New Semiconductor Photocatalysts Designed for CO_2 Reduction and Water Oxidation under Visible Light

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Conversion of solar energy into useful fuels using a semiconductor photocatalyst through CO_2 fixation or water splitting has drawn significant attention in recent years due to a growing interest in artificial photosynthesis. Because the main component of sunlight is visible light, the development of a photocatalytic system that efficiently works under visible light is an important subject. In this presentation, recent progress on the development of new photocatalysts that are active for such artificial photosynthetic reactions will be given.

A hybrid material that consists of a semiconductor and a binuclear metal complex having a redox photosensitizer and a catalytic unit was employed as a photocatalyst for CO_2 reduction under visible light (Fig. 1). This hybrid was capable of reducing CO_2 into HCOOH (or CO) according to two-step photoexcitation of the semiconductor and the photosensitizer unit of the metal complex. It was found that semiconductors of TaON, $CaTaO_2N$, $Y_2Ta_2O_5N_2$ and C_3N_4 became active component for this system driven by visible light (> 400 nm) in combination with a suitable binuclear metal complex [1–7].

We also developed a new photocatalyst consisting of $Co(OH)_2$ and TiO_2 [8,9]. It is well known that TiO_2 is an active photocatalyst, but only works under UV irradiation. By contrast, the $Co(OH)_2/TiO_2$ hybrid photocatalyst was capable of absorbing visible light with wavelengths of up to 850 nm and oxidizing water into oxygen gas, even though it consisted of only earth-abundant elements only. To our knowledge, this system provides the first demonstration of a photocatalytic material capable of water oxidation upon excitation by visible light up to such a long wavelength.

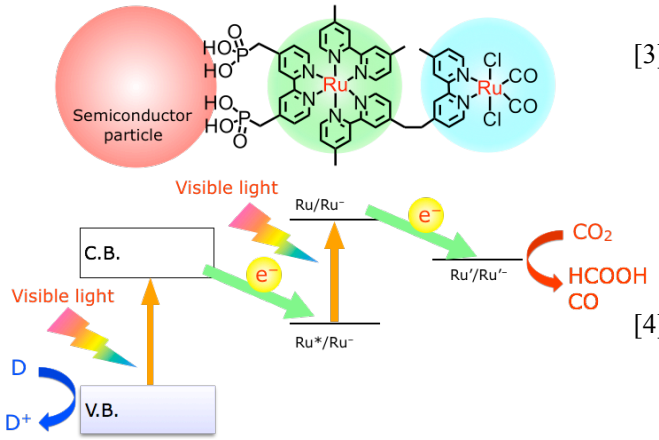

Fig.1 Z-scheme CO_2 reduction using a semiconductor and a binuclear metal complex having photosensitizing and catalytic units. The binuclear Ru(II) complex shown here is known to work as an efficient homogeneous photocatalyst to produce HCOOH.

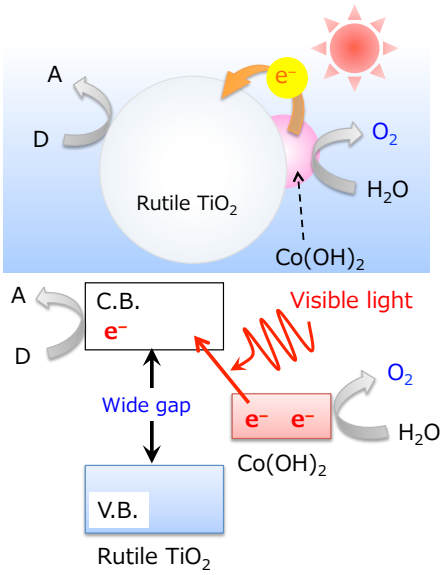

Fig. 2 Visible-light-driven water oxidation using $Co(OH)_2$-modified rutile TiO_2.

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