

Visible light driven NADH regeneration using a system of water-soluble zinc porphyrin and homogeneously polymer-dispersed rhodium nanoparticles and application to CO₂ fixation with enzyme

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Enzymes have high catalytic activity and selectivity in ambient conditions. NADH is widely used as a cofactor with the function of electron donor in enzymatic redox reactions. In general, the supply of NADH is a major challenging factor due to its high cost and low stability, which have stimulated the development of NADH regeneration systems.¹ Recently, photochemical NADH regeneration has attracted much attention because solar energy is clean, inexpensive, abundant, and renewable. However, in the direct NAD⁺ photoreduction, it has been frequently reported that enzymatically inactive byproducts (1,2- or 1,6-NADH isomers, and NAD dimer) can be formed.² In this study, we devoted to constructing the novel and simple visible light driven regioselective NADH regeneration system. As far as we have surveyed, we discovered the catalytic activity of Rh nanoparticles dispersed by polyvinylpyrrolidone (Rh-PVP) in the visible light driven selective NADH regeneration for the first time. This system consists of triethanolamine (TEOA) as an electron donor, zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) as a photosensitizer, and Rh-PVP (Fig. 1). Only 1,4-NADH was produced as the reduction product of NAD⁺, which was validated by HPLC analysis and an enzymatic assay. It was also proposed an NADH regeneration mechanism. First, NAD⁺ was adsorbed to the surface of Rh-PVP with the carbonyl of amide. A hydride species at the surface of Rh-PVP could attack the C4 position of nicotinamide and form 1,4-NADH directly. The hydride transfer is the key to avoiding the radical intermediate and NAD dimer formation. In addition, we constructed the photochemical conversion system combined NADH regeneration system and NAD⁺-dependent malate dehydrogenase. By using this system, we have successfully achieved the L-malate synthesis based on the CO₂ fixation to pyruvate with visible light energy.

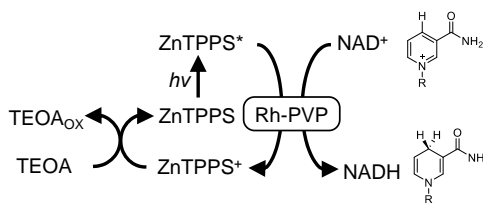


Fig. 1. Scheme of visible light driven NADH regeneration with the system consisted of TEOA, ZnTPPS, Rh-PVP, and NAD⁺.

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