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Single atom catalyst towards ammonia synthesis at mild conditions

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Nitrogen is an essential nutrient element for all living organisms, however in its sufficient molecular form, nitrogen could not be utilized to meet the crucial need for global food requirements or industrial production due to its strong nonpolar N≡N triple bond. Therefore, nitrogen fixation is an essential transformation but this only occurs in the nature with the help of nitrogenases [1]. Although nitrogen can be artificially transformed into ammonia through the well-established Haber-Bosch process, the reaction is accomplished under drastic conditions, such as high temperature (300–500 °C) and pressure (150–250 atmosphere), consuming the scarce fossil fuel and creating a large amount of greenhouse gas emission [2]. In the view of the fuel shortage and global climate situation, achieving nitrogen fixation under mild conditions to overcome such high energy consumption is a crucial subject in chemistry and has fascinated the scientists for many years.

Polymeric carbon nitride (p-CN) has emerged as a potential photocatalyst for various chemical reactions, including water splitting, CO_2 reduction and selective oxidation of aromatic alcohols due to its suitable electronic band structure, good chemical stability, molecular tenability and low cost [3,4]. The pristine photocatalytic activity of carbon nitride is quite low owing to its intrinsic drawback from the conjugated quasi two dimensional π system. Though numerous attempts have been made to functionalize the photocatalyst through copolymerization, doping and hybridization, the photoexcited electrons are still constrained in the π bond. Through hetero-homogeneous co-catalyst could we improve the interfacial charge transfer and contribute to the relevant photocatalytic reactions [5].

Single metal atom catalysts have recently attracted increasing research attention due to their unique catalytic properties and maximized atom utilization. Based on the theoretical calculations and experiments, Xie's research group [6] first deployed the non-noble single metal atoms onto the p-CN to fabricate the copper modified ultrathin carbon nitride nanosheets, achieving high performance photoilluminated synthesis of ammonia under ambient conditions. They obtained the single dispersion of copper atoms from the high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) characterization. The X-ray absorption fine structure (XAFS) spectra results revealed the novel three-fold coordination of Cu atoms in the T-defect of p-CN, which resulted in the single valence electron of the coordinated N atom delocalized even isolated from the π conjugated electron cloud due to the charge density difference (Figure 1). The isolated single electron is more easily activated for involvement in the relevant photocatalytic reactions, which was confirmed by electron spin resonance (ESR) experiments. Xie and coworkers' encouraging results show the photocatalytic ammonia synthesis activity of copper modified CN was improved by 7 times compared with that of pristine p-CN, achieving 186 μmol g^{-1} h^{-1} under visible light irradiation, demonstrating the manipulation of lone-pair electrons to realize the effective isolation of conjugated valence electrons is an effortless approach for superior photocatalytic performance

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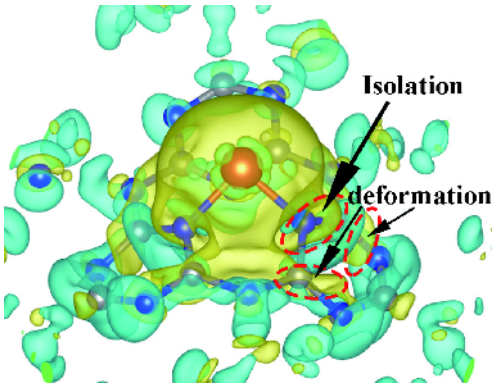

Figure 1 Side view of the electron density distribution. Schematic of the π electron deformation and the valence electron isolation [6] (color online).

and the scarce non-noble metal loaded catalyst could be a strong candidate for exciting performance of ammonia synthesis at mild conditions.

Xie's group [6] believes that the delicate manipulation of lone-pair electrons in conjugated polymer undoubtedly offers a new avenue for ammonia synthesis under mild conditions. Furthermore, this approach provides deeper insight into alternative pathways for many other photocatalytic reactions.

Conflict of interest The authors declare that they have no conflict of interest.

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