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Synthesis of high-value chemicals through selective photocatalytic conversion of waste products

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Abstract

One of the key scientific challenges is the development of innovative photocatalytic processes driven solely by (sun)light under mild conditions. During this project, we have developed a new type of composite photocatalyst for use in selective photocatalytic oxidation of glycerol to 1,3-dihydroxyacetone (DHA). While glycerol is a cheap and abundant waste product of biodiesel production, DHA is a high-value chemical compound used, for example, in cosmetic industry and with a high prospect of being used in the synthesis of new biodegradable polymers.

Introduction

The production of biodiesel is nowadays typically based on transesterification of vegetable oils or of animal or waste fats, whereby glycerol is the main by-product and represents thus an important renewable and readily available feedstock. The development of efficient chemical routes for utilization of glycerol has therefore recently attracted significant scientific interest.[1] One of the most attractive strategies seems to be the selective conversion of glycerol (market price ~ 0.6 US$/kg) to high-value compounds like 1,3-dihydroxyacetone (DHA; ~150 US$/kg) (Figure 1).[1-4] DHA is a 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.[5]

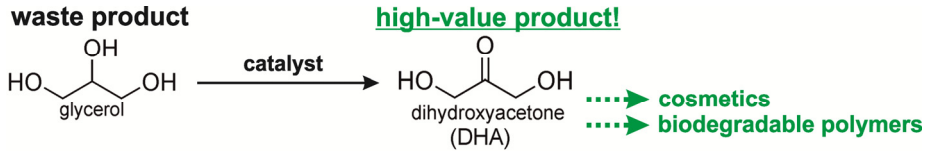

Figure 1: Catalytic conversion of glycerol as a waste product to DHA as a valuable feedstock for chemical industry.

From the chemical point of view, the major challenge in oxidation of glycerol to DHA is to achieve selective oxidation of the secondary hydroxyl group while inhibiting the oxidation of the (normally more reactive) primary hydroxyl group, as well as avoiding any subsequent reactions of the DHA formed. Currently, the industrial production of DHA from glycerol is based solely on biological fermentation processes. Such microbial enzymatic reactions allow for high selectivity but suffer from very low space-time yields and overall high costs since the reaction times are long and only low concentrations of glycerol can be used. The development of alternative catalytic processes is therefore highly desirable. Obviously, in an ideal case, the catalytic conversion system for DHA production should be operative not only at room temperature and using easily available oxidizing agents (water or aerial oxygen), but also without any external electric input. Therefore, we decided to investigate *photocatalytic* conversion of glycerol to DHA.

Results and discussion

More or less selective oxidation of glycerol to DHA has been recently observed to proceed *electrochemically* at room temperature,[6-7] whereby the highest selectivity was reported recently for a carbon-supported Pt electrode saturated at the surface with Bi^{3+} ions.[7] While the presence of bismuth was found to be crucial for favouring the oxidation of the secondary hydroxyl group, the mechanism and the exact role of bismuth ions in driving the chemoselectivity of the process is still not clarified. Drawing on the these developments in the electrochemical selective oxidation of glycerol and on our group's expertise in heterogeneous photocatalysis, we have successfully performed some proof-of-principle investigations of selective *photocatalytic* oxidation of glycerol to DHA. The main idea was to avoid the need for any external electric energy input by driving the selective oxidation of glycerol photocatalytically, *i.e.* by utilizing the charges generated in a semiconductor upon irradiation with sunlight.[8-10] In terms of the photocatalyst design, our idea was to effectively reverse the scenario known to be at work in the electrochemical selective oxidation of glycerol (Pt electrodes covered with Bi^{3+} ions)[7] by employing bismuth oxide (□-Bi_2O_3) powders modified at the surface with platinum nanoparticles. Bismuth oxide is known to be a semiconductor with absorption in the UV and near visible region (bandgap of ca. 2.9 eV; ~430 nm). The concurrent presence of Pt nanoparticles and Bi ions at the surface of the photocatalyst was expected to ensure the selectivity of the process.

