

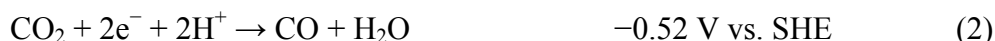
Photochemistry of CO₂ Reduction

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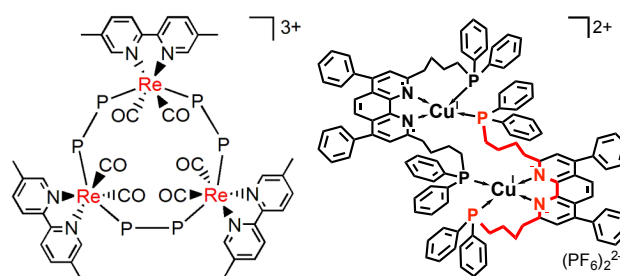
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How can we reduce CO₂ with light energy? This is one of the key questions for constructing artificial photosynthesis. Since CO₂ is the most oxidized state of carbon, one-electron reduction of CO₂ is an extraordinarily high endergonic reaction (eq. 1). From the viewpoints of low-energy light application, the multi-electron reduction of CO₂ via chemical reactions promises to be a more valuable process (eqs. 2, 3).



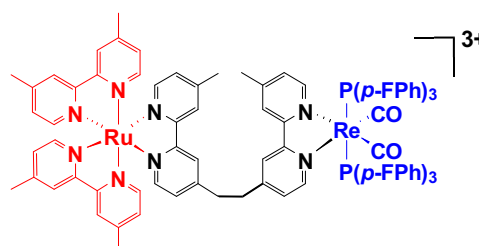
It is undeniable that photoinduced electron transfer reactions can be used for the photocatalytic reduction of CO₂. However, since excitation of a molecule with one photon can, in principle, induce only one-electron transfer, conversion systems from the photoinduced one-electron transfer processes to multi-electron reductions of CO₂ are necessary. From viewpoints of these requirements, outstanding results have been afforded by photocatalytic systems consisting of transition metal complexes as both a redox photosensitizer which initiates photochemical one-electron transfer and a catalyst, which accepts the electron from the photosensitizer, “accumulates” two electrons, and introduces them to the CO₂ molecule.^[1]

I will start this topic in my lecture. We successfully developed two novel types of redox photosensitizers (Scheme 1); (1) ring-shaped Re(I) multinuclear complexes, which achieved the highest efficiency of CO₂ reduction with a Re(I) diimine carbonyl complex as the catalyst ($\Phi_{\text{CO}} = 82\%$),^[2] and (2) a Cu(I) dimer, which works as a very stable photosensitizer and CO₂ reduction proceeded with Fe(II) and Mn(I) complexes as the catalysts.^[3]



Scheme 1. Photosensitizers

We have also developed so-called supramolecular photocatalysts where the photosensitizer and the catalyst are combined to each other with a bridging ligand. This bonding in the supramolecular photocatalysts can accelerate electron transfer between the two components, which improves the

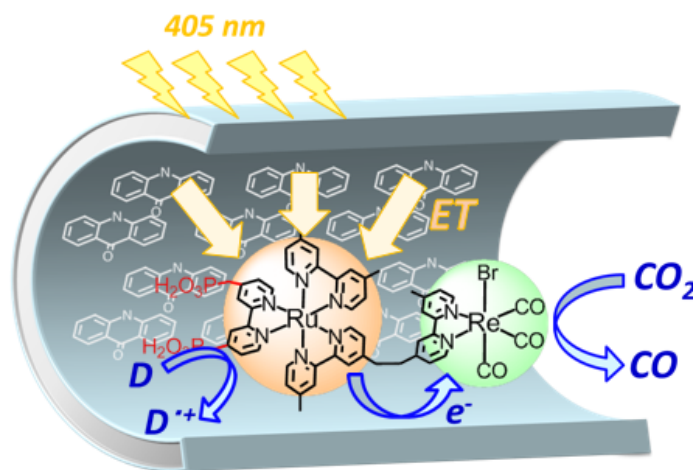


Scheme 2. Supramolecular photocatalyst

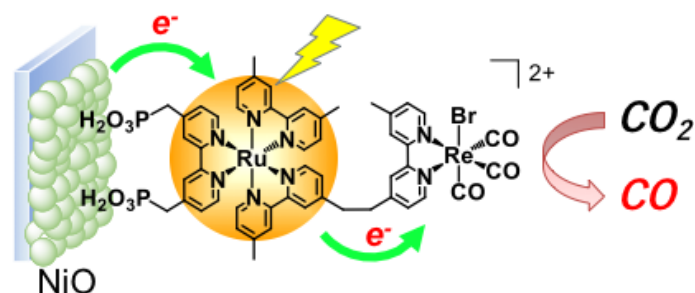
performance of the photocatalytic system.^[4] In particular, this advantage should be heightened on the surface of photofunctional solid materials as described below.

If we try to use sun light, molecular photocatalytic systems should require light-harvesting units because the light flux in the sun light is low and the light-absorption abilities of one molecule is too low to use dilute light for efficient photocatalytic reactions. For this purpose, we have developed hybrid systems of the supramolecular photocatalyst with mesoporous organosilica (PMO).^[5] The organic moieties in the walls of the PMO absorbed light and then energy transfer to the photosensitizer unit of the supramolecular photocatalyst efficiently proceeded to initiate photocatalytic CO₂ reduction.

The molecular photocatalytic systems have another weakness, i.e., weak oxidation power in the excited state. For practical application, water should be used as an electron donor. For overcoming this problem, we have developed a hybrid system consisting of the supramolecular photocatalyst and semiconductor electrodes.^[7] The hybrid photoelectrochemical cell consisting of a NiO-RuRe hybrid photocathode and a CoO_x/TaON photoanode showed the activity for visible-light-driven CO₂ reduction with water as a reductant to generate CO and O₂.^[8]



Scheme 3. Photocatalyst having light-harvesting function.



Scheme 4. Photocathode consisting of a NiO electrode and a Ru(II)-Re(I) supramolecular photocatalyst

References:

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