2-2-2. Water Oxidation Reaction

Overview

In artificial photosynthesis as a chemical conversion and storage of light energy, the oxidation of water as an ideal electron source is essential from the perspective of "Resource circulation" and "Energy storage" with "Zero-emission". Compared to a direct light irradiation of semiconductor photocatalysts (the Honda-Fujishima effect) and an oxygen evolution via four-electron oxidation of water through hole injection into metal oxides, the water oxidation using molecular catalysts by the stepwise four-photon excitation has suffered much difficulty due to the rarefied photon-flux density of sunlight. However, in recent years, the discovery of a two-electron oxidation of water by a single photon to produce hydrogen peroxide has attracted attention.

Current Status and Frontiers

In artificial photosynthesis, in order to extract electrons from water molecules as an ideal electron source, attention has been mostly focused on the oxygen-evolving reaction via four-electron oxidation, mimicking natural photosynthesis. However, since single-photon irradiation of sensitizers or molecular catalysts is limited to one-electron oxidation/reduction, four-electron oxidation of water requires stepwise four-photon excitation to reach the active four-electron oxidation state of the molecular catalyst (Eq. 1).

$$S_0 \xrightarrow[-e^-]{h\nu} S_1(+1) \xrightarrow[-e^-]{h\nu} S_2(+2) \xrightarrow[-e^-]{h\nu} S_3(+3) \xrightarrow[-e^-]{h\nu} S_4(+4) \qquad (1)$$

Under the sunlight photon-flux density conditions (AM1.5), for example, when Sn-porphyrin, a typical molecular catalyst, is immobilized on a device, the time interval between the photon reaching the molecule and the next photon's arrival is approximately 0.17 seconds, meaning that stepwise four-photon excitation takes approximately 0.7 seconds. This is extremely long compared to the time scale inherent to the molecule. In other words, each oxidation state (S_1 to S_4 in eq. 1) climbing up to the activated state capable of oxidizing water is decomposed or transformed while waiting for the next photon's arrival, losing its activity, resulting in a low overall reaction efficiency for the four-electron oxidation of water into O_2. This problem, known as the "Photon-flux density problem" of sunlight, has long been a bottleneck in the realization of artificial photosynthesis with molecular catalyst.[1,2] However, in recent years, a methodology for two-electron oxidation of water induced by one-electron oxidation has been discovered that circumvents this problem.[3] The axial ligand water molecule of aluminum porphyrin (AP) is one-electron oxidized into an oxyl radical by visible light irradiation, and reacts with water/hydroxide ions to form a hydroperoxide radical anion, which is further one-electron oxidized to generate H_2O_2 as the two-electron oxidation product (Fig. 1). The formation of H_2O_2 by one photon can store approximately 2.9 times more energy than the

generation of O_2 by four photons. If titanium dioxide (TiO_2) is used as an electron relay agent in water, H_2 is generated simultaneously with H_2O_2 by irradiating AP adsorbed on the TiO_2 surface with one-photon of visible light.[4] In artificial photosynthesis, simultaneous production of H_2 (gas) and O_2 (gas) by four-photon irradiation results in explosive gases, which must be separated immediately after the production. However, the combination of H_2 (gas) and H_2O_2 (liquid) separates spontaneously, eliminating the need for external energy input for the separation. Hydrogen peroxide is an important oxidizing agent and is in widespread industrial demand (4 million tons/year in 2022, 7.8 million tons/year forecast for 2032). Furthermore, it is possible to construct a visible-light artificial photosynthesis system incorporating carbon dioxide reduction on the reduction side.[5] The two-electron oxidation of water by one photon can also be induced in earth abundant Si-, Sn-, Ge-, and Zn-porphyrins, raising hopes for the development of next-generation artificial photosynthesis that can circumvent the photon-flux density problem of sunlight.

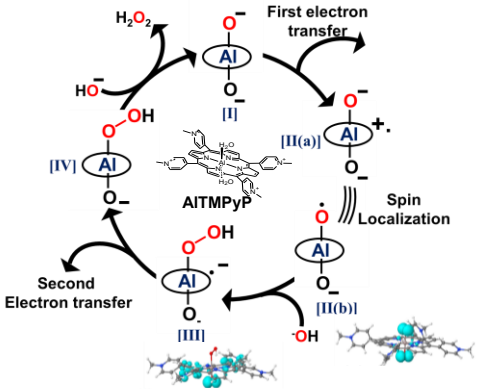

Figure 1. Two-electron oxidation of water catalyzed by Al-porphyrins.

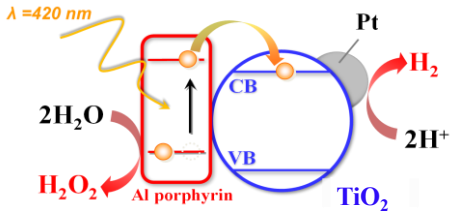

Figure 2. Artificial photosynthesis by molecular catalyst upon visible light irradiation: Water splitting into H_2/H_2O_2.

References

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Future Perspectives and Directions

Problem to be solved and realized within the next 10 years: By further improving the reactivity of the H_2O_2 formation reaction through the two-electron oxidation of water driven by a single photon of visible light to further improve the light energy conversion efficiency, we will realize comprehensive artificial photosynthesis with a renewable energy factor exceeding 1, making it possible to implement it in society.

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