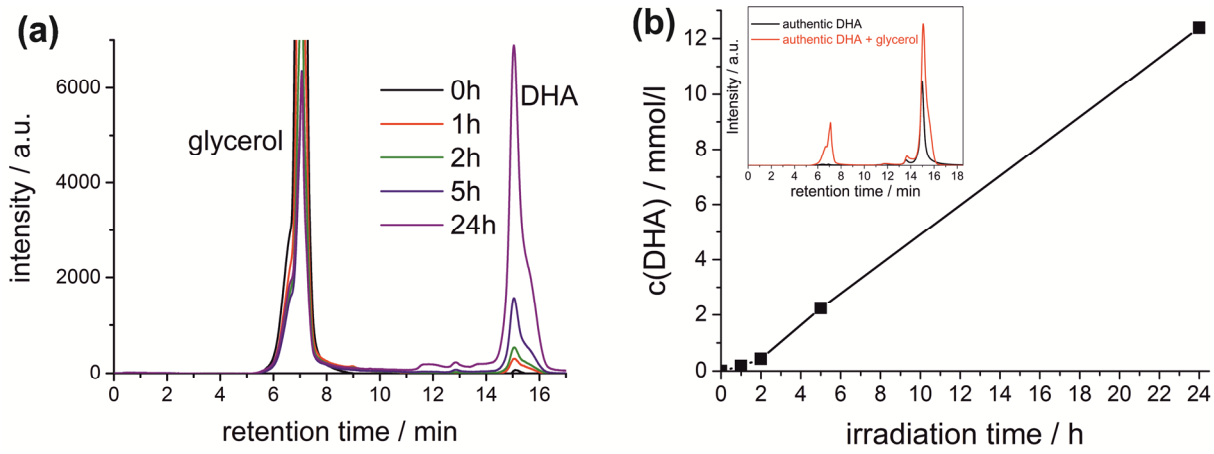

Figure 2: HPLC chromatograms (a) and DHA concentration changes during glycerol oxidation at α-Bi_2O_3/Pt photocatalyst under UV + visible light (λ > 320 nm) irradiation. ***Note**:* The small "shoulder" of the DHA peak at longer retention times is an artefact due to the concurrent presence of glycerol (presumably formation of dimers), and it appears when analyzing authentic DHA/glycerol mixtures (see the inset).

The proof-of-principle photocatalytic investigations have been carried out using α-Bi_2O_3 powders (synthesized by heating bismuthyl nitrate) modified at the surface with different platinum nanoparticles (deposited by *in-situ* photoreduction of hexachloroplatinic acid). The selective photocatalytic oxidation of glycerol to DHA (using 1:1 vol. glycerol/water mixtures) is demonstrated in Figure 2. The HPLC chromatograms show that DHA is formed with high selectivity as the main oxidation product. Notably, in terms of the possibility of carrying out the reaction using solar light, the reaction proceeds not only under irradiation with polychromatic *UV + visible* light (λ > 320 nm), but also under irradiation with *visible light only* (λ > 420 nm). As expected, no DHA was formed without irradiation. It should be also noted that *no DHA* was formed when using conventional platinized TiO_2 (anatase, Hombikat UV 100) photocatalyst, which is in line with the literature reports on photooxidation of glycerol on TiO_2 exhibiting very low selectivity towards DHA.[11-13]

During irradiation of α-Bi_2O_3/Pt suspensions the concentration of DHA increases continuously (Figure 2b), with a slight induction period which might be related to formation of Pt nanoparticles by photoreduction of H_2PtCl_6 or surface restructuring of the photocatalyst in the initial stage of reaction. Notably, when irradiation is stopped after several hours, the production of DHA also stops, ruling out the possibility of solely thermal (non-photon) catalysis at work. The presence of Pt as co-catalyst was found to be absolutely crucial, negligible amounts of DHA were formed without Pt.

Conclusions

To the best of our knowledge, we have found first experimental evidence for selective *photocatalytic* oxidation of glycerol to DHA in highly concentrated glycerol solution. From the technological point of view, there are several advantages of such photocatalytic reaction: **i)** it can be carried at room temperature simply by irradiation with sunlight or cost-effective light sources (e.g. LED arrays); **ii)** easily available oxidizing agent (aerial oxygen) can be used; **iii)** the use of a *heterogeneous* photocatalyst promises easier processing and product isolation than in case of homogeneous catalysis; **iv)** as compared to the enzymatic process, relatively much higher concentrations of glycerol can be used leading possibly to much higher space-time yields. A German patent application has been filed,[14] and a publication manuscript is in preparation. Further investigations are currently underway which are directed to mechanistic understanding of the process bottlenecks and optimizing the photocatalyst design (a research funding through a DFG grant has been recently successfully applied for).

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