Artificial photosynthesis as a new energy resource

Masao Kaneko
Solar Energy Science Research Group

Artificial photosynthesis is described as one of the candidates for new energy resource. Energy cycle on the earth is represented by the electron cycle pumped up by solar irradiation. Such electron pumping is achieved by photosynthesis in the nature. Since water is the electron source for the whole system, abstraction of electron from water (resulting in O_2 evolution) is the most important primary step for such an energy cycle. Study on the catalytic water oxidation using a polymer-confined metal complex is described, and an artificial photosynthetic model is proposed which couples a water oxidation catalyst membrane with a narrow bandgap semiconductor photoexcitation center. Electrocatalytic CO_2 reduction is also shown as a reduction site for the future artificial photosynthesis.

Global environmental problem is becoming serious with the increase of atmospheric CO_2 concentration. In order to solve this, a new energy resource has to be introduced instead of the present fossil fuels. To this aim, it is important to at first understand the energy cycle on the earth including biological and our social activities.

The energy cycle on the earth is represented by the electron cycle pumped up by solar irradiation as shown in Fig. 1.[1,2] The "engine" to achieve this cycle is photosynthesis in the nature. It is important that the electron source is water; dioxygen (O_2) is liberated when electrons are abstracted from water which is a four-electron process ($2H_2O \rightarrow O_2 + 4e^- + 4H^+$). The electrons from water are pumped up by solar visible light to higher potentials and then reduce CO_2 to produce carbohydrates ($C_6H_{12}O_6$). The high energy electrons stored in the products are ingested by animals as foods and combine again with O_2 to liberate free energy which is used for biological activities (respiration) reproducing water and CO_2. Free energy is also liberated and used for our social activities when the high energy electrons stored as fossil fuels combine with O_2 by combustion reproducing again water and CO_2. The most important are the solar energy and water in such energy cycle; CO_2 is just used to form materials which,can be utilized by biological existence. It is important to follow such energy cycle in order to develop a renewable energy source which is safe, clean, and compatible with the nature. Artificial photosynthesis is one of the most promising future energy resources which can produce fuels only from sunshine and water.

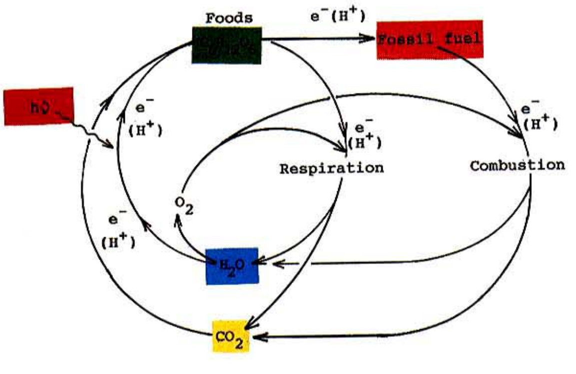

Fig. 1. Energy cycle on the earth as represented by electron cycle pumped up by solar irradiation.

In construction an artificial photosynthesis, three fundamental steps are important:[1,2] (1) electron abstraction from water (O_2 is evolved), (2) visible light excitation of the electrons from water, and (3) reduction of CO_2 by high energy electrons to form reduction products. The third reduction step can be substituted by proton reduction for the formation of H_2 which is the most fundamental reduction compound as fuel. The total reaction in this case is the water photolysis by visible light to produce H_2 and O_2.

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad (1)$$

$$4e^- \xrightarrow{h\nu} [4e^-]^* \quad (2)$$

$$4H^+ + [4^-]^* \rightarrow 2H_2 \quad (3)$$

$$\text{Overall reaction}: 2H_2O \xrightarrow{h\nu} O_2 + 2H_2 \quad (4)$$

In any case water oxidation and photoexcitation of the electrons abstracted from water are the most important processes in artificial photosynthesis. It is of importance to construct an artificial photosynthesis in a heterogeneous system because in a homogeneous solution, energy-consuming back electron transfer (corresponding to charge recombination) inevitably occurs. We have adopted polymer membrane systems for costructing a heterogeneous system.

Although catalytic water oxidation is the primary step for photosynthesis, only a few artificial catalysts have been known. Tetrakis (bipyridine)-di-μ-oxo-dimanganese complex

Table 1. Water oxidation catalysts.

$[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+}$

$[(bpy)_2Ru\text{-}O\text{-}Ru(bpy)_2]^{4+}$

$[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$

$[Ru(NH_3)_5X]^{3+}$

(Table 1) has been regarded as a photosynthetic water oxidation center model, but to our surprise it does not work as a water oxidation catalyst in a homogeneous aqueous solution. We have now found that this complex can catalyze water oxidation to evolve O_2 when used as a heterogeneous catalyst.[3] This finding is interesting because in the photosynthetic oxygen evolving center, Mn ions from a heterogeneous protein complex. We have also found that many of the Ru complexes such as shown in Table 1 are catalytically active for water oxidation not only in a homogeneous aqueous solution but also in a heterogeneous state in polymer or in clay.[1,3] This finding is important for constructing a heterogeneous artificial photosynthesis.

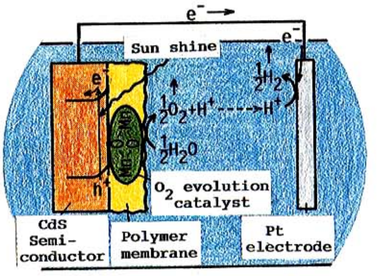

Fig. 2. Artificial photosynthetic model.

Such a heterogeneous water oxidation catalyst was effective for achieving visible light water cleavage as an artificial photosynthesis model in combination with a small bandgap semiconductor photoanode. A single crystalline n-CdS photoanode was at first coated with a Nafion (perfluoroalkyl sulfonate polyanion polymer) membrane, and then the coated electrode was soaked in an aqueous solution of water oxidation catalyst to adsorb the complex in the polymer layer. Irradiation of the coated CdS brought about O_2 evolution on the membrane surface, and at the same time H_2 was evolved at the counter Pt electrode (Fig. 2).[4] The light-to-chemical conversion yield was 16% based on the total incident 500 nm light.

In order to combine a catalytic CO_2 reduction site in future with the above water photolysis system to realize an artificial photosynthesis, electrocatalytic CO_2 reduction was studied in water using a metal complex such as $[CO(terpy)_3]^{2+}$ or $Re(bpy)(CO)_3$ Br by incorporating it into a Nafion membrane coated on a graphite electrode.[5] Proton reduction was successfully suppressed by this system, and electrocatalytic CO_2 reduction was attained to produce formic acid or CO. This CO_2 reduction site will be coupled in the future with a water photolysis system to achieve an artificial photosynthesis.

References

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