Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Photocatalytically Active Oligomeric Graphitic Carbon Nitride: Conformational Flexibility, Electronic Levels, Carrier Localization

VOLKER BLUM, Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, USA, VINCENT LAU, Max Planck Institute for Solid State Research, Stuttgart, Germany, TIAGO BOTARI, WILLIAM HUHN, Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, USA, BETTINA V. LOTSCH, Max Planck Institute for Solid State Research, Stuttgart, Germany and University of Munich (LMU), Munich, Germany

— Polymers consisting of bridged heptazine units (often called “graphitic carbon nitride” or “g-C_3N_4”) show considerable promise as photocatalysts for solar hydrogen evolution. Recent experimental evidence suggests that oligomeric rather than fully polymerized “g-C_3N_4” exhibits increased intrinsic photocatalytic activity. Using density-functional theory (DFT; van der Waals corrected PBE functional for conformers, hybrid DFT and *GW* for electronic levels), we show that considerable conformational flexibility exists for the heptazine trimers and tetramers. Analysis of HOMO and LUMO locations as well as trends in photocatalytic activity among heptazine oligomers and polymers reveals the NH_2 groups of the oligomers as potential charge-transfer sites. We show that conformational variations of the oligomers can lead to significant, electrostatically motivated carrier localization effects. We suggest that NH_2 side groups and the intrinsic conformational variations of the oligomeric species lead to the observed enhanced catalytic activity.

Volker Blum
Department of Mechanical Engineering and Materials Science,
Duke University, Durham, NC, USA

Date submitted: 14 Nov 2014 Electronic form version 1.4