Effect of palladium chemical states on CO2 photocatalytic reduction over g-C3N4

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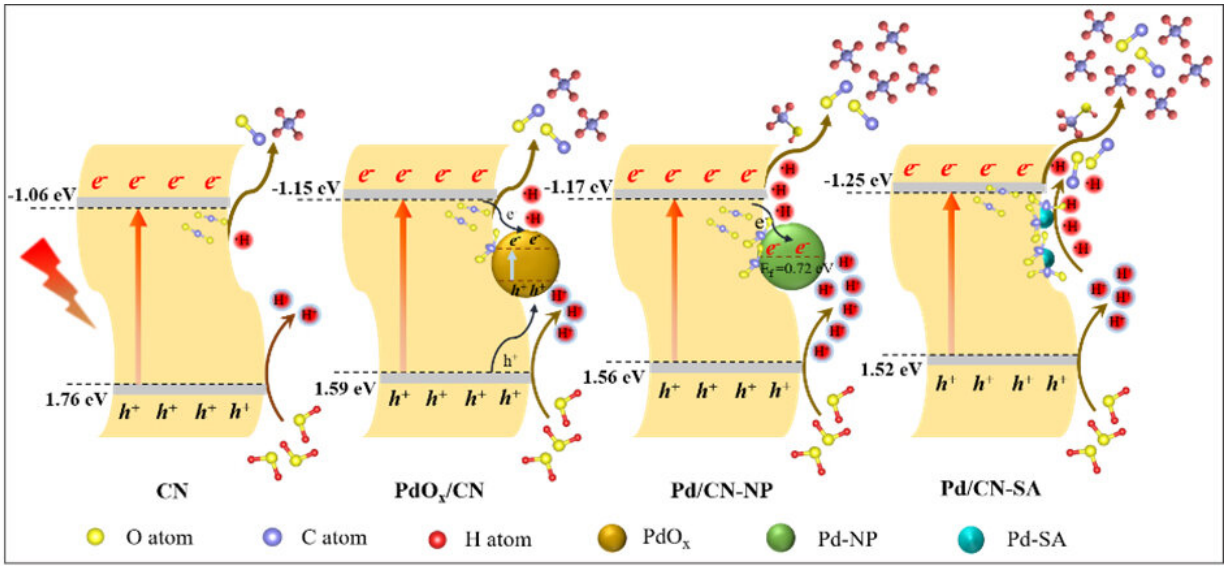

Cocatalyst decoration has demonstrated to be effective in boosting CO_2 photocatalytic conversion, yet the critical role of sing-atomic state on CO_2 photocatalytic reduction, distinguished from the oxide and elemental states, remains a mystery. Herein, palladium single-atoms, palladium oxides, and palladium nanoparticles were homogeneously anchored on g-C_3N_4 to investigate their CO_2 photocatalytic reduction behaviors. And the mechanism behind their significantly different activities, especially the role of Pd-SA in boosting CH_4 production were comprehensively revealed. Credit: *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(22)64199-8

Using solar energy and photocatalysts to convert CO_2 into high value-

added chemicals can simultaneously alleviate the greenhouse effect and energy crisis. Single atom cocatalysts decoration has been demonstrated to be an effective strategy to improve the CO_2 photocatalytic reduction efficiency.

Unfortunately, when unraveling the mechanism behind performance promotion, most studies mainly focus on clarifying the superior physicochemical and photoelectrical properties of SACs in comparison with the substrate. The critical role of the sing-atomic state distinguished from those oxide and elemental states was often neglected and remains a mystery.

Recently, a research team led by Prof. Zhongbiao Wu and Haiqiang Wang from Zhejiang University, China, comprehensively investigated the effect of Pd chemical states on CO_2 photocatalytic reduction of g-C_3N_4 (CN) under visible light irradiation, especially the critical role of Pd-SA in boosting CH_4 production. The results were published in the *Chinese Journal of Catalysis*.

Performance tests showed Pd species decoration improved the CH_4 production of CN, with Pd/CN-SA exhibiting the optimum yields (2.25 μmol g^{-1}), markedly higher than that of PdO_x/CN (1.08 μmol g^{-1}) and Pd/CN-NP (0.44 μmol g^{-1}). After comprehensive mechanism analysis with various characterization techniques, in-situ FTIR spectra and DFT calculations, it was found that the conducive activation of CO_2, negative conduction band potentials, and excellent •H utilization efficiency, collaboratively contributed to the superior CO_2 reduction performance of Pd/CN-SA, especially in the remarkably boosted CH_4 production.

In addition, despite the larger electron density of Pd/CN-NP and PdO_x/CN, the moderate reduction ability of their photogenerated electrons restricted the further reduction of adsorbed CO_2 species and CO intermediate, limiting the enhancement of CO_2 reduction activity.

Furthermore, the CH_4 evolutions of Pd/CN-NP and PdO_x/CN were also limited by the poor •H supply and inferior •H utilization efficiency, respectively.

The new insights may advance the understanding of CO_2 reduction process and inspire the design of efficient photocatalysts for CO_2 photocatalytic conversion.

More information: Qian Li et al, Effect of palladium chemical states on CO2 photocatalytic reduction over g-C3N4: Distinct role of single-atomic state in boosting CH4 production, *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(22)64199-8

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