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Synthesis, properties and photocatalytic activity of porous carbon nitride

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Porous carbon nitrides of different morphology were obtained via bulk and hard template (SBA-15 and MCF) pyrolysis of melamine. It was shown that acetaldehyde was the main product of the photoreduction reaction of CO_2 regardless the morphology of carbon nitride. The using of hydrochloric acid during the impregnation of the initial matrices with melamine's solution allowed obtaining ordered porous carbon nitride with higher bandgap (2.87 eV for carbon nitride received in MCF) in the contrary to bulk sample (2.45 eV). Sponge-like C_3N_4–MCF possessing spatially ordering, developed surface and the higher bandgap in this regard revealed the highest photocatalytic activity in the photoreduction of carbon dioxide with the formation of acetaldehyde.

Photocatalytic reduction of carbon dioxide in the presence of water vapor on S-doped and non-doped carbon nitrides was investigated. Utilization of sulfuric acid results not only in doping of carbon nitride with sulfur but also in a significant decrease of particle size (from 31 nm to 6 nm) and changes in textural characteristics (S_{BET} from 75 to 25 m^2/g). S-doped carbon nitride demonstrated much higher photocatalytic activity in photoreduction of carbon dioxide to acetaldehyde (from 0.6 to 5 μmol/g) and methane (from 0.03 to 0.27 μmol/g) compared to non-doped C_3N_4. The increased photocatalytic activity of S-doped carbon nitride is a result of the expansion and shift of the valence band due to doping impurity of sulfur, as well as a shift of the conduction band of carbon nitride to more negative potentials (relatively to the electrochemical scale) caused by the quantum size effects. The obtained results give new possibilities for development of efficient and cheap photocatalysts on the basis of graphitic carbon nitride.