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PHOTOELECTROCHEMICAL NADH REGENERATION FOR ENZYMATIC CO₂ REDUCTION: INCREASING EFFICIENCY AT METAL-MODIFIED SEMICONDUCTORS

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Abstract

The mimicry of the photosynthetic process has inspired the enzymatic reduction of carbon dioxide into methanol through the dehydrogenase enzyme cascade: *F_{ate}DH*, *F_{ald}DH* and *ADH*. Although, this process occurs under very mild conditions (water, 37°C, pH=7) and with optimal yield and selectivity (close to 100%), there still is a limitation associated with the consumption of the cofactor NADH. Although enzymatic, chemical and photo-chemical approaches have been attempted electrochemical regeneration is considered the most attractive solution. Herein we report the use of p-type semiconductor electrodes in order to utilize solar energy for photoelectrochemical NADH regeneration. While bare semiconductors were shown to produce only enzymatically inactive dimers (NAD₂), modification of the surface by electro-deposition of a thin layer of Pt or Ru metal caused the formation of 1,4-NADH as the main product. In particular red-light illuminated (>600 nm) of Pt/p-GaAs showed an increased efficiency at low overpotentials (-0.75V vs Ag/AgCl) when compared to metal electrodes (> 7 fold), with no dimer detection. This study represents the first example of NADH regeneration at an illuminated semiconductor electrode. The absence of a mediator allows the direct coupling of this regeneration system with the enzymatic CO₂ reduction apparatus, modeling the light and dark reactions occurring in a chloroplast.
