Hydrogen bonding promotes photocatalytic alcohol coupling

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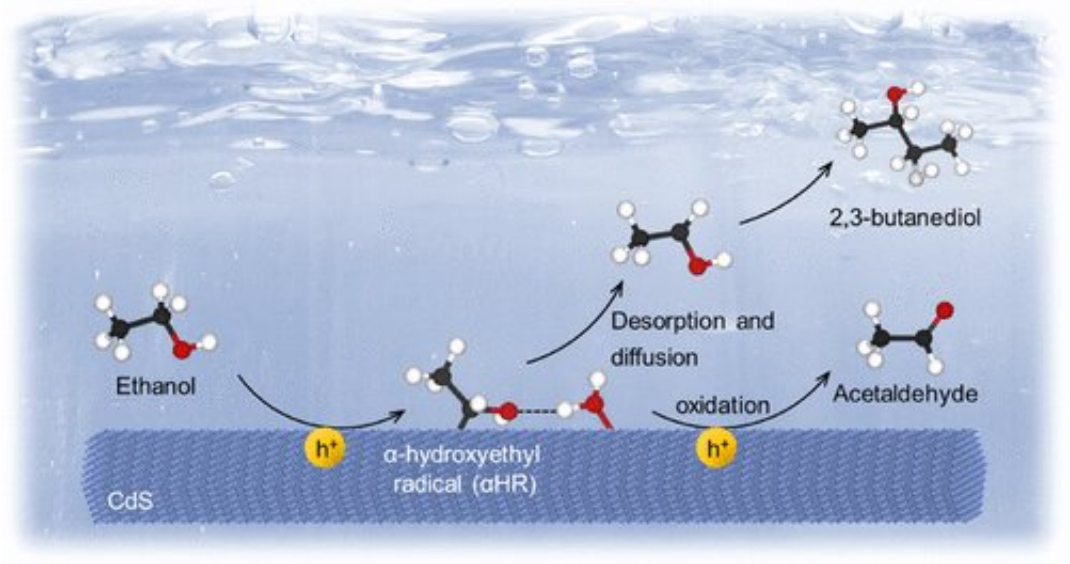

Graphical abstract. Credit: *Journal of the American Chemical Society* (2022). DOI: 10.1021/jacs.2c07410

A research group led by Assoc. Prof. Luo Nengchao and Prof. Wang Feng from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences realized selective control of photocatalytic coupling reaction of alcohols.

This study was published in *Journal of the American Chemical Society* on Oct. 10.

Radicals are common intermediates in photocatalytic conversions, with open-shell electronic structures. They are highly active and readily adsorb on the surface of semiconductors strongly, resulting in a variety of reactions. Solution can influence the product selectivity and quantum yield of the photocatalytic reaction.

In this work, the researchers found that adding 5 vol% water to ethanol solution could increase the selectivity of 2,3-butanediol generated by photocatalytic coupling of ethanol from 37% to 57%, with a reaction rate 2.4 times of the original.

Using radical trapping experiments, deuterium experiments, DFT calculations, and molecular dynamics simulations, they found that the introduction of a small amount of water enabled the intermediate α-hydroxyethyl radical (αHR) to form hydrogen bonds with solvent molecules both on the catalyst surface and in bulk solution.

With the help of hydrogen bonding, αHR tended to desorb from the catalyst surface and was stabilized in solution, avoiding the predominant oxidation of αHR to acetaldehyde and reverse reaction between αHRs and H· that recovered ethanol.

"Our study reveals that non-chemical bonding interactions can steer the reaction paths of radicals for selective photocatalysis," said Luo.

More information: Zhuyan Gao et al, Hydrogen Bonding Promotes Alcohol C–C Coupling, *Journal of the American Chemical Society* (2022). DOI: 10.1021/jacs.2c07410

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