

Supplementary Information for

Facile synthesis of in-situ phosphorus-doped g-C₃N₄ with enhanced visible light photocatalytic NO purification

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● Experimental Section

1.1 Synthesis of P doped g-C₃N₄

All chemicals used in this study reached analytical grade and no further treatment was carried out afterwards. In a typical synthesis, 10 g of thiourea was mixed with a certain amount (0.3, 0.5 and 1.0 g) of phosphonitrilic chloride trimer (Cl₆N₃P₃). The mixture was transferred into a semi-closed alumina crucible with a cover after grounded for 20 mins, and then heated to 550 °C in a muffle furnace for 2 hours at a heating rate of 10 °C min⁻¹. The pure g-C₃N₄ with no addition of Cl₆N₃P₃ was prepared under the same thermal conditions. After the reaction, the resultant samples were collected and grounded into powders when the alumina crucible was cooled to room temperature for further use. The samples were named as CN and CN-P-X (X=3, 5 and 10), respectively.

1.2 Characterization

The crystal phase was analyzed by X-ray diffraction with Cu K α radiation (XRD: model D/max RA, Japan). The scan rate was 0.02 degree/s. The accelerating voltage and the emission current were 40 kV and 40 mA, respectively. X-ray photoelectron spectroscopy with Al K α X-rays (h ν = 1486.6 eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.8 eV as an internal standard. The morphology and structure were characterized by transmission electron microscopy (TEM: JEM-2010, Japan). The

UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV-vis spectrophotometer (UV-vis DRS: UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, using BaSO₄ as reflectance sample. The photoluminescence spectra were measured with a fluorescence spectrophotometer (PL, F-7000, Japan) using a Xe lamp as excitation source with optical filters. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 150 °C prior to measurements.

1.3 Visible light photocatalytic capability for NO purification

The photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A 150 W commercial tungsten halogen lamp was vertically placed outside the reactor. A UV cutoff filter (420 nm) was adopted to remove UV light in the light beam. Photocatalyst (0.2 g) was coated onto a dish with a diameter of 12.0 cm. The coated dish was then pretreated at 70 °C to remove water in the suspension. The catalyst adhesion on the dish was firm enough to avoid the erosion (or removal) of the catalyst during air flowing. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N₂ balance, BOC gas). The initial concentration of NO was diluted to about 500 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L/min by a mass flow controller. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated by η (%) = $(1-C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet stream and the feeding stream, respectively.