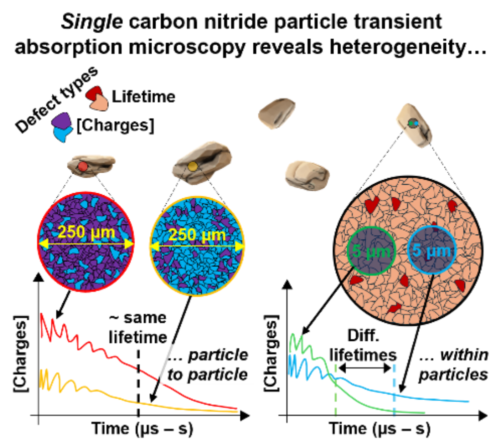
Deciphering Charge Carrier Dynamics in Carbon Nitride Photocatalysts for Improved Energy, Environmental, and Synthetic Applications

Abstract

Polymeric photocatalysts made of Earth-abundant elements have been extensively developed over the past decade to take advantage of their synthetic tunability.[1] Within this family, carbon nitrides (CN_x) are emerging as leading photocatalysts because of their high photocatalytic performance combined with good stability and facile synthesis.[2] However, significant gaps remain in our knowledge of the photophysical properties of these organic polymeric materials. Determining the pathways and mechanism of photoinduced processes will greatly aid our efforts to engineer better CN_x photocatalysts for solar fuel production, environmental remediation, and synthetic photochemistry.[3]

We have developed a first-of-its-kind transient absorption microscopy (TAM) system that can monitor charge carrier dynamics on the microsecond – second timescales together with spatial resolution on the micron scale. Spatial mapping of the charge carrier dynamics with this system provides novel insights into the particle-to-particle heterogeneity and heterogeneity within individual CN_x particles. Our observations point to the presence of at least two different types of trap states that dictate the density of trapped charges and the charge carrier lifetime, respectively.



Photocatalysts are often surface-modified with cocatalysts to enhance their photocatalytic activity and drive specific chemical transformations. We use transient absorption spectroscopy (TAS) on these types of systems where CN_x have been modified by cocatalysts containing metals such as Pt, Ni, and Co.[4,5] We can observe the impact of these surface modifications on the charge carrier dynamics and glean information on charge transfer pathways and reaction mechanisms. These new insights into the charge carrier dynamics of CN_x can push the field of photocatalyst into uncovering the optimal structure and local environment in defect-rich organic semiconductors such as CN_x.

1 Y. Wang, A. Vogel, M. Sachs, R. S. Sprick, L. Wilbraham, S. J. A. Moniz, R. Godin, M. A. Zwijnenburg, J. R. Durrant, A. I. Cooper and J. Tang, *Nat. Energy*, 2019, **4**, 746–760.

2 P. O. Ohemeng and R. Godin, *Sustainable Energy Fuels*, 2023, **7**, 3250–3265.

3 R. Godin and J. R. Durrant, *Chem. Soc. Rev.*, 2021, **50**, 13372–13409.

4 C. Liu, J. Liu and R. Godin, *ACS Catal.*, 2023, **13**, 573–586.

5 M. Beckedorf, J. Holland and R. Godin, *Artif. Photosynth.*, 2024, DOI:10.1021/aps.4c00007.

Bio

Dr. Robert Godin established the SolarSpec group (Solar Energy Conversion and Spectroscopy) in 2018 at UBC Okanagan in Kelowna, British Columbia, Canada. The group develops time-resolved spectroscopic tools to better understand carbon-based semiconductors for sustainable energy production, with a healthy dose of physical organic chemistry concepts. Born in Bathurst, New Brunswick, Robert has fostered an interest in photochemistry since the start of his higher education career. He first got introduced to photochemistry and spectroscopy techniques working with Prof. Tito Scaiano during his B.Sc. at the University of Ottawa. He continued to learn advanced optical techniques with Prof. Gonzalo Cosa during his Ph.D. on single molecule spectroscopy at McGill University. Robert then completed a FRQNT-funded postdoctoral stint from 2015 to 2018 with Prof. James Durrant at Imperial College London, UK, to fully enter the field of solar energy conversion.