

Communications

Photocatalytic Systems of Pt Nanoparticles and Molecular Co Complexes for NADH Regeneration and Enzyme-coupled CO₂ Conversion

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ABSTRACT : Natural photosynthesis utilizes solar energy to convert carbon dioxide and water to energy-rich carbohydrates. Substantial use of sunlight to meet world energy demands requires energy storage in useful fuels via chemical bonds because sunlight is intermittent. Artificial photosynthesis research focuses the fundamental natural process to design solar energy conversion systems. Nicotinamide adenine dinucleotide (NAD⁺) and NADP⁺ are ubiquitous as electron transporters in biological systems. Enzymatic, chemical, and electrochemical methods have been reported for NADH regeneration. As photochemical systems, visible light-driven catalytic activity of NADH regeneration was carried out using platinum nanoparticles, molecular rhodium and cobalt complexes in the presence of triethanolamine as a sacrificial electron donor. Pt nanoparticles showed photochemical NADH regeneration activity without additional visible light collector molecules, demonstrating that both photoactivating and catalytic activities exist together in Pt nanoparticles. The NADH regeneration of the Pt nanoparticle system was not interfered with the reduction of O₂. Molecular cobalt complexes containing dimethylglyoxime ligands also transfer their hydrides to NAD⁺ with photoactivation of eosin Y in the presence of TEOA. In this photocatalytic reaction, the NAD⁺ reduction process competed with a proton reduction.

As a result of gradational depletion of fossil fuels in the near future, various efforts have been made to develop alternative energy sources. Radiant electromagnetic light energy can be transformed by a photochemical system to yield chemical energy in the formation of chemical bonds. Dihyronicotinamide adenine dinucleotide (NADH) is used as a cofactor in various biological reactions. Many redox enzymes use NAD(P)H as cofactors to perform regio- and stereo-selective biological reactions. Since cofactors used in stoichiometric amounts in biological reactions are quite expensive, the development of efficient catalytic systems that can carry out solar energy capture and NADH regeneration attracts scientist's attention. Furthermore, visible light-driven catalytic systems have attracted significant interest because about half of total solar light is within the visible energy range.¹

Most NADH regeneration systems consist with molecular Rh catalysts which are supposed to produce rhodium(III)-hydride intermediates. Such Rh(III)-hydride species can be generated by chemical, electrochemical, and photochemical reactions, in which two electrons are provided by formate, electrode, and photosensitizer, respectively.²⁻⁷ In order to collect visible light, organic and inorganic photosensitizers, such as eosin Y, phloxine B, Ru(bpy)₃²⁺, C- and P-doped TiO₂, CdS, and CdSe, have been used.⁷⁻⁹ To utilize wider range of visible light, graphene oxides covalently attached with benzophenone coupled porphyrins are used as a light collector for reduction of NAD⁺ and conversion of carbon dioxide.¹⁰

Based on the processes occurring in natural

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photosynthesis, which couples the absorption of light energy to rapid electron-transfer events, artificial photocatalytic systems for NADH regeneration typically consist of three main components, photosensitizer, electron relay, and catalyst. As examples of the three component systems for the NADH photoproduction by visible light, light-harvesting inorganic dyes were coupled with methyl viologen and dehydrogenases as an electron carrier/catalyst pair, in the presence of a sacrificial electron donor.^{5,6} In a few attempts for non-enzymatic photochemical regeneration of NADH, organometallic Rh complexes were used as both an electron relay and hydride transfer catalyst in the presence of Ru(bpy)₃²⁺ as a photosensitizer.⁵ In order to assemble all components together for more practical applications, co-immobilization of photosensitizing compounds, redox mediators, catalysts or enzymes were also investigated. For example, hydrogenase immobilized on photosensitizing CdS particles was reported to produce NADH.⁶ We introduced a simple system employing Pt nanoparticles (PtNPs) for the efficient photochemical regeneration of NADH. This system demonstrated that PtNPs can be used as a visible light collector in the visible light-driven photoregeneration of NADH, and can have the capacity of relaying electrons and catalyzing the reduction of NAD⁺ in aqueous media.

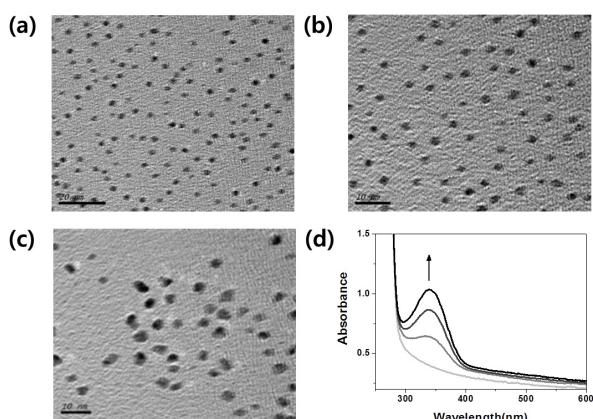
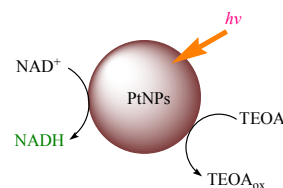


Figure 1. TEM images of PtNPs: (a) 5 nm, (b) 7 nm, (c) 10 nm. (d) UV-visible absorption spectral changes of NADH regeneration at different time intervals (0, 2, 4, and 8 h) of illumination: 20 nM Pt nanoparticles (7 nm), 0.2 mM NAD, 0.4 M TEOA, and 0.2 M phosphate buffer (pH 7.0) at room temperature, 420 nm band-pass filter.

