Visible-Light CO₂ Reduction Using Carbon Nitride and Metal Complex Hybrid Photocatalysts

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Converting CO₂ into energy-rich chemicals using water and sunlight as an electron donor and energy source, respectively, is of great interest as a means of addressing the depletion of fossil fuels and concomitant CO₂ emission. Our group has recently developed a visible-light-driven photocatalyst for CO₂ reduction, which consisted of an organic semiconductor, graphitic carbon nitride (abbreviation for g-C₃N₄) and a Ru(II) mononuclear complex [1]. In this system, g-C₃N₄ serves as a light absorber and works as oxidation sites, while the combined Ru(II) complex acts as an active site for CO₂ reduction. This system is expected to be promising because of the excellent electrochemical (and/or photocatalytic) ability of metal complexes for CO₂ reduction and the high efficiency of semiconductors for water oxidation. In order to conduct photocatalytic CO₂ reduction using this hybrid system, electron transfer from g-C₃N₄ to the loaded Ru complex is necessary. Since the efficiency of the interfacial electron transfer is influenced by the energy level of the Ru complex, we examined the structure of Ru complexes in detail. As a result, we revealed that larger potential difference between electron donor (i.e., conduction band minimum of g-C₃N₄) and acceptor (i.e., LUMO potential of Ru complex) is important to achieve high photocatalytic ability [2]. However, it is difficult to achieve larger potential difference using this system due to the lack of suitable structures of a Ru(II) mononuclear complex.

In this work, as another system, photocatalytic CO₂ reduction using g-C₃N₄ and a Ru(II) binuclear complex hybrid is presented (Fig.1). This system is expected to photocatalyze CO₂ reduction through a Z-schematic electron-transfer mechanism with a two-step photoexcitation of the semiconductor and binuclear Ru(II) complex. We could get larger potential difference between electron donor (i.e., g-C₃N₄) and acceptor (i.e., Ru complex) using this hybrid system, which may induce high photocatalytic ability.

Photocatalytic CO₂ reduction was conducted using this system. As a result, HCOOH was detected catalytically under visible light in the presence of a suitable electron donor. Control experiments indicated that no HCOOH occurred in the absence of either light, CO₂ or a Ru(II) binuclear complex. In addition, no HCOOH occurred using Al₂O₃, which is an insulator, and a Ru(II) binuclear complex hybrid. These results led to the conclusion that g-C₃N₄ and a Ru(II) binuclear complex hybrid functioned as a CO₂ reduction photocatalyst.

In addition, we also found that the ability was improved dramatically, when g-C₃N₄ was modified with Ag nanoparticles. Importantly, the amount of formed HCOOH using this Z-schematic system was higher than that achieved using Ag-loaded g-C₃N₄ and an optimized Ru(II) mononuclear complex hybrid. These results indicated the importance of Z-schematic system to achieve high photocatalytic performance. CO₂ reduction with high selectivity (>95%) was achieved both in organic solvent and aqueous solution. In addition, a TON_HCOOH (with respect to the amount of Ru complex) of greater than 33,000 and 2,000 were obtained in organic solvent and aqueous solution, respectively. These are the highest among visible-light-driven heterogeneous CO₂ reduction photocatalysts ever reported [3].

Fig.1 Carbon nitride and a Ru(II) binuclear complex hybrid photocatalyst.