Visible-light-driven N_2 fixation by a metal-free single atom catalyst

With the support by the National Natural Science Foundation of China and China Scholarship Council, the research team led by Prof. Wang JinLan (王金兰) at the School of Physics, Southeast University, collaborated with Prof. Du AiJun (杜爱军) from Queensland University of Technology, designed single B atom decorated g-C_3N_4 (B/g-C_3N_4) as a promising metal-free single atom catalyst for N_2 fixation driven by visible light, which was published in *Journal of the American Chemical Society* (2018, 140: 14161—14168).

The element nitrogen is essential for the plants, animals and other life forms on Earth. Although the atmosphere consists of more than 78% of N_2, its utilization is very difficult due to its inherent inert character. Alternatively, NH_3, as the reduction product of N_2, is an important chemical in various fields. Photocatalytic N_2 reduction is the most attractive way for sustainable NH_3 production as it can directly produce NH_3 from N_2 and H_2O driven by the sunlight at ambient conditions. However, its practical application is hindered by the development of an efficient catalyst, which remains a great challenge. During the past decade, various transition metal-based catalysts have been fabricated for photocatalytic or electrocatalytic N_2 fixation, while the metal-free catalyst has been rarely explored. This can be ascribed to the coexistence of empty and occupied d orbitals in transition metals, which on one hand can accept the lone pair electrons of N_2 and on the other hand can donate electrons into antibonding orbitals of N_2 to weaken the N≡N triple bond.

On the basis of the concept of electron "acceptance-donation" driven by the coexistence of empty and occupied orbitals, Wang et al. found that the B atom with sp^3 hybridization may serve as a center for N_2 fixation as it also contains occupied and empty orbitals simultaneously. Meanwhile, graphitic-carbon nitride (g-C_3N_4), which consists of C and N only, is a well-known metal-free photocatalyst for various reactions. Therefore, the incorporation of the single B atom into g-C_3N_4 (B/g-C_3N_4) may achieve the goal of metal-free N_2 fixation driven by solar. Their comprehensive calculations show that the as-designed B/g-C_3N_4 indeed possesses excellent catalytic performance for N_2 fixation with a record low onset potential (0.20 V). More interestingly, the decoration of the B atom can significantly enhance the visible light absorption, rendering them ideal for solar-driven reduction of N_2. Importantly, the whole process occurs on a single B site for the as-designed catalyst, indicating that B/g-C_3N_4 can actually serve as a "metal-free single atom catalyst". This is a fully new concept not only for N_2 fixation, but also for other reactions. Their work provides a very compelling photocatalyst for N_2 fixation, offering cost-effective opportunities for advancing sustainable NH_3 production.

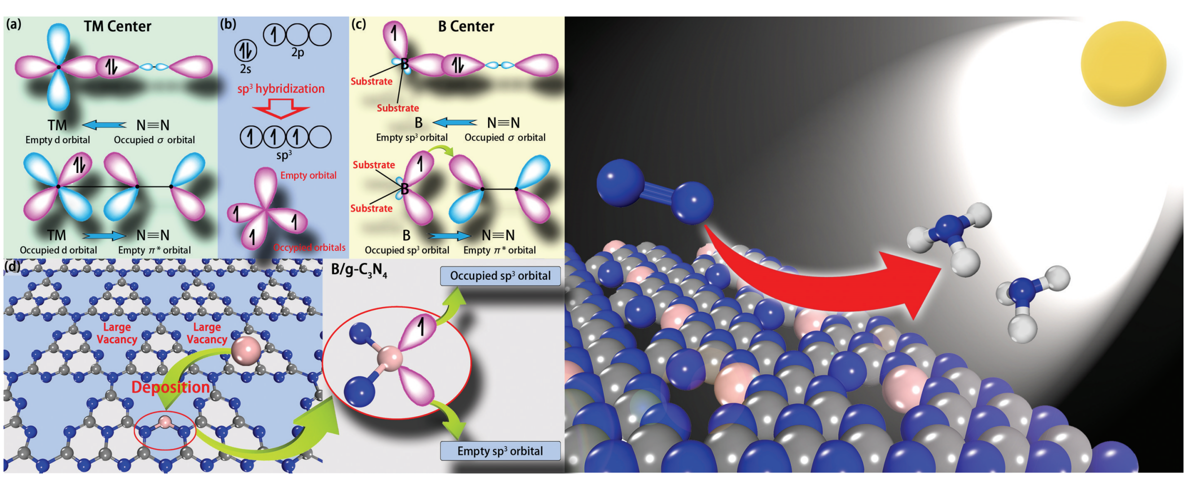

Figure Schematic of the design of B/g-C_3N_4 as photocatalyst for N_2 fixation.