

Selectivity in heterogeneous photocatalysis: achievements and challenges

Radim Beránek

Institute of Electrochemistry, Ulm University, Albert Einstein-Allee 47, 89069 Ulm, Germany

radim.beranek@uni-ulm.de

<https://www.uni-ulm.de/nawi/nawi-elektrochemie/>

Photocatalysis is a powerful method for driving useful chemical transformations by sunlight or low-cost operating light sources (e.g., LEDs) under otherwise completely mild conditions: at ambient pressure and temperature, and using ubiquitous and sustainable reagents like water or aerial oxygen.^{1,2} Moreover, the distinct feature of photocatalytic reactions as being initiated by highly reactive excited states often translates into unprecedented reactivities which are not easily achieved in thermal catalysis, as exemplified particularly by a plethora of *homogeneous* photocatalytic systems for selective organic transformations developed in recent years.²⁻⁵ In the field of *heterogeneous* photocatalysis, while significant progress has been made in the development of photocatalysts for solar water splitting and the decontamination of water and air, much less is known about *selective* photocatalytic synthetic reactions leading to high-value organic compounds. Several more or less selective photocatalytic organic transformations reported so far include, for example, decarboxylation,^{6,7} selective fluorination,⁸ cyanation,⁹ sulfoxidation,¹⁰ C–C¹¹⁻¹³ and C–N coupling reactions,¹⁴ or selective oxidation reactions,¹⁵⁻¹⁹ typically utilizing semiconductors like TiO₂, ZnS, CdS or carbon nitride as light absorbers. However, the factors governing the selectivity in heterogeneous photocatalysis are still poorly understood, particularly due to the complex interplay of various processes involved in photochemical charge generation and catalysis of chemical reactions at solid surfaces.^{7,20-24}

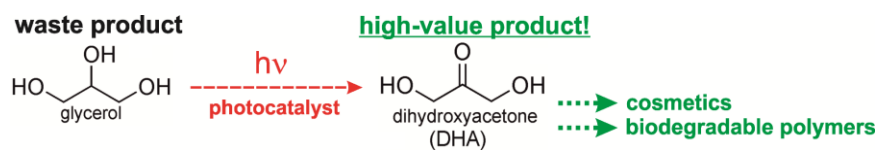


Figure 1: Selective photocatalytic conversion of glycerol to DHA

The talk will summarize the current state of our knowledge of factors governing the selectivity in heterogeneous photocatalytic systems, with a special focus on selective photocatalytic oxidation of glycerol to 1,3-dihydroxyacetone (DHA) developed recently in our lab (**Figure 1**). DHA is a high-value (by the factor of ~500 as compared to glycerol) chemical compound used extensively, for example, in the cosmetics industry, and with a high prospect of being used in synthesis of new biodegradable polymers if the market price were lower. In

particular, the role of model systems, theoretical calculations, photoelectrochemical and spectroscopic methods for elucidation of the mechanistic aspects of the selective photocatalytic transformation of glycerol to DHA will be discussed, and design rules for the development of more efficient photocatalysts for selective conversions will be suggested.

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