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Supporting information

For

Graphitic Carbon Nitride for Photocatalytic Degradation of Sulfamethazine in Aqueous Solution under Simulated Sunlight Irradiation

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Experimental

Catalysts' preparation

Bulk g-CN was prepared by direct polycondensation of guanidine hydrochloride (GndCl, analytically pure, Sinopharm Chemical Reagent Co., Ltd) in an oven (protected by nitrogen) at 550 °C for 4 h, with a heating rate of 2 °C/min. Supported g-CN/SBA-15 was prepared by first dissolving GndCl in de-ionized water until the material was fully dissolved. Thereafter, a prepared SBA-15 [see Microporous and Mesoporous Materials, 2016, 221, 159-166] was added to impregnate the precursor. The mass ratio of SBA-15 to GndCl is 1:1. The mixture was stirred continuously at 90 °C until water was evaporated. The resulting material was dried at 100 °C in an air oven overnight and thermal treated in N₂ atmosphere at 500 °C for 4 h (heating rate: 2 °C/min). Mesoporous mpg-CN was prepared by a templating method using silica gel (chemical pure, percentage: 25-30%, particle size: 17 nm, Tianjin Guangfu Fine Chemical Research Institute) as template and GndCl as precursor. The impregnation process is similar to that for the preparation of g-CN/SBA-15, except that the mass ratio of silica to GndCl is 0.7:1. The obtained g-CN/SiO₂ composite was treated with 50 mL 4 M NH₄HF₂ for 48 h, and then filtrated, washed three times with deionized water and twice with ethanol, and finally dried in a vacuum oven at 50 °C for 6 h.

Characterizations

X-Ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer (Cu Kα irradiation). Transmission electron microscopy (TEM) image was obtained on a Tecnai G2 20 S-Twin apparatus with high-resolution transmission electron microscope (200 kV). N₂ physisorption isotherms were determined at liquid-nitrogen temperature (-196 °C) with an Autosorb-1 apparatus. The sample was degassed at 150 °C overnight before measurement. Thermal gravimetric analysis (TGA) was conducted on a NETZSCH TG 209F3 apparatus. 10 mg

samples were first put in an alumina crucible, thereafter air with flow rate of 20 mL min⁻¹ was passed. After reaching a stable baseline, the sample was heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹, to record the profile. Diffuse reflectance spectroscopy (DRS) was obtained from a UV–vis spectrophotometer (Lambda, Bio 35, PE Co., USA).

Photocatalytic tests

Photocatalytic degradation of SMT was conducted on a XPA-7 photochemical reactor (Xujiang Electromechanical plant, Nanjing, China). Simulated sunlight irradiation was provided by a 350W xenon lamp (Institute of Electric Light Source, Beijing). The reaction system was cooled by circulating water and maintained at room temperature. 200 mL SMT aqueous solution (10 mg L⁻¹) were divided homogeneously into 10 parallel quartz-tube reactors (20 mL for each) and, to each reactor 20 mg catalysts (1 g L⁻¹) were added. Before irradiation, the suspension was stirred in dark for 30 min in order to achieve an adsorption–desorption equilibrium of SMT on the catalysts. In the tests, 1.5 mL of aqueous sample was withdrawn from the parallel experiments at desired time intervals and filtered before the analysis, in order to ensure that the activity was tested under identical reaction conditions. Thus 10 points were obtained from the 10 parallel reactors. The concentrations of SMT were determined by a reverse-phase HPLC (Shimadzu LC-20AT) equipped with a 250 mm × 4.6 mm Waters C18 column. A Waters guard column (C18, 4.6 mm × 20 mm) was used to protect the analytical column. The injection volume of sample was 10 μ L. The mobile phase was mixtures of 55% HPLC-grade methanol and 45% ultra-water, with a flow rate of 1.0 mL·min⁻¹. The detection wavelength was set at 266 nm.

In the calculation of the contribution of h^+ , $\bullet O_2^-$ and $\bullet OH$, if we assume that their contribution to the reaction is 100% (corresponding to the activity of 70% in Figure 1D), then we can have the equation:

 $h^{+} + \bullet O_{2}^{-} = 30\% * 100\% / 70\%$ (Isopropanol is added) $h^{+} + \bullet OH = 19\% * 100\% / 70\%$ (BQ is added) $\bullet O_{2}^{-} + \bullet OH = 8\% * 100\% / 70\%$ (KI is added) After simplication, the equations can be presented as:

 $h^+ + \bullet O_2^- = 0.43$ $h^+ + \bullet OH = 0.27$

$$\bullet O_2^{-} + h^+ + \bullet O_2^{-} = 0.12$$

By calculation, we can obtain the contribution of each species, as below:

 $h^+ = 29\%; \bullet O_2^- = 14\%; \bullet OH = -2\%$



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