Plasma surface modification of C_3N_4 improves durability of photocatalytic CO_2 reduction with RuRu supramolecular photocatalyst

([1]*Tokyo Institute of Technology*, [2]*High Energy Accelerator Research Organization,* [3]*Toyota Technological Institute,* [4]*The University of Tokyo*) ○Noritaka Sakakibara,[1] Mitsuhiko Shizuno,[1] Tomoki Kanazawa,[2] , Kosaku Kato,[3] Akira Yamakata,[3] Shunsuke Nozawa,[2] Tsuyohito Ito,[4] Kazuo Terashima,[4] Kazuhiko Maeda,[1] Osamu Ishitani[1]

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For realizing sustainable energy management, hybrid photocatalyst combined with a supramolecular photocatalyst and a semiconductor is one of the promising concepts.[1] In the design of hybrid photocatalyst, the control of interface should be essential for the photocatalytic activity. Here, we performed surface modification of C_3N_4 nanosheet by using plasma in hydroquinone-containing aqueous solution[2] to gain better interfacial affinity between C_3N_4 and a supramolecular photocatalyst. Plasma in aqueous solution is a promising technique that can modify surface properties of inorganic particles such as carbon nanotube and boron nitride, without changing the original bulk properties.

By the plasma surface modification of C_3N_4 nanosheet, uniform deposition of oxygen-rich carbon layer based on sp^2 bonding structure was tentatively identified with a TEM observation and an XPS measurement, while bulk properties of C_3N_4 was maintained after the plasma surface modification. In the photocatalytic CO_2 reduction under visible light irradiation with C_3N_4 on which a Ru(II)-Ru(II) supramolecular photocatalyst was fixed via phosphonic anchoring groups[3] (Fig. 1), the plasma surface modification improved the durability of formic acid production by three times. Turnover number of HCOOH production recorded ~50000 in an optimal condition. This result demonstrates positive effect of the plasma surface modification on the photocatalytic activity in the hybrid system.

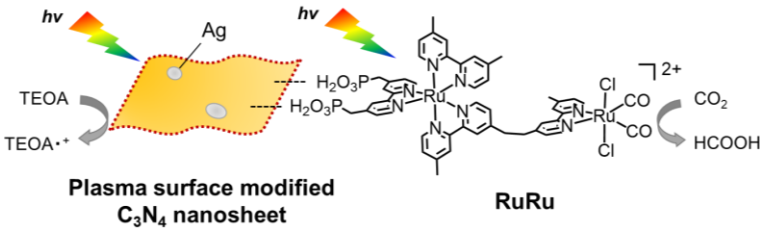

Figure 1 Illustration of the hybrid photocatalyst composed of plasma surface modified C_3N_4 nanosheet and RuRu.

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