Reduction of NAD⁺ was carried out using a photocatalytic system including PtNPs as a catalyst was investigated in the presence of triethanolamine (TEOA) as a sacrificial electron donor (Scheme 1). A 450W Xe lamp equipped with a 420 nm band pass filter was used as a light source. The NADH regeneration with PtNPs that have a particle size of 5 nm was determined to be 69 % (Fig. 1). The 58 % yield observed for PtNPs with an average diameter of 7 nm was less than that observed for 5 nm PtNPs (Fig. 1d). When 10 nm PtNPs was used, the yield was even lower as obtained 41 %. Such a particle size dependence for catalytic reactions can be explained from a quantum-size effect, which is theoretically based on the electronic structure of PtNPs.¹¹ Under the same conditions, the NADH regeneration using 5 nm PtNPs was even higher than [Cp*Rh(bpy)(H₂O)]²⁺ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) which is well known catalyst for NADH.¹¹

Scheme 1



When eosin Y often used as an additional visible light collector in hydrogen production with homogeneous or heterogeneous catalysts was used in this system, an even lower yield was obtained, indicating that eosin Y disturbed the photo-reactivity of PtNPs. The fluorescence of eosin Y was quenched upon addition of PtNPs, but this energy transfer had no synergy effect. A further study is needed to understand this effect. Instead of 420 nm band pass filter, use of 420 nm cut-off filter with PtNPs and TEOA reduced the NADH yield significantly. The NADH reduction was compensated with hydrogen production with 420 nm cut-off filter. These data demonstrate that photochemical hydrogen production process also occurs with NADH regeneration and the produced NADH may be used directly to produce hydrogen. Such a hydrogen production using PtNPs was reported visible light-driven photoactivation of 9-methyl-10-methylacridinium ion.¹² However, our system of PtNPs alone afforded hydrogen without any organic chromophore. For more efficient NADH regeneration using this system, the reduction of

protons should be controlled by optimizing reaction conditions.

Eosin Y as a photosensitizer provided a best yield of NADH relative to Rose Bengal and Phloxine B, and $\text{Ru}(\text{bpy})_3^{2+}$ in the hydrogen production and NADH regeneration reactions. When eosin Y was used, the NADH regeneration was limited due to gradual decomposition of eosin Y during irradiation. New stable photo-collector materials should be developed to increase quantum efficiency and conversion yield.

In photocatalytic systems using molecular metal catalysts for NADH regeneration, Rh and Co complexes are used.^{7,13} Various cobalt complexes are used to produce hydrogen electrochemically and photochemically. In proposed reaction mechanisms for hydrogen production, Co(III)-hydride intermediates are reported as reactive intermediates in the course of catalytic reactions. Among many Co catalysts developed for H_2 production in order to transfer a hydride to NAD^+ , $[\text{Co}(\text{dmgH})_2\text{pyCl}]$ (dmgH = dimethylglyoximate, py = pyridine) was used for photochemical regeneration of NADH under aqueous solution.

NADH production was carried out by employing $[\text{Co}(\text{dmgH})_2\text{pyCl}]$ and visible light irradiation (a 420 nm band pass filter) under nitrogen. The formation of enzymatically active NADH was followed by monitoring absorbance at 340 nm.

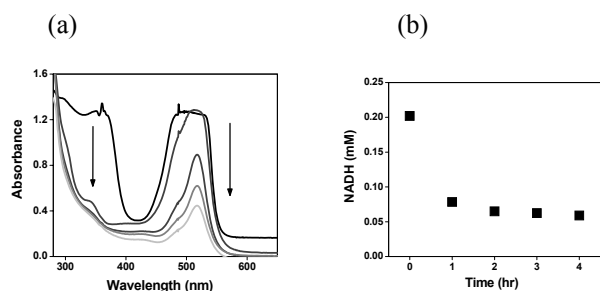


Figure 2. (a) Decomposition of 0.2 mM NADH, 0.13 mM $[\text{Co}(\text{dmgH})_2\text{pyCl}]$, 0.5 mM eosin Y in phosphate buffer (pH 7.0) upon irradiation with time (1 hr) and (b) NADH changes according to time in the photochemical reaction with eosin Y. Irradiation conditions; 450 W, 420 band-pass filter.

When the photocatalytic reaction system contained Co catalyst, eosin Y, and triethanolamine (TEOA) in the presence of NAD^+ in phosphate buffer (pH = 7.0), the conversion yield of NAD^+ turned out to be around 38 % after 9 h of irradiation. No NADH was

detected in the absence of the Co catalyst, indicating that the Co complex was a key component of the NADH production system. In the absence of eosin Y, only trace amount of NADH was observed under the same reaction conditions, demonstrating that the visible light collecting molecule should be activated for this reaction. The low yield of NADH obtained in this system might derive from decomposition of NADH generated photochemically through activation of eosin Y. In fact, NADH was decomposed to produce hydrogen upon irradiation in the presence of Co complex (Fig. 2).

The catalytic conversion of carbon dioxide to liquid or solid fuels is a fascinating challenge to fulfill the global energy demands. Carbon dioxide which is a stable molecule is mostly produced from fossil fuel combustion and biological respiration. Returning CO_2 to useful chemicals back utilizing solar energy is an urgent issue that we are facing, and the system requires efficient catalysts and energy input. Formate dehydrogenase was often used to convert CO_2 to formic acid selectively and utilize NAD(P)H regenerated by electrochemical and photochemical methods. The conversion of carbon dioxide to formic acid was performed using NADH in-situ generated using PtNPs or Co catalysts in the presence of FDH. However, the low equilibrium constant for the conversion of CO_2 to formic acid in the presence of FDH is the crux of the matter. In the end, new metal based materials are needed for an efficient and selective conversion of carbon dioxide.

KEYWORDS : Pt nanoparticle, photochemical NADH regeneration, cobalt complex, formate dehydrogenase, carbon dioxide

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