

PHOTOCATALYSIS

g/C₃N₄-based photocatalysis*Adv. Funct. Mater.*, **30**, 2002353 (2020)

Photocatalysis has been regarded as a sustainable and environmentally friendly technique for the degradation of contaminants. Graphitic carbon nitride (g/C₃N₄), an efficient metal-free polymeric semiconductor photocatalyst, has attracted extensive attention, but the practical applications of intrinsic g/C₃N₄ are usually limited by its insufficient visible-light absorption (the band absorption edge is about 460 nm), high recombination rate of charge carriers and low electrical conductivity. Various strategies, including doping with elements to narrow the bandgap, coupling with cocatalysts to enhance the reaction kinetics, and loading on substrates with excellent mobility of charge carriers to realize the efficient charge extraction, have been developed to overcome these drawbacks. However, the systematic optimization on the photocatalytic behaviors of g/C₃N₄ for degrading complicated chemicals is lack of deserved attention.

Deng *et al.* optimized the photocatalytic performance of g/C₃N₄-based metal-free photocatalysts, via doping of oxygen, decorating with CDs (carbon quantum dots), and loading on the rGO (reduced graphene oxide) for degradation of a representative antibiotic, lincomycin. The combination showed a synergistic effect both in the degradation rate and the degree of decomposition of lincomycin. The bandgap of g/C₃N₄ has been narrowed efficiently by doping of oxygen, which enhanced the utilization of visible light. CDs were introduced as cocatalysts to boost the production of reactive species of ·O₂⁻. rGO was used to optimize the charge extraction. In comparison with the intrinsic g/C₃N₄, the structurally optimized photocatalyst showed a tenfold enhancement in degradation rate. In the degradation, the active species, including ·O₂⁻, ·OH, and h⁺, had different contributions in the different photocatalysts. The intermediate, H₂O₂, played an important role in the photocatalytic process, and the detailed functions and originations were clarified for the first time. ·O₂⁻ was the main active species for all the systems, but its production pathways were different for g/C₃N₄ and O-g/C₃N₄ (oxygen doped g/C₃N₄). It came from the O₂ reduction in g/C₃N₄, while from the H₂O₂ decomposition in the systems containing O-g/C₃N₄. The H₂O₂ production was very important, and it originated from H₂O oxidation in the systems of O-g/C₃N₄ and CD-O-g/C₃N₄, and from both H₂O oxidation and O₂ reduction in the systems of rGO-O-g/C₃N₄ and CD-rGO-O-g/C₃N₄. Another reactive species of ·OH was generated by the h⁺ in the active sites of rGO. In addition, decorating of CDs could promote the production of ·O₂⁻ from H₂O₂ by chemical catalysis without light on account of the peroxidase-mimetic activity of them. Thus, a new metal-free g/C₃N₄-based photocatalyst of high efficiency has been provided by engineering the components efficaciously.

Chao Zhao (Institute of Semiconductors, CAS, Beijing, China)

doi: [10.1088/1674-4926/41/9/090201](https://doi.org/10.1088/1674-4926/41/9/090201)

PHOTOCATALYSIS

Reactive facet of carbon nitride single crystals*Nat. Catal.*, **3**, 649 (2020)

Reactive facets of heterogeneous photocatalysts play an important role during the water photolysis process since they afford the active sites/planes for the photoredox splitting of water or loading of co-catalysts. Recent studies indicated that the facets also play additional roles during charge separation. Therefore, identifying and exploring how the reactive facets facilitate the reactivity is considered to be a crucial step for developing high-performance photocatalysts for solar to chemical energy conversion. Investigations of the reactive facets have mainly focused on inorganic photocatalysts. There are only few reports about the exact reactive facets of polymeric carbon nitride (PCN) due to its low crystallinity and instability under the irradiation of high-energy electron beams. The PTI (polytriazine imide) intercalated with LiCl (PTI/Li⁺Cl⁻), which is synthesized by ionothermal methods, forms an ideal system for exploring the reactive facets of conjugated polymers because of its high crystallinity.

Wang *et al.* studied the surface structures of PTI/Li⁺Cl⁻ under an extremely low electron dose rate via aberration-corrected integrated differential phase contrast (AC-iDPC) imaging. The photodeposition of Co and Pt co-catalysts was used to probe the reactive facets of PTI/Li⁺Cl⁻ in overall water photolysis. First-principles calculations were performed to understand the electronic structures and confirm the electron-hole transition among the prismatic {10 $\bar{1}$ 0} planes of the PTI/Li⁺Cl⁻. Unlike conventional view on PCN nanosheets, all those experiments demonstrated that the side prismatic planes {10 $\bar{1}$ 0} were the major reactive facets because of two factors: the photogenerated electron-hole pairs can easily migrate along with the conjugated layers to the {10 $\bar{1}$ 0} facets, and the co-catalysts are mostly photodeposited on the {10 $\bar{1}$ 0} facets due to the more electrons or holes available on the prismatic surfaces. Upon this discovery, PTI/Li⁺Cl⁻ crystals with different aspect ratios were prepared at different synthetic temperatures. It is found that the overall water splitting performance followed a linear correlation with the relative surface areas of the {10 $\bar{1}$ 0} and {0001} planes. The photocatalytic overall water splitting performance on PTI-550 (samples synthesized at 550 °C) showed an AQY (apparent quantum yield) of 8% at 365 nm. In contrast with the conventional application of PCN nanosheets, this work provides a new design strategy to boost the photoactivity of layered conjugated polymers in a one-step-excitation overall water splitting reaction.

Kong Liu (Institute of Semiconductors, CAS, Beijing, China)

doi: [10.1088/1674-4926/41/9/090202](https://doi.org/10.1088/1674-4926/41/9/090202)