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Review

Cobalt complexes as artificial hydrogenases for the reductive side of water splitting☆

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ABSTRACT

The generation of H_2 from protons and electrons by complexes of cobalt has an extensive history. During the past decade, interest in this subject has increased as a result of developments in hydrogen generation that are driven electrochemically or photochemically. This article reviews the subject of hydrogen generation using Co complexes as catalysts and discusses the mechanistic implications of the systems studied for making H_2. This article is part of a Special Issue entitled: Metals in Bioenergetics and Biomimetics Systems.

1. Introduction

1.1. Background

In nature, photosynthesis plays the essential role of converting solar energy into stored chemical energy in the form of fuels and oxygen that sustains life on Earth. Through photosynthesis in plants and photosynthetic bacteria, CO_2 and water (H_2O) are converted into carbohydrates and oxygen via a series of photochemical and thermally-driven electron transfer reactions and dark catalytic reactions [1–3]. There are two related photosystems in photosynthesis [2,4] (Fig. 1, Z-scheme): Photosystem I (P700) and Photosystem II (P680). When Photosystem I is excited by sunlight, an electron transfer (ET) process is induced to reduce a series of electron acceptors, such as, phylloquinone and ferredoxin, ultimately reducing the cofactor $NADP^+$ (nicotinamide adenine dinucleotide phosphate) to NADPH (biological hydrogen) and Photosystem I is oxidized. NADPH is both the electron source and a partial proton source for CO_2 transformation into carbohydrates in the Calvin cycle [5]. Oxidized Photosystem I is regenerated by obtaining electrons from Photosystem II through several electron relays, such as, plastoquinone, cytochrome *f* and plastocyanine. The oxidized Photosystem II mediates another important reaction — water oxidation to produce oxygen, catalyzed by a $CaMn_4O_4$ cluster [6–8].

Inspired by nature, the development of renewable carbon-free energy using the sun is a major scientific and technological challenge in meeting the energy needs of the future. Efficient solar cells (that is, solid state photovoltaic devices and dye-sensitized solar cells) and solar-driven water splitting systems represent two major objectives in utilizing solar energy [9]. While solar cells can directly convert solar radiation into electricity, they cannot store energy [10]. On the other hand, solar-driven water splitting can store energy in the form of fuel (H_2) and oxidant (O_2) [11,12]. Energy storage in chemical bonds is most efficient, and as a consequence, this strategy for solar energy storage has attracted great attention during the past three decades. Hydrogen is an environmentally-friendly energy carrier because its only oxidation product is H_2O. Through widespread use of H_2 as a fuel, generated either directly in an artificial photosynthetic system or by electrolysis using solar-generated electricity, dependence on fossil fuels can be decreased, with a corresponding decrease in CO_2 emissions.

Water splitting is actually an oxidation–reduction reaction that can be divided into its two half reactions — the reduction of water protons to H_2 and the oxidation of water to O_2. For each half reaction, the following components are needed: (1) a light absorber that undergoes electron transfer upon excitation; (2) an electron relay or

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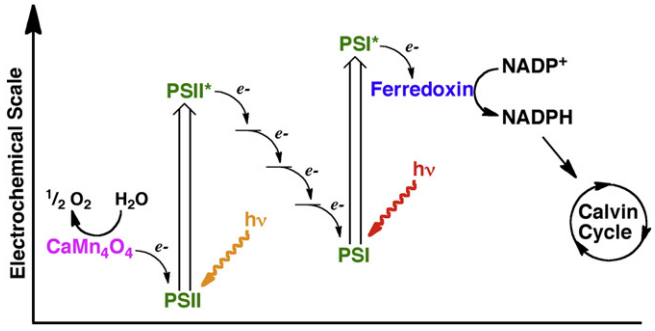

Fig. 1. Z-scheme of biological photosynthesis.

pathway that proceeds favorably in one direction so that reducing equivalents or oxidizing equivalents are transferred to the respective catalysts; and (3) a catalyst for carrying out the desired oxidative or reductive half reactions. The half reaction systems may also have other components such as an antennae assembly so that a greater fraction of incident photons are absorbed with the energy subsequently transferred to the light absorber that undergoes electron transfer upon excitation.

It is generally acknowledged that because water oxidation to O_2 involves an overall four-electron transformation coupled with the loss of four protons from two water molecules and the formation of an oxygen–oxygen bond [13], it is the more difficult half reaction to carry out. However, a viable system for the light driven generation of H_2 from water has not been achieved to date in terms of the levels of activity and robustness for real development into a practical water splitting system.

