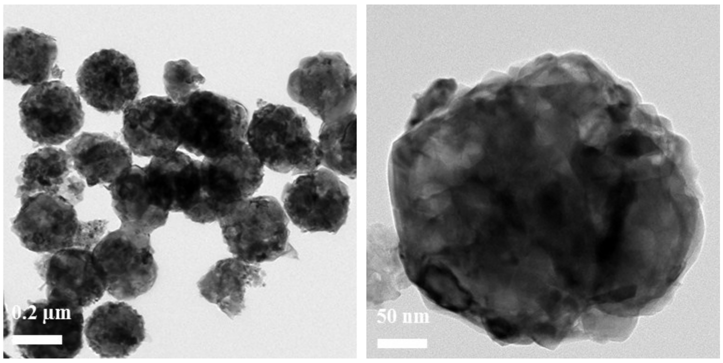

Fig. S1. TEM images of $TiO_2@TiO_{1-x}N_x$ nitrided at 900 ^oC for 24 h. The spherical shape was almost collapsed.

Materials	Lattice parameter
Ref-TiO (JCPDS NO. 089-3660)	a= 4.1705 Å
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 4 h	a= 4.1774 Å
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 7 h	a= 4.1876 Å
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 10 h	a= 4.1945 Å
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 24 h	a= 4.2066 Å
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 48 h	a= 4.2103 Å
Ref-TiN (JCPDS NO. 074-1214)	a= 4.3937 Å

Table. S1. Calculated lattice parameters for $TiO_2@TiO_{1-x}N_x$ samples nitrided at 700 °C in a NH_3 atmosphere for different periods of time. For comparison, lattice parameters of TiN and TiO were included, which were taken from the JCPDS file.

Materials	Elements	Atomic (%)	Weight (%)
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 10 h	Ti	30.73	58.50
	O	37.01	23.53
	N	32.27	17.96
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 24 h	Ti	30.59	58.84
	O	26.45	17.00
	N	42.95	24.16
$TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 48 h	Ti	26.45	54.37
	O	16.45	11.30
	N	57.10	34.33

Table. S2. Atomic and weight percentages of the three $TiO_2@TiO_{1-x}N_x$ samples were obtained from the EDX data.

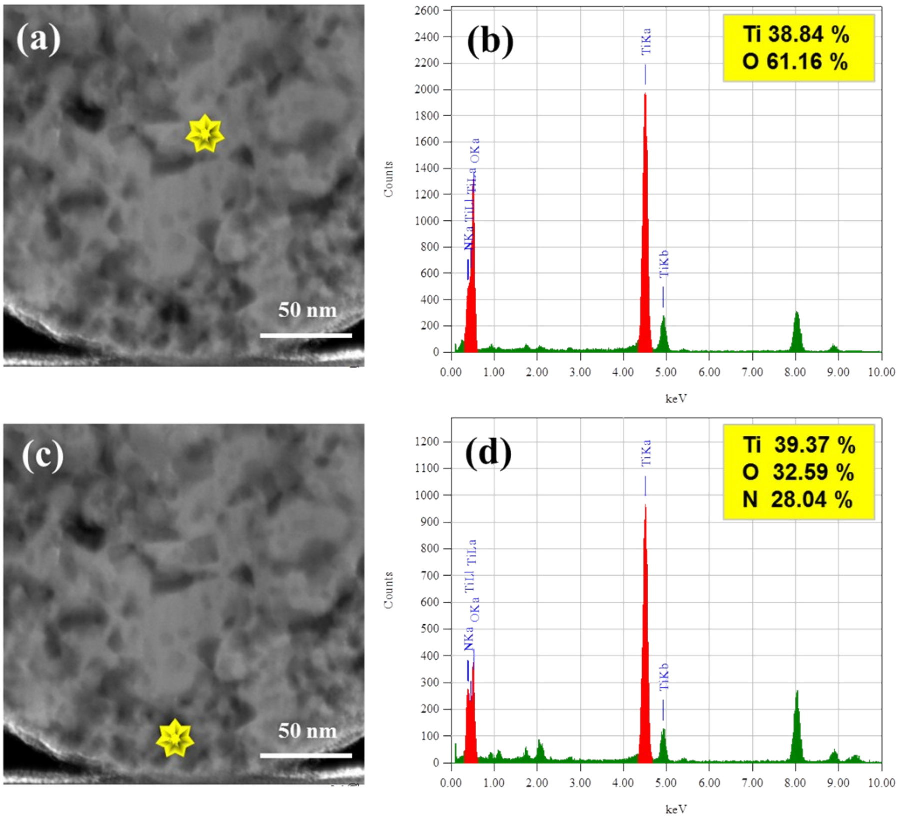

Fig. S2. STEM images (a, c) of a bisected $TiO_2@TiO_{1-x}N_x$ microsphere. EDS data of (b) and (d) are collected from corresponding yellow spots of (a) and (c), respectively. (b) and (d) represent core and shell signals, respectively.

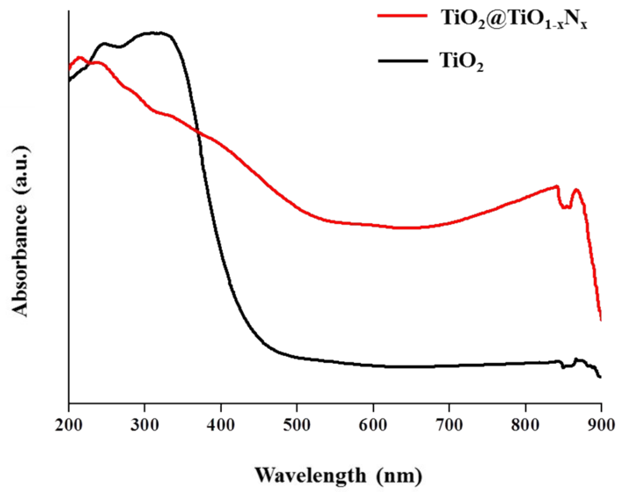

Fig. S3. The DRUVS spectrum of $TiO_2@TiO_{1-x}N_x$ nitrided at 700 °C for 24 h clearly shows that the sample absorbs light in the broad visible region. For comparison, the DRUVS spectrum of TiO_2 was included.

References

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