abstract
Photocatalytic water splitting over suspended nanoparticles represents a potential solution for achieving CO2-neutral energy generation and storage. To design efficient photocatalysts, a fundamental understanding of the material’s structure, electronic properties, defects, and how these are controlled via synthesis is essential. Both bulk and nanoscale materials characterization, in addition to various performance metrics, can be combined to elucidate functionality at multiple length scales. In this work, two promising visible light harvesting systems are studied in detail: Pt-functionalized graphitic carbon nitrides (g-CNxHys) and TiO2-supported CeO2-x composites.

Electron energy-loss spectroscopy (EELS) is used to sense variations in the local concentration of amine moieties (defects believed to facilitate interfacial charge transfer) at the surface of a g-CNxHy flake. Using an aloof-beam configuration, spatial resolution is maximized while minimizing damage thus providing nanoscale vibrational fingerprints similar to infrared absorption spectra. Structural disorder in g-CNxHys is further studied using transmission electron microscopy at low electron fluence rates. In-plane structural fluctuations revealed variations in the local azimuthal orientation of the heptazine building blocks, allowing planar domain sizes to be related to the average polymer chain length. Furthermore, competing factors regulating photocatalytic performance in a series of Pt/g-CNxHys is elucidated. Increased polymer condensation in the g-CNxHy support enhances the rate of charge transfer to reactants owing to higher electronic mobility. However, active site densities are over 3x lower on the most condensed g-CNxHy which ultimately limits its H2 evolution rate (HER). Based on these findings, strategies to improve the cocatalyst configuration on intrinsically active supports are given.

In TiO2/CeO2-x photocatalysts, the effect of the support particle size on the bulk/nanoscale properties and photocatalytic performance is investigated. Small anatase supports facilitate highly dispersed CeO2-x species, leading to increased visible light absorption and HERs resulting from a higher density of mixed metal oxide (MMO) interfaces with Ce3+ species. Using monochromated EELS, bandgap states associated with MMO interfaces are detected, revealing electronic transitions from 0.5 eV up to the bulk bandgap onset of anatase. Overall, the electron microscopy/spectroscopy techniques developed and applied herein sheds light onto the relevant defects and limiting processes operating within these photocatalyst systems thus suggesting rational design strategies.