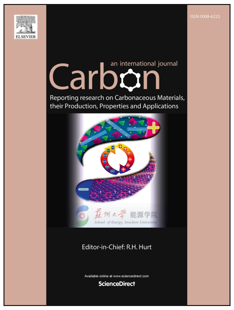

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Pore confinement effects and stabilization of carbon nitride oligomers in macroporous silica for photocatalytic hydrogen production

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Abstract

An ordered macroporous host (mac-SiO_2) has been used to prevent aggregation of layered photocatalysts based on carbon nitride. Using typical carbon nitride synthesis conditions, cyanamide was condensed at 550 ^oC in the presence and absence of mac-SiO_2. Condensation in the absence of mac-SiO_2 results in materials with structural characteristics consistent with the carbon nitride, melon, accompanied by ca. 2 wt% carbonization. For mac-SiO_2 supported materials, condensation occurs with greater carbonization (ca. 6 wt%). On addition of 3wt% Pt cocatalyst photocatalytic hydrogen production under visible light is found to be up to 10 times greater for the supported composites. Time-resolved photoluminescence spectroscopy shows that excited state relaxation is more rapid for the mac-SiO_2 supported materials suggesting faster electron-hole recombination and that supported carbon nitride does not exhibit improved charge separation. CO_2 temperature programmed desorption indicates that enhanced photoactivity of supported carbon nitride is attributable to an increased surface area compared to bulk carbon nitride and an increase in the concentration of weakly basic catalytic sites, consistent with carbon nitride oligomers.

1. Introduction

The specific activity (per unit mass) of a heterogeneous catalyst can be increased by controlling morphology, typically by increasing the geometric surface area. For heterogeneous photocatalysts there are the additional considerations of photon absorption and subsequent electron/hole migration that precede surface reactions.[1] In the absence of significant surface reconstruction, increasing the specific surface area of a photocatalyst typically enhances the number of catalytically active sites, while suppressing bulk electron-hole recombination. High surface areas can also be stabilized by dispersing active phases

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