Modification of organic molecule structure for photocatalytic hydrogen production in water medium

Motonori Watanabe

International Institute of Carbon Neutral Energy Research, Kyushu University, Fukuoka, Motooka744, Japan
Corresponding author: mwata@i2cner.kyushu-u.ac.jp

Renewable hydrogen production is key for establishing clean energy systems because hydrogen can be used as a clean energy source in hydrogen fuel cells and a hydrogen-driven society. We have developed the novel donor-bridge-acceptor type organic molecule for dye-sensitizer [1-4] on metal oxide semiconducting photocatalyst for photocatalytic hydrogen production (Fig. 1). TiO₂ is a known UV-light-responsive photocatalyst and when the surface of TiO₂ is coated with a donor-acceptor organic dye and is simply irradiated with visible light (>420 nm), it produces hydrogen gas in water that contains sacrificial reagents. To increase the hydrogen productivity and photocatalytic stability, we systematically investigated modifications of the organic-dye sensitizer using a synthetic organic approach. When the dye sensitizer introduced a terthiophene group as a "charge separation spacer," the dye showed good hydrogen productivity at 4400 turn of number (TON) and an apparent quantum efficiency of 1.6% at 420 nm. The dye showed a longer charge-recombination lifetime of 85 ps, whereas without a spacer group, the recombination lifetime of the dye was 0.2 ps with a nine-times lower TON of 483 [1]. This value is higher than that of a commercially available rare-metal-organic complex dye at

438 TON (Ru-dye called N719). I covered the photocatalyst with a hydrophobic group. The hydrophobic group reduced electron leakage from the photocatalyst to the water solution. This improved charge collection at the hydrogen-production site, thereby improving the hydrogen productivity by as much as a factor of two compared with materials without a hydrophobic coating [2]. Generally, a carboxylic group is used as the coordination-anchoring group at the interface between a dye sensitizer and the TiO₂. Instead, a multi-pyridyl group is used as the hydrogen-bonding anchoring group for TiO₂. This group showed high stability during photocatalytic reactions, with no delamination occurring, in contrast to the case of chemical coordination with a carboxylic group. The hydrogen-bonding system showed no change in the rate of hydrogen production, even after 80h [3].

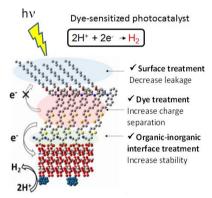


Fig. 1: Summary of organic dye sensitized photocatalytic hydrogen production

References

- [1] M. Watanabe, H. Hagiwara, I. Aoi, Y. Ogata, K. Shiomi, A. Staykov, S. Ida, K. Tanaka, T. Ishihara, J. Mater. Chem. A, 2 (2014) 12952-12961.
- [2] M. Watanabe, H. Hagiwara, Y. Ogata, A. Staykov, S. R. Bishop, N. H. Perry, Y. J. Chang, S. Ida, K. Tanaka, T. Ishihara, *J. Mater. Chem. A*, 3 (2015) 21713-21721.
- [3] M. Watanabe, S. Sun, T. Ishihara, T. Kamimura, M. Nishimura, F. Tani, ACS Appl. Energy Mater., 1 (2018) 6072-6081.
- [4] M. Watanabe, Sci. Tech. Adv. Mater., 18 (2017) 705–723.