Supplementary Information for

(NH₄)₂SO₄-assisted polycondensation of dicyandiamide for porous g-C₃N₄ with enhanced photocatalytic NO removal

Peidong Li¹, Wendong Zhang², Yuxin Zhang³, Yanjuan Sun*¹,a, Fan Dong*¹,a

¹ Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, College of Environment and Resources, Chongqing Technology and Business University, 400067 Chongqing, China.
² Department of Scientific Research Management, Chongqing Normal University, Chongqing, 401331, China.
³ College of Materials Science and Engineering, National Key Laboratory of Fundamental Science of Micro/Nano-Devices and System Technology, Chongqing University, Chongqing 400044, China.

● Experimental Section

1.1 Preparation of bulk g-C₃N₄ and (NH₄)₂SO₄-modified g-C₃N₄

All chemicals were reagent grade and used without further treatment. The bulk g-C₃N₄ (CN) was prepared by the polycondensation of dicyandiamide (2g) loaded in a crucible at 550 °C for 2 h in a muffle furnace. The ramping rate was 5 °C/min. The sample was cooled naturally to room temperature. To prepare (NH₄)₂SO₄-modified g-C₃N₄, 2g of dicyandiamide powder and different amount of (NH₄)₂SO₄ were dissolved with 30 mL water in an alumina crucible. The solution of dicyandiamide and ammonium sulfate were then dried at 60 °C overnight to get the composite precursors. The composite precursors loaded in a crucible were heated to 550 °C at a heating rate of 5 °C min⁻¹ in a muffle furnace and maintained for 2 h. According to the molar ratios of dicyandiamide: (NH₄)₂SO₄ (2:1, 2:1.5, 2:2, and 2:2.5), these samples were named as CN-1, CN-1.5, CN-2 and CN-2.5, respectively.

1.2 Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer equipped with intense Cu Kα radiation (Model D/max RA, Rigaku Co., Japan). The morphological structure was analyzed using scanning electron microscope (SEM, JEOL model JSM-6490, Japan) and transmission electron
microscope (TEM, JEM-2010, Japan). The Brunauer–Emmett–Teller (BET) specific surface area (SBET) of the samples were determined using a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 100 °C for 12 h prior to measurements. X-ray photoelectron spectroscopy (XPS) measurement was carried out to investigate the surface chemical compositions and states with Al Kα X-ray (hν = 1486.6 eV) radiation source operated at 150 W (Thermo ESCALAB 250, USA). The UV-vis diffuse reflection spectra (UV-vis DRS) were obtained for the dry-pressed disk samples by using a Scan UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) with 100% BaSO₄ as the standard sample. The photoluminescence spectra (PL) for the samples were measured with a fluorescence spectrophotometer (FS-2500, Japan) using a Xe lamp as excitation source with optical filters.

1.3 Visible light photocatalytic capability for NO purification

The visible light responsive photocatalytic activity was evaluated by removal of NO at ppb-level in a continuous flow reactor. The reactor had a capacity of 4.5 L (30×15×10 cm), made of polymeric glass and covered with Quartz-Glass. A commercial tungsten halogen lamp (150 W) was vertically placed outside and 20 cm above the reactor. A UV cut-off filter (420 nm) was used to remove UV light from the lamp. The as-prepared sample (0.20 g) was dispersed in distilled water (50 mL) in two beakers via ultrasonic treatment for 10 min and then spread on two glass dishes. The coated dishes were dried at 60 °C and were placed at the center of the reactor after being cooled to room temperature. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N₂ balance). The initial concentration of NO was diluted to about 600 ppb by air streaming. The flow rates of the air stream and NO were controlled at 2.4 L min⁻¹ and 15 mL min⁻¹, respectively. The gas streams were premixed completely by a gas blender. The relative humidity was controlled at 50% in the air stream. When the adsorption–desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was measured every minute by a NOx analyzer (Thermo Scientific, 42i-TL), which also monitored the concentrations of NO, NO₂ and NOx. The removal ratio (η) of NO was calculated using \( \eta(\%) = (1 - C/C_0) \times 100\% \), where C and C₀ represents the outlet and inlet concentration of NO.