In order to study each half-reaction system in detail and optimize the performance of individual components contained therein, a source of electrons for the reductive side or oxidizing equivalents (holes) for the oxidation side is added to the system as well. If this is done by the addition of another chemical component to the system, it is best done with a compound that undergoes irreversible decomposition upon oxidation or reduction to prevent back electron transfer. If the former, the component is a sacrificial electron donor, and if the latter, it is a sacrificial electron acceptor, but neither of these components is capable of driving the respective half reaction from a thermodynamic standpoint.

The key challenge for each light-driven half reaction includes the following: (1) whether the excited state of the light absorber is capable of electron transfer at the potential need for the particular catalyst to carry out the half-reaction; (2) whether the catalyst is capable of accumulating charge for the desired transformation; (3) the long-term stability of all system components during irradiation to see if they are viable for long-term operation; (4) the levels of activity for photoinduced electron transfer and product generation; and (5) the mechanism by which the system operates to prolong overall system stability.

In earlier studies of the light-driven generation of H_2, colloidal Pt was employed as the catalyst, either stabilized in solution by different polymers such as polyvinyl alcohol or polyvinylpyrrolidone or attached to semiconductor nanoparticles by platinization (one example is platinized TiO_2). Platinum as an electrode material has a low overpotential for the electrochemical generation of H_2 in aqueous or aqueous/organic solutions of different levels of acidity, and it was found to operate satisfactorily in colloidal form for the light-driven production of H_2 from water. However, it is widely accepted that platinum must be replaced by cheaper materials because of its high price and very low earth abundance [14]. Hence, the development of efficient catalysts for water reduction to H_2 made from of inexpensive, earth-abundant elements has become a prime focus of research on artificial photosynthesis and light-driven hydrogen generation.

During the past 15 years, efforts on this front have focused on complexes of iron, nickel and cobalt as possible catalysts [15–17]. The studies involving iron-containing catalysts are generally related to models of the active sites of hydrogenase enzymes that feature two iron atoms bridged by a dithiolate ligand such as 2-aza-1, 3-propanedithiolate or benzene-1,2-dithiolate. The other ligands bound to the iron centers in these model compounds include CO and CN^- with other coordination sites occupied by cysteine or phosphine. A second class of hydrogenase enzymes contain Fe and Ni ions, which are similarly bridged by thiolate donors and contain CO and possibly CN^- bound to the Fe center. The catalytic properties of Ni complexes for H_2 generation electrocatalytically has been developed most extensively over the past decade by DuBois and coworkers beginning with a mononuclear complex that possesses chelating ligands capable of functioning in a manner similar to 2-aza-1,3-propanedithiolate for proton delivery to a Ni-bound hydride ligand. The chemistry and electrocatalytic studies of the Fe hydrogenase model compounds is reviewed in Chapter 8 while the Ni systems are covered in Chapter 9.

In this section, we focus on the recent progress achieved using cobalt complexes as artificial hydrogenases for the generation of H_2 from protons and electrons. Complexes of cobalt, their interactions with hydrogen and the existence of cobalt hydride species have a long history from the original discoveries of $Co_2(CO)_8$ reacting with H_2 to form $CoH(CO)_4$ by Hieber [18] and the seminal work on hydrogenation catalysis by $Co(CN)_5^{3-}$ that involved the formation of $CoH(CN)_5^{3-}$ [19–21]. In the 1970s, work by Schrauzer on model compounds for the active site of Vitamin B_{12} led to the study of bis(dimethylglyoximate)cobalt complexes termed cobaloximes (Fig. 2), hydridocobaloximes and the observation of hydrogen evolution from such species [22]. In 1986, Espenson and Connelly found that hydrogen was formed by reaction of the related complex **3** (Fig. 4) with Cr^{2+} reductants in an acidic medium [23]. These reports set the stage for the numerous studies that have been published in the past decade dealing with hydrogen generation promoted by cobalt complexes upon electrochemical reduction or as part of photochemical systems in which electrons are supplied chemically by a sacrificial electron donor. Different series of Co catalysts that have been employed in electrocatalytic and photocatalytic water splitting will be described in detail, and the mechanisms of the catalysis of hydrogen formation will be analyzed based on most recent information. A review article by Artero has recently been published on the electrocatalytic generation of H_2 using Co complexes, but much of the emphasis in that article is on studies in non-aqueous media in which protons are supplied in the form of weak or strong acids [24]. In this section, we will concentrate more on both photochemical and electrochemical work in which the proton source is water or acid and either aqueous or aqueous organic solvents are employed.

1.2. Key considerations for H_2 formation in photochemical and electrochemical systems

With a number of different photochemical systems described using various Co complexes as catalysts and with an even greater

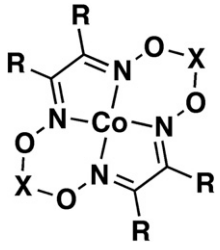

Fig. 2. Generic cobaloxime complex.