



Applications of Porphyrins as Photosensitizers in the CO₂ Reduction Reaction

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DESCRIPTION

Metal complexes are promising candidates as CO₂ reduction catalysts because they can have multiple accessible redox states and high activation energies for proton reduction. Moreover, their catalytic properties and reactive sites can be manipulated at the molecular level by choosing appropriate metals and ligands. Most metal complexes produce CO or HCOOH as two-electron reduction products of CO₂, but some form oxalates (oxalic acid) and methane [1]. Diimine carbonyl complexes are advantageous as CO₂ reduction catalysts because the Re complexes almost completely generate CO without forming HCOOH or H₂ even in aqueous solution. Since the complex exhibits absorption in the near-ultraviolet to visible region, it also works as a photosensitizer in the photocatalytic CO₂ reduction reaction, but its durability is low. A hybrid system of semiconductors and metal complexes has been developed that can extract electrons from water and selectively reduce CO₂. A two-step dual excitation process is required to achieve both water oxidation and CO₂ reduction with visible light [2]. Visible light irradiation of immobilized Ru-Re complexes to CO₂ via selective CO₂ reduction by semiconductor catalysts using electrons donated by visible light-driven semiconductors to oxidize water with high efficiency and selectivity [3]. Ru-Re complexes are widely used in the presence of sacrificial reducing reagents such as 1-benzyl-1,4-dihydronicotinamide and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]. being studied [4]. It is imidazole (BIH) and has high catalytic activity for photocatalytic CO₂ reduction. When BIH was used as the electron donor for N,N-Dimethylformamide (DMF) and Triethanolamine (TEOA), the Turnover Number (TONCO) and reaction quantum yield for photocatalytic CO₂ reduction were 3000 and 45%, respectively. Homogeneous reactions, catalysts can be directly characterized without considering their combination with oxidation sites, and it is relatively easy to investigate reaction mechanisms using spectroscopic techniques. The various catalysts, photosensitizers, electron donors, solvents and catalytic properties used in homogeneous catalytic systems have not been described in detail. Ru-Re complexes showed high activity and durability for photocatalytic CO₂ reduction, but the absorbance of Ru-tris-

diiminecomplexes is insufficient for full utilization of sunlight in semiconductors [5]. Therefore, accumulation of photosensitizers and development of photosensitizers that absorb more visible light are required. This perspective focuses on porphyrins, one of the organic compounds most capable of absorbing visible light, and describes a system that combines porphyrins with his Re complex catalyst to reduce his CO₂. Zn(II) porphyrins are widely used alternatives to magnesium tetrapyrrole compounds as synthetic analogues and model molecules of chlorophylls and bacteriochlorophylls (Mg complexes).

CONCLUSION

Magnesium porphyrins are very acid sensitive and demetallation of magnesium ions can easily occur even on silica gel columns. The free base and Zn porphyrins have strong absorption bands in the visible region and can retain fluorescent singlet excited states, enabling the long-range singlet energy transfer observed in photosynthetic systems. Here, Zn(II) has a closed-shell d10 configuration and does not give rise to low-energy states that facilitate thermal deactivation of excitation energy. On the other hand, for example, Ni(II) porphyrins in the d8 configuration give a metastable dd excited state and return to the ground state. Porphyrins have been used as photosensitizers in photocatalytic CO₂ reduction systems.

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