A new strategy for enhancing hydrogen peroxide utilization in photocatalytic reactions

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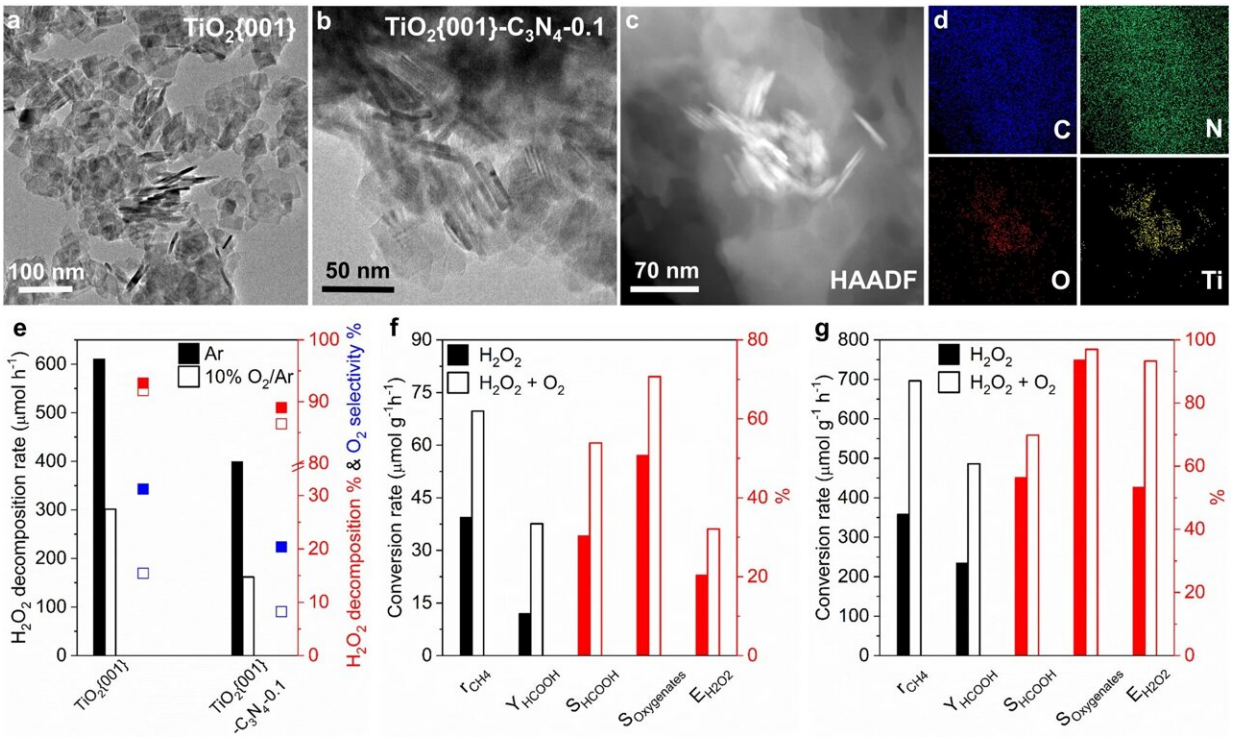

Photocatalysts and photocatalytic performance. **a** TEM image of TiO_2{001}. **b** TEM, (**c**) HAADF and (**d**) element mapping images of TiO_2{001}-C_3N_4–0.1. **e** H_2O_2 decomposition rate, H_2O_2 decomposition and O_2 selectivity of photocatalytic H_2O_2 decomposition over TiO_2{001} and TiO_2{001}-C_3N_4–0.1 under the reaction condition of 165 μL H_2O_2 + 20 mL H_2O in Ar or 10%O_2/Ar. CH_4 conversion rate (r_{CH4}), yield(Y_{HCOOH}) and selectivity (S_{HCOOH}) of formic acid, selectivity of oxygenates ($S_{Oxygenates}$), and H_2O_2 utilization efficiency (E_{H2O2}) of photocatalytic CH_4 conversion over (**f**) 20 mg TiO_2{001} under the

reaction condition of 8%CH_4 + 92%Ar + 110 μL H_2O_2 + 20 mL H_2O or 8%CH_4 + 1.6%O_2 + 90.4%Ar + 110 μL H_2O_2 + 20 mL H_2O for 5 h and over (**g**) 20 mg TiO_2{001}-C_3N_4–0.1 under the reaction condition of 8%CH_4 + 92%Ar + 165 μL H_2O_2 + 20 mL H_2O or 8%CH_4 + 4%O_2 + 88%Ar + 165 μL H_2O_2 + 20 mL H_2O for 8 h at 298 K. Credit: *Nature Communications* (2022). DOI: 10.1038/s41467-022-34563-4

Recently, a research team led by Prof. Huang Weixin from the University of Science and Technology of China (USTC) of the Chinese Academy of Sciences (CAS) realized the production of oxygenated chemicals from methane and H_2O_2 with oxide semiconductor as photocatalyst, revealed a new strategy for improving H_2O_2 utilization and photocatalytic conversion efficiency from methane to oxygenates, and studied the photocatalytic activity and selectivity by tuning TiO_2 facets.

This work was published in *Nature Communications*.

Methane has been increasingly considered as a possible carbon resource, but it is a major challenge to convert methane to value-added chemicals with both high activity and selectivity.

H_2O_2 is a common oxidant that could photocatalytically convert liquid-phase methane to value-added chemicals. It reacts with photogenerated electrons and produce ·OH radicals or ·OOH radicals, which is an effective activation method. Unfortunately, H_2O_2 is subject to side reactions with photogenerated holes and tends to convert itself to O_2, reducing its utilization.

In this study, the researchers aerated O_2 into the semiconductor photocatalytic reaction system containing methane and H_2O_2, and found that H_2O_2 utilization was enhanced. They discovered that the adsorption

of O_2 onto the surface of TiO_2 inhibited the adsorption of H_2O_2, which suppressed side reactions.

In addition, the researchers observed that photocatalytic activity and selectivity was determined by TiO_2 facets. In virtue of theoretical calculation, they discovered that it was the desorption energy of different products on different TiO_2 facets that accounted for the different catalytic selectivity. For example, CH_3OOH had low desorption energy on $TiO_2\{101\}$, thus it was the only liquid-phase product of $TiO_2\{101\}$-C_3N_4 composite.

This work offered a new strategy for improving H_2O_2 utilization and conversion efficiency in the photocatalytic conversion from methane to oxygenates. It also manifested the role that the catalyst facets played during photocatalytic reactions.

More information: Xiao Sun et al, Molecular oxygen enhances H2O2 utilization for the photocatalytic conversion of methane to liquid-phase oxygenates, *Nature Communications* (2022). DOI: 10.1038/s41467-022-34563-4

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