2-2-6. Photocatalytic CO_2 Reduction

Overview

The technology that converts CO_2 into valuable resources using solar energy occupies an important position in artificial photosynthesis. During the oil crisis of the 1970s, it was discussed as a response to energy shortages and carbon resource scarcity; today, it is often highlighted as a measure against global warming. This technology has the potential to address the three critical issues that cast a shadow over humanity's future. Research on CO_2 reduction photocatalysts temporarily slowed in the early 2000s as crude oil prices fell after the oil shock subsided. However, Japan continued research during this period and is now one of the leading countries in this field. Since 2010, related publications have increased rapidly (Fig. 1). Although studies began soon after the oil shock, full-scale research started around 1983 when J.-M. Lehn and colleagues demonstrated that products originated from CO_2 as the carbon source by using $^{13}CO_2$. In Japan, research has been ongoing since the 1990s. For a comprehensive overview up to the mid-2000s, refer to "2-2-5. Photocatalytic CO_2 Reduction" in the Photochemical Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0220205.pdf

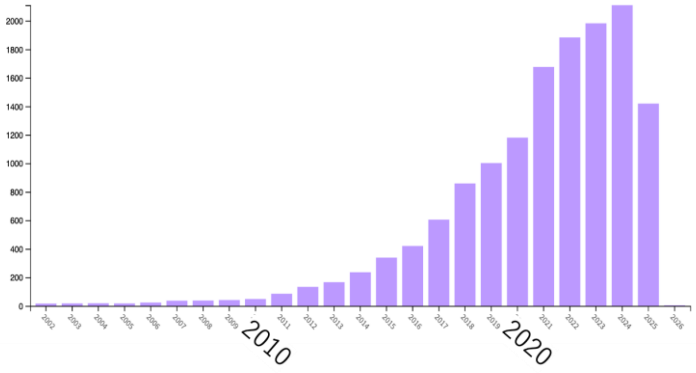

Figure 1. Numbers of papers related to "photocatalytic CO_2 reduction".

Current Status and Frontiers

Recently, research has focused on three major types of photocatalytic systems.

First is molecular systems using metal complexes. In these systems, photoinduced electron transfer typically moves only one electron per absorbed photon. However, reducing CO_2 to stable compounds requires at least a two-electron reduction per CO_2 molecule. Therefore, molecular photocatalyst systems generally employ two types of molecules: a redox photosensitizer to drive electron transfer and a catalyst. Suppressing proton reduction, which leads to hydrogen evolution due to its lower reduction potential, is essential. Complexes with Ru(II) or Re(I) as central metals have been extensively studied as highly selective CO_2 reduction catalysts. Japan has reported the most efficient (highest quantum yield) and most durable (largest turnover number) photocatalysts in this

category.[1] Recently, research has shifted toward catalysts of abundant and inexpensive metals such as Mn(I), Fe(II), and Co(II).[2] Initially, noble metal complexes (Ru(II), Ir(III), Os(II), Re(I)) were used as redox photosensitizers, but current studies increasingly focus on Cu(I) complexes and organic molecules with TADF properties (utilizing triplet excited states). Japanese researchers remain at the forefront, reporting the most efficient and durable systems composed solely of inexpensive elements.

Second is semiconductor photocatalysts. Although numerous studies have been reported, very few have clearly demonstrated CO_2 reduction using water as the electron source. Against this backdrop, Ag was identified as an effective cocatalyst for photocatalytic CO_2 reduction.[3] UV-responsive metal oxide photocatalysts such as $BaLa_4Ti_4O_{15}$ and $NaTaO_3$:Sr loaded with the Ag cocatalyst can produce CO with nearly 90% selectivity over H_2 formation accompanied with stoichiometric O_2 in aqueous solution.[4] Furthermore, when Rh–Ru cocatalysts are used instead of Ag, CH_4 of an eight-electron reduction product is formed with approximately 10% selectivity instead of CO. In addition, Z-scheme photocatalytic systems employing metal sulfide photocatalysts have successfully achieved CO generation from CO_2 reduction under visible light irradiation using water as the electron donor.

In recent years, research on MOF-based systems, which are the third category here, has surged. The first report, by Kajiwara, Tanaka, and Kitagawa at Kyoto University in 2016, demonstrated a system capable of capturing and reducing low-concentration CO_2.[5]

Since 2013, hybrid systems combining the three approaches have also been reported.[6]

References

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Future Perspectives and Directions

Over the next decade, key challenges to be addressed include achieving efficient reduction of low-concentration CO_2, improving the performance of photocatalytic systems, and advancing process and chemical engineering to enable the effective utilization of newly developed photocatalysts